

Unit 43: Plant and Process Principles

Unit code: H/601 442

QCF level: 5

Credit value:

15

OUTCOME 4 - COMBUSTION PROCESSES

4 Understand combustion processes associated with plant engineering.

Combustion chemistry: composition of air and simple hydrocarbon fuels; combustion equations; stoichiometric and actual air:fuel ratios; mixture strength: excess air

Energy of combustion: calorific values; higher and lower; thermal and boiler efficiency; practical determination of calorific value of various solid, liquid and gaseous fuels

Products of combustion: instrumentation for flue gas and exhaust products; volumetric analysis; variation of proportions of products dependent on air:fuel ratio and combustion quality

You should judge your progress by completing the self assessment exercises. These may be sent for marking at a cost (see home page).

On completion of this tutorial you should be able to do the following.

- Write down combustion equations.
- Solve the oxygen and air requirements for the combustion of solid, liquid and gaseous fuels.
- Determine the products of combustion.
- Determine the air/fuel ratio from the products of combustion.
- Solve problems involving energy released by combustion.
- Describe basic instruments used in flue gas analysis.
- Explain the use of calorimeters.

In order to complete this tutorial you should be already familiar with the following.

- The molecular nature of substances.
- Basic chemistry.
- The properties of gas and vapours.
- The use of steam tables.

1. INTRODUCTION

Combustion is the process of chemical reaction between fuel and oxygen (the 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 1 m³ 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 as follows.

	Symbol	Atomic Mass	Molecular Mass	Product
Carbon	C	12		CO ₂
Hydrogen	H ₂	1	2	H ₂ O
Sulphur	S	32		SO ₂
Oxygen	O ₂	16	32	
Nitrogen	N ₂	14	28	

If the water formed during combustion leaves as vapour, 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 vapour condenses, the latent heat is given up and the calorific value is then the higher calorific value (HCV).

Solid and liquid fuels are normally analysed 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 the process. The silica leaves deposits of slag on the heat transfer surfaces in boilers.

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

COMPOSITION OF AIR. For purposes of calculation, the composition of air is considered to be as follows.

	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 CO₂. The resulting products contain water H₂O. Industrial equipment for measuring the contents of the products usually removes the water from the sample and the products are then called the dry products.

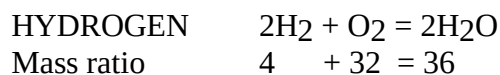
2. COMBUSTION CHEMISTRY

2.1 SOLID AND LIQUID FUELS

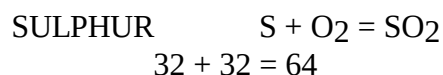
In the case of solid and liquid fuels, we do the combustion of each element separately. The important rule is that you must have the same number of atoms of each substance before and after the process. This may be obtained by juggling with the number of molecules.



Hence 1kg of C needs 32/12kg of O₂ and makes 44/12kg of CO₂



Hence 1kg of H₂ needs 8kg of O₂ and makes 9 kg of H₂O



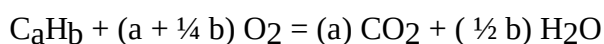
Hence 1 kg of S needs 1kg of O₂ and makes 2kg of SO₂.

2.2. GASEOUS FUELS.

Typical hydrocarbons are:

Methane	CH ₄
Ethane	C ₂ H ₆
Propane	C ₃ H ₈
Butane	C ₄ H ₁₀
Pentane	C ₅ H ₁₂
Hexane	C ₆ H ₁₄
Heptane	C ₇ H ₁₆
Octane	C ₈ H ₁₈
Ethene	C ₂ H ₄ (Ethylene)
Propene	C ₃ H ₆ (Propylene)
Ethyne	C ₂ H ₂ (Acetylene)
Benzenol	C ₆ H ₆ (Benzene)
Cyclohexane	C ₆ H ₁₂

The combustion equation follows the following rule:



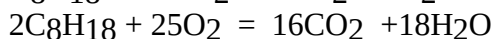
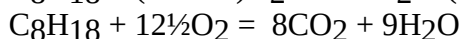
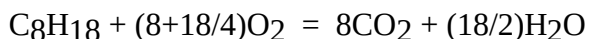
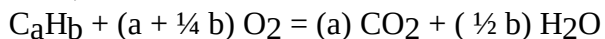
If this results in fractional numbers of molecules, then the whole equation may be multiplied up.

WORKED EXAMPLE No.1

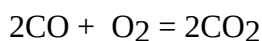
Write out the combustion equation for C₈H₁₈

SOLUTION

$$a = 8, b = 18$$



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:



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.

WORKED EXAMPLE No.2

A fuel contains by mass 88% C, 8%H₂, 1%S and 3% ash (silica). Calculate the stoichiometric air.

SOLUTION

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

Hence 0.88kg of C needs $(32/12) \times 0.88 = 2.347$ kg of oxygen.
It makes $(44/12) \times 0.88 = 3.227$ kg of carbon dioxide.

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

hence 0.08kg of hydrogen needs $(32/4) \times 0.08 = 0.64$ kg of oxygen.

SULPHUR	$S + O_2 = SO_2$
Mass ratio	$32 + 32 = 64$

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

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

TOTAL AIR needed is $2.997/23\% = 13.03$ kg

The STOICHIOMETRIC air/fuel ratio is 13.03/1

WORKED 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:

$$120\% \times 13.03 = 15.637 \text{ kg}$$

Oxygen is also 20% excess so $0.2 \times 2.997 = 0.599\text{kg}$ is left over.

Nitrogen in the air is $77\% \times 15.637 = 12.04\text{kg}$

List of products :

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

SELF ASSESSMENT EXERCISE No.1 – COMBUSTION BY MASS

Complete the following problems.

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

80% C 18% H₂ 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% CO₂)

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

75% C 15% H₂ 7%S remainder ash

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

(16.5% CO₂)

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

80% C 10% H₂ 5% S and 5% ash.

(76.7%N, 22.5% CO₂ 0.8% SO₂)

4. 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 Avogadro'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 O₂ and 2 kg of H₂ and 28 kg of N₂.

The molecular mass of a substance is expressed as kg/kmol so the molecular mass of O₂, for example, is 32 kg/kmol.

Avogadro's Law states:

1m³ 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:

$$p_A V_A = m_A R_0 T / \tilde{N}_A \quad p_B V_B = m_B R_0 T / \tilde{N}_B$$

$\tilde{N}$ is the relative molecular mass.

$$p_A / p_B = m_A \tilde{N}_B / m_B \tilde{N}_A = \text{ratio of the kmol fractions.}$$

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 $V_A / V_B = p_A / p_B$

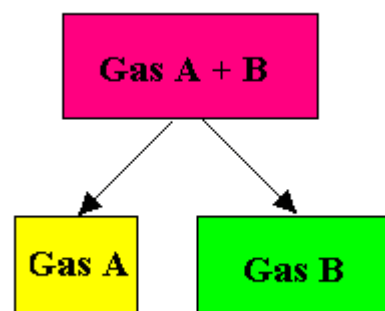


Figure 1

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

$$pV_A/T = m_A R_0 / \tilde{N}_A \quad p = m_A R_0 T / \tilde{N}_A V_A \dots\dots\dots(1)$$

$$pV_B/T = m_B R_0 / \tilde{N}_B \quad p = m_B R_0 T / \tilde{N}_B V_B \dots\dots\dots(2)$$

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:

$$p_A = m_A R_0 T / \tilde{N}_A V \dots\dots\dots(3)$$

$$p_B = m_B R_0 T / \tilde{N}_B V \dots\dots\dots(4)$$

(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. $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{H}_2\text{O}$

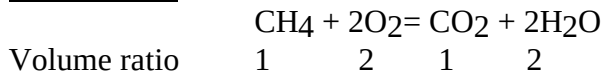
Since the volumetric content of each gas is in the same ratio as the kmol fractions then the volumetric content is in the same proportion as the molecules. Hence it needs 2 volumes of oxygen to burn 1 volume of methane.

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.

WORKED EXAMPLE No.4

Calculate the % CO₂ in the dry products when methane is burned with 15% excess air by volume.

SOLUTION



The stoichiometric air is $2/21\% = 9.524 \text{ m}^3$

The actual air is $9.524 \times 115\% = 10.95 \text{ m}^3$

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 = $(1/9.95) \times 100 = 10\%$

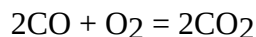
When the fuel is a mixture of gases, the procedure outlined must be repeated for each combustible gas and the oxygen deduced for the volume of each in 1 m³ of total fuel.

WORKED 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 m³ of methane is 2m³. To burn 0.6m³ needs 1.2m³ of oxygen. For carbon monoxide we use the combustion equation:



Hence to burn 1 m³ of CO need 0.5 m³ of oxygen, so to burn 0.3 m³ needs 0.15 m³ of oxygen.

The total oxygen needed is $1.2 + 0.15 = 1.35 \text{ m}^3$. However there is already 0.1 m³ in the fuel so the **stoichiometric oxygen needed 1.25m³**

SELF ASSESSMENT EXERCISE No.2 - COMBUSTION BY VOLUME

1. Find the air fuel ratio for stoichiometric combustion of Ethene by volume.
(14.28/1)
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% CO₂, 40% H₂ , 40% CH₄, 15% N₂

Determine the stoichiometric air and the % content of each dry product.

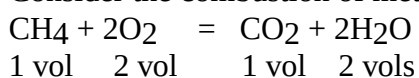
(4.76 m³, 89.7%,N₂ 10.3% CO₂).

5. RELATIONSHIP BETWEEN PRODUCT AND EXCESS AIR.

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

WORKED EXAMPLE No.6

Consider the combustion of methane again.



SOLUTION

Let the excess air be x (as a decimal)

The stoichiometric air is 9.52 vols. Actual air is $9.52(1 + x)$

Dry Products:

Nitrogen	$0.79 \times 9.52(1 + x) =$	$7.524x + 7.524$
Oxygen		$2.000x$
Carbon Dioxide		1.000
Total		$9.524x + 8.524$

$$\% \text{ Carbon monoxide} = 100 \{1/(9.524x + 8.524)\}$$

$$\% \text{ Oxygen} = 100\{2/(9.524x + 8.524)\}$$

For example if the % CO_2 is 10% then the excess air is found as follows:

$$10\% = 100 \{1/(9.524x + 8.524)\}$$

$$0.1 = 1/(9.524x + 8.524)$$

$$(9.524x + 8.524) = 10$$

$$9.524x = 1.476$$

$$x = 0.155 \text{ or } 15.5\%$$

Similarly if the O_2 is 10% then the excess air is 81% (show this for yourself)

If the analysis of the fuel is by mass, then a different approach is needed. The following examples show two ways to solve problems.

WORKED EXAMPLE No.7

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% H₂ 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 H₂. Converting these into kmol we have 0.9/12 kmol of C and 0.1/2 kmol of H₂. For 1 kmol of dry exhaust gas we have :

0.15 kmol of CO₂
Y kmol of excess O₂

$$1 - 0.15 - Y = 0.85 - Y \text{ kmol of N}_2$$

1 kmol of CO₂ is 44 kg

1 kmol of N₂ is 28 kg

1 kmol of O is 32 kg

0.15 kmol of CO₂ 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 $0.9 / (0.15 \times 12) = 0.5$

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 :

$$(23.3/76.7) \times 28 \times (0.85 - Y) = 7.24 - 8.5Y \text{ kg per kmol of DEG.}$$

(using precise proportions of air for accuracy).

The oxygen contained within the carbon dioxide is:

$$(32/44) \times 0.15 \times 44 = 4.8 \text{ kg per kmol DEG}$$

1 kmol of CO₂ contains 44 kg and 32/44 of this is oxygen. The oxygen in the CO₂ is hence 32 x 0.15 kg per kmol DEG.

The excess oxygen is

$$32Y \text{ kg per kmol DEG}$$

Total oxygen in the products excluding that used to make H₂O is :

$$32 \times 0.15 + 32Y$$

The oxygen used to burn hydrogen is hence :

$$7.24 - 8.5Y - (32 \times 0.15 + 32Y)$$

O₂ used to burn H₂ is

$$2.44 - 40.5Y \text{ kg per kmol DEG}$$

For 0.5 kmol this is

$$1.22 - 20.25Y \text{ kg}$$

To burn hydrogen requires oxygen in a ratio of 8/1. There is 0.1 kg of H₂ in each kmol of fuel so 0.8 kg of O₂ is needed. Hence :

$$0.8 = 1.22 - 20.25Y$$

$$Y = 0.0208 \text{ kmol per kmol DEG}$$

The nitrogen in the DEG is $0.85 - Y = 0.8292 \text{ kmol per kmol DEG}$

The actual Nitrogen = $0.8292 \times 0.5 \times 28 = 11.61 \text{ kg}$

The air supplied must be $11.61/0.767 = 15.14 \text{ kg per kg of fuel}$. A simple calculation shows the stoichiometric mass of air is 13.73 so there is 10.3% excess air.

WORKED EXAMPLE No.8

A fuel oil contains by mass 86.2% C, 12.8% H₂ and 0.9% S by mass. The dry exhaust gas contains 9% CO₂ by volume. Calculate the excess air by mass.

SOLUTION

CARBON	$C + O_2 \rightarrow CO_2$
Mass ratio	$12 + 32 \rightarrow 44$
	$0.862 + 2.299 \rightarrow 3.16$
HYDROGEN	$2H_2 + O_2 \rightarrow 2H_2O$
Mass ratio	$4 + 32 \rightarrow 36$
	$0.128 + 1.024 \rightarrow 1.152$
SULPHUR	$S + O_2 \rightarrow SO_2$
Mass ratio	$32 + 32 \rightarrow 64$
	$0.09 + 0.09 \rightarrow 0.18$

TOTAL OXYGEN needed is 3.413 kg
 Ideal Air (stoichiometric ratio) = $3.413/0.233 = 14.65$ kg
 Nitrogen is $0.767 \times 14.65 = 11.23$
 Let the excess air be x Calculate dry products by mass

		% of total
CO ₂	3.16 kg	316/T
O ₂	3.413x kg	341.3x/T
SO ₂	0.18	18/T
N ₂	11.23(1+ x)	1123(1+ x)/T
Total = T = 3.34 + 3.413x + 11.23(1+ x)		

Now convert these into % by volume by dividing by the molecular mass

CO ₂	$316/44T = 7.18/T$
O ₂	$341.3x/32T = 10.67x/T$
SO ₂	$18/64T = 0.56/T$
N ₂	$1123(1+ x)/28T = 40.11(1+ x)/T$
Total = $(1/T)(7.18 + 10.67x + 0.56 + 40.11 + 40.11x)$	
Total = $(1/T)(47.85 + 50.78 x)$	

$$\begin{aligned} \%CO_2 &= 9 = (7.18/T)100/(1/T)(47.85 + 50.78 x) \\ 0.09 &= (7.18)/(47.85 + 50.78 x) \\ 47.85 + 50.78 x &= 79.78 \\ 50.78 x &= 79.78 - 47.85 = 31.92 \\ x &= 0.63 \end{aligned}$$

Answer the % excess air is 63%

SELF ASSESSMENT EXERCISE No.3 - EXCESS AIR.

1. C₂H₆ is burned in a boiler and the dry products are found to contain 8% CO₂ by volume. Determine the excess air supplied. (59%)
2. The analysis of the dry exhaust gas from a boiler shows 10% carbon dioxide. Assuming the rest is Oxygen and Nitrogen; determine the excess air supplied to the process and the % excess air. The fuel contains 85% C and 15% H₂
(21.5 kg , 44.5%)
3. A fuel oil contains by mass 85% C and 15% H₂. The dry exhaust gas contains 11% CO₂ by volume. Calculate the excess air by mass.
(32%)

6. ENERGY RELEASED BY THE REACTION

This is complex subject and the following is very much simplified. Students wishing to study this in full should refer to advanced text books and/or the level 2 tutorial on combustion. The contents of the fuel and air or oxygen prior to combustion are called the reactants. The resulting material is called the products. In the process energy is released. This is taken as the enthalpy of reaction Δh

In simple terms we may say: $h(\text{reactants}) = h(\text{products}) + \Delta h_o$

Since $h(\text{products}) > h(\text{reactants})$ it follows that Δh_o is a negative value.

In order to make more sense of this, we assume that the products and reactants end up at the same temperature. The values of Δh_o for various reactants may be found in standard tables. These are normally stated for 1 kmol of substance at 25°C. We will be more practical here and quote values for 1 kg (solid and liquid fuels) and 1 m³ for gaseous fuels. You will also find values for internal energy of reaction but we will not go into this here.

A fuel containing hydrogen will produce water vapour in the products. If the vapour condenses, more energy is released to the process. In practical combustion it is undesirable to allow this to happen as the condensed vapours form acids with the sulphur and corrodes the plant, especially the flue.

The energy released when water vapour is not condensed is called the Lower Calorific Value (L.C.V.). If the vapour is condensed then it is normally assumed that an extra 2441.8 kJ is released per kg of water, this being the latent enthalpy of evaporation at 25°C. If this energy is added we get the Higher Calorific Value (H.C.V.). Typical L.C.V.s are as follows.

Coal	30 – 36 MJ/kg
Fuel Oils	43 – 46 MJ/kg
Natural Gas	38 MJ/m ³

The calorific values of fuels are found with **CALORIMETERS**. In the case of solid and liquid fuels the **BOMB CALORIMETER** is used. For gaseous fuels the **BOY'S CALORIMETER** is used.

HESS' LAW

This is useful when you need to work out the enthalpy of reaction Δh_o (energy released) when a particular chemical reaction takes place. The law states "if a reaction is carried out in a series of steps, Δh_o for the reaction will be equal to the sum of the enthalpy changes for the individual steps".

For the level being studied here, we can apply it in two ways.

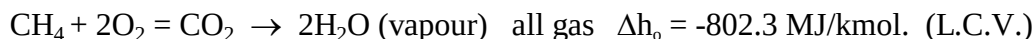
CHANGE OF STATE

When a change of state occurs we can use the law to link the H.C.V. and the L.C.V.

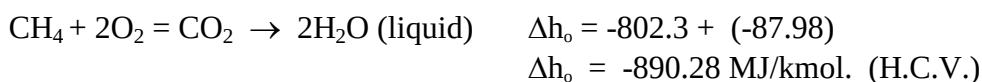
WORKED EXAMPLE No.9

When methane CH_4 in its gaseous form is completely burned to form CO_2 and H_2O (both in the gaseous form) the enthalpy of reaction is -802.3 kJ/kmol . When vapour is condensed to water at standard conditions the energy released is 87.98 kJ/kmol . Determine the H.C.V. for methane gas.

SOLUTION



We need the figure for two atoms of water.



PARTIAL COMBUSTION

If a substance is partially burned, energy E_1 is released.

If the partially burned substance is then completely burned the energy released is E_2 .

If the substance is completely burned in one step, the energy released is $E = E_1 + E_2$.

WORKED EXAMPLE No.10

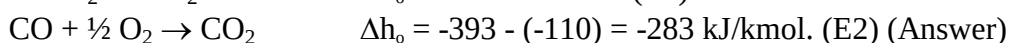
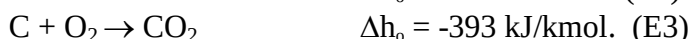
The enthalpy of reaction for solid carbon being burned to form carbon monoxide gas is -110 kJ/kmol .

The enthalpy of reaction for solid carbon into carbon dioxide gas is -393 kJ/mol .

What is the enthalpy of reaction when carbon monoxide gas is burned to form carbon dioxide gas?

SOLUTION

Base the solution on 1 atom of carbon throughout.



BOMB CALORIMETER

A sample of solid or liquid fuel (about 1 gram) is accurately weighed and placed in a crucible. This is fitted inside the bomb with an ignition wire (platinum) passing through the fuel. Special tools are used to create pellets of coal dust. The lid is screwed on and the bomb is pressurised with oxygen. The bomb is placed inside the outer container containing exactly 1 kg of water.



Figure 2

The outer container is placed inside an insulated box to prevent heat loss. A very accurate thermometer is placed in the water. The temperature is recorded against time. When the temperature is stable, the bomb is fired by passing an electric current through the wire. All the time the water is stirred by an electric motor and stirrer.

The fuel in the crucible is completely burned and the energy released causes a rapid rise in the temperature of the water. This is recorded until it starts to cool again. The bomb may be depressurised and the contents examined. A small amount of condensate will be found in it from the water formed during combustion. This may be weighed and used to find the L.C.V.

The graph produced is similar to that shown. Because of slow cooling and possibly initial warming, the straight lines are drawn as shown to find the true temperature change ΔT .

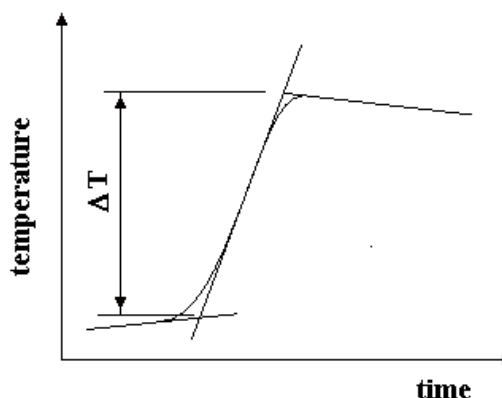


Figure 3

Because the metal of the bomb and container is warmed as well as the water, the manufacturer will certify that the bomb has an equivalent mass of water. The effective mass of water heated up is the actual mass plus the equivalent mass.

The resulting calorific value is the higher value because the gaseous H_2O is condensed to water.

M_f = mass of fuel.

M_w = total effective mass of water.

c = specific heat capacity of water.

Higher Calorific value = $M_w C \Delta T / m_f$

WORKED EXAMPLE No.11

A bomb calorimeter is used to determine the Higher Calorific Value of an oil sample. The mass of the sample is 1.01 g. The total equivalent mass of water is 1.32kg. The increase in temperature after ignition is 7.8 K. Calculate the higher calorific value. The specific heat of water is 4.186 kJ/kg K.

SOLUTION

$$\text{H.C.V} = M_w C \Delta T / m_f = 1.32 \times 4.186 \times 7.8 / 0.00101 = 42672 \text{ kJ/kg or } 42.672 \text{ MJ/kg}$$

BOY'S CALORIMETER

THE Boy's calorimeter is in effect a highly efficient gas boiler. The following is a simplified description of it. Gas is burned in the bottom and as it forces its way out to the top, it has to make several passes over a coiled pipe with many fins on it to absorb the heat. Water is heated as it flows through the pipe. Condensate from the burned gas is also collected from the bottom. The volume of gas burned and the mass of water heated is accurately measured over the same period of time. Thermometers measure the water temperature at inlet and outlet and the flue gas temperature is also measured accurately



Figure 4

Heat released = volume of gas x higher calorific value.

Heat given to water = $M_w c \Delta T$

Assuming 100% efficiency we may equate and get H.C.V. = $(M_w c \Delta T)/\text{Volume of gas}$

This is over simplified and is only true if the flue gas is cooled back to the same temperature as the unburned gas. The laboratory procedure is detailed in standards.

WORKED EXAMPLE No.12

The results of a test with a Boy's calorimeter are as follows.

Volume of gas burned (at standard conditions) = 0.004 m^3

Volume of water heated in the same time = 1.8 kg

Temperature rise of the water = 20.17 K

Specific heat of water = 4.186 kJ/kg K

Calculate the Higher calorific value.

SOLUTION

$$\text{H.C.V.} = (M_w c \Delta T)/\text{Volume of gas} = (1.8 \times 4.186 \times 20.17)/0.004 = 38\,000 \text{ kJ/m}^3$$

COMBUSTION EFFICIENCY

The efficiency of a combustion process is found from the following basic relationship.

$$\eta_{th} \% = \frac{\text{Energy gained by the working fluid}}{\text{Energy released by the fuel}} \times 100$$

The efficiency of the process is a maximum when all the fuel is burned and the resultant gaseous products give up all its energy to the process. To this end, the minimum amount of air necessary for complete combustion should be used as excess air takes away energy with it in the flue and exhaust. Because cooling the gas too much produces condensation, a minimum flue temperature is maintained and some heat loss must be expected. Heat loss from combustion equipment should be minimised by lagging. The following principles could apply to engines or boilers.

The flue gas or exhaust from the process should be monitored for some or all the following features.

- Temperature
- Oxygen content
- Carbon Monoxide content
- Carbon dioxide content
- Sulphur dioxide content

The presence of carbon monoxide indicates that the fuel is not completely burned and energy is being wasted as unburned fuel.

The presence of oxygen is an indication of the excess air and the correct figure should be maintained.

The presence of carbon dioxide is another indication of the excess air and the correct figure should be maintained.

Sulphur dioxide is a pollutant and this indicates the quality of the fuel.

INSTRUMENTS

Old technology used an instrument called the Orsat Apparatus to analyse flue gas. This used chemical absorbents to determine the oxygen, carbon monoxide and carbon dioxide content of a flue gas (by volume).

Modern instruments like that shown here complete with its probe can measure the flue gas content and compute the combustion efficiency.

A fully controlled system would adjust the air/fuel ratio and match it to the load required. These principles are used in modern boilers and in engine management systems.



Figure 5

In the case of a boiler, the energy gained by the working fluid is the increase in enthalpy of the water or steam.

WORKED EXAMPLE No.13

A hot water boiler produces 0.24 kg/s of hot water at 80°C from cold water at 18°C. The boiler burns fuel oil at a rate of 1.6 g/s with a calorific value of 44 MJ/kg. Calculate the thermal efficiency of the boiler.

SOLUTION

The easiest way to find the increase in enthalpy of the water is to use the specific heat assumed to be 4.186 kJ/kg K.

$$\Phi = m c \Delta\theta = 0.24 \times 4.186 \times (80 - 18) = 62.29 \text{ kW}$$

$$\text{Heat released by combustion} = m_f \times \text{C.V.}$$

$$= 1.6 \times 10^{-3} \text{ (kg/s)} \times 44\,000 \text{ (kJ/kg)} = 70.4 \text{ kW}$$

$$\eta_{\text{th}} = (62.29/70.4) \times 100 = 88.5\%$$

WORKED EXAMPLE No.14

A steam boiler produces 0.2 kg/s at 50 bar and 400°C from water at 50 bar and 100°C. The boiler burns 5.3 m³/min of natural gas with a calorific value of 38 MJ/m³. Calculate the thermal efficiency of the boiler.

SOLUTION

The enthalpy of the steam produced is found in tables at 50 bar and 400°C.

$$h_2 = 3196 \text{ kJ/kg}$$

The enthalpy of the water is found as follows.

$$h_1 = \text{Flow energy} + \text{internal energy}$$

$$h_1 = (\text{pressure} \times \text{volume}) + 4186 \times \text{temp. } ^\circ\text{C.}$$

The volume of water is about 0.001 m³ per kg.

$$h_1 = 50 \times 10^5 \times 0.001 + 4186 \times 100 = 423600 \text{ J/kg or } 423.6 \text{ kJ/kg}$$

$$\text{Energy given to the water and steam} = m (h_2 - h_1) = 0.2 (3196 - 423.6) = 3111.3 \text{ kW}$$

$$\text{Energy from burning the fuel} = \text{Vol/s} \times \text{C.V.}$$

$$= (5.3/60)(\text{m}^3/\text{s}) \times 38\,000 \text{ (kJ/m}^3\text{)} = 3356.7 \text{ kW}$$

$$\eta_{\text{th}} = (3111.3/3356.7) \times 100 = 92.7\%$$

SELF ASSESSMENT EXERCISE No. 4 - ENERGY OF COMBUSTION

1. When solid sulphur is burned to form sulphur dioxide gas (SO_2), the enthalpy of reaction is -297 kJ/kmol . When burned to form sulphur trioxide gas (SO_3) it is -396 kJ/kmol . Determine the enthalpy of reaction when SO_2 gas is burned to form SO_3 gas. **(-99 kJ/kmol)**
2. A bomb calorimeter is used to determine the Higher Calorific Value of a coal sample. The mass of the sample is 0.98 g . The total equivalent mass of water is 1.32 kg . The increase in temperature after ignition is 5.7 K . Calculate the higher calorific value. **(32.14 MJ/kg)**
3. A Boy's calorimeter gave the following results.

Volume of gas burned (at standard conditions) = 0.004 m^3
Volume of water heated in the same time = 1.9 kg
Temperature rise of the water = 18.6 K
Specific heat of water = 4.186 kJ/kg K

Calculate the Higher calorific value. **(36.98 MJ/m^3)**
4. A hot water boiler produces 0.4 kg/s of hot water at 70°C from cold water at 10°C . The boiler burns fuel oil at a rate of 3.2 g/s with a calorific value of 44 MJ/kg . The specific heat of water is 4.186 kJ/kg K . Calculate the thermal efficiency of the boiler. **(71.4%)**
5. A steam boiler produces 3 kg/s at 70 bar and 500°C from water at 70 bar and 120°C . The boiler burns $17 \text{ m}^3/\text{min}$ of natural gas with a calorific value of 38 MJ/m^3 . Calculate the thermal efficiency of the boiler. **(80.8%)**