## PLANT and PROCESS PRINCIPLES

## COMBUSTION PROCESSES

This work covers Outcome 4 of the syllabus for the Edexcel HNC/D module Plant Process Principles 21725P and part of the Engineering Council Certificate Exam C106 Thermodynamic, Fluid and Process Engineering.

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:

$$
\begin{array}{ll}
\text { o } & \text { CARBON } \\
\text { o } & \text { HYDROGEN } \\
\text { o } & \text { SULPHUR }
\end{array}
$$

The heat released by 1 kg or $1 \mathrm{~m}^{3}$ 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 as follows.

|  | Symbol | Atomic Mass | Molecular Mass | Product |
| :--- | :--- | :--- | :--- | :--- |
|  |  |  |  | $\mathrm{CO}_{2}$ |
| Carbon | C | 12 | 2 | $\mathrm{H}_{2} \mathrm{O}$ |
| Hydrogen | $\mathrm{H}_{2}$ | 1 |  | $\mathrm{SO}_{2}$ |
| Sulphur | S | 32 | 32 |  |
| Oxygen | $\mathrm{O}_{2}$ | 16 | 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 $\mathrm{CO}_{2}$. The resulting products contain water $\mathrm{H}_{2} \mathrm{O}$. 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.

$$
\begin{array}{ll}
\text { CARBON } & \mathrm{C}+\mathrm{O}_{2}=\mathrm{CO}_{2} \\
\text { Mass ratio } & 12+32=44
\end{array}
$$

Hence 1 kg of C needs $32 / 12 \mathrm{~kg}$ of $\mathrm{O}_{2}$ and makes $44 / 12 \mathrm{~kg}$ of $\mathrm{CO}_{2}$

| HYDROGEN | $2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}$ |
| :--- | :--- |
| Mass ratio | $4+32=36$ |

Hence 1 kg of $\mathrm{H}_{2}$ needs 8 kg of $\mathrm{O}_{2}$ and makes 9 kg of $\mathrm{H}_{2} \mathrm{O}$

$$
\begin{gathered}
\text { SULPHUR } \quad \mathrm{S}+\mathrm{O}_{2}=\mathrm{SO}_{2} \\
32+32=64
\end{gathered}
$$

Hence 1 kg of S needs 1 kg of $\mathrm{O}_{2}$ and makes 2 kg of $\mathrm{SO}_{2}$.

### 2.2. GASEOUS FUELS.

Typical hydrocarbons are:

| Methane | $\mathrm{CH}_{4}$ |
| :--- | :--- |
| Ethane |  |
| Propane | $\mathrm{C}_{2} \mathrm{H}_{6}$ |
| Butane | $\mathrm{C}_{3} \mathrm{H}_{8}$ |
| Pentane | $\mathrm{C}_{4} \mathrm{H}_{10}$ |
| Hexane | $\mathrm{C}_{5} \mathrm{H}_{12}$ |
| Heptane | $\mathrm{C}_{6} \mathrm{H}_{14}$ |
| Octane | $\mathrm{C}_{4} \mathrm{H}_{16}$ |
| Ethene | $\mathrm{C}_{8} \mathrm{H}_{18}$ |
| Propene | $\mathrm{C}_{2} \mathrm{H}_{4}$ (Ethylene) |
| Ethyne | $\mathrm{C} 3_{3}$ (Propylene) |
| Benzenol | $\mathrm{C}_{2} \mathrm{H}_{2}$ (Acetylene) |
| Cyclohexane | $\mathrm{C}_{6} \mathrm{H}_{6}$ (Benzene) |
| $\mathrm{C}_{6} \mathrm{H}_{12}$ |  |

The combustion equation follows the following rule:

$$
\mathrm{C}_{\mathrm{a}} \mathrm{Hb}_{\mathrm{b}}+(\mathrm{a}+1 / 4 \mathrm{~b}) \mathrm{O}_{2}=(\mathrm{a}) \mathrm{CO}_{2}+(1 / 2 \mathrm{~b}) \mathrm{H}_{2} \mathrm{O}
$$

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 $\mathrm{C}_{8} \mathrm{H}_{18}$

## SOLUTION

$\mathrm{a}=8, \mathrm{~b}=18$
$\mathrm{CaHb}_{\mathrm{a}}+(\mathrm{a}+1 / 4 \mathrm{~b}) \mathrm{O}_{2}=(\mathrm{a}) \mathrm{CO}_{2}+(1 / 2 \mathrm{~b}) \mathrm{H}_{2} \mathrm{O}$
$\mathrm{C}_{8} \mathrm{H}_{18}+(8+18 / 4) \mathrm{O}_{2}=8 \mathrm{CO}_{2}+(18 / 2) \mathrm{H}_{2} \mathrm{O}$
$\mathrm{C}_{8} \mathrm{H}_{18}+12 \frac{1}{2} \mathrm{O}_{2}=8 \mathrm{CO}_{2}+9 \mathrm{H}_{2} \mathrm{O}$
$2 \mathrm{C}_{8} \mathrm{H}_{18}+25 \mathrm{O}_{2}=16 \mathrm{CO}_{2}+18 \mathrm{H}_{2} \mathrm{O}$

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:

$$
2 \mathrm{CO}+\mathrm{O}_{2}=2 \mathrm{CO}_{2}
$$

## 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.

## WORKED EXAMPLE No. 2

A fuel contains by mass $88 \% \mathrm{C}, 8 \% \mathrm{H}_{2}, 1 \% \mathrm{~S}$ and $3 \%$ ash (silica). Calculate the stoichiometric air.

## SOLUTION

CARBON $\quad \mathrm{C}+\mathrm{O}_{2}=\mathrm{CO}_{2}$
Mass ratio

$$
12+32=44
$$

Hence 0.88 kg of C needs ( $32 / 12$ ) $\mathrm{x} 0.88=2.347 \mathrm{~kg}$ of oxygen.
It makes (44/12) x $0.88=3.227 \mathrm{~kg}$ of carbon dioxide.
HYDROGEN

$$
2 \mathrm{H}_{2}+\mathrm{O}_{2}=2 \mathrm{H}_{2} \mathrm{O}
$$

Mass ratio
$4+32=36$
hence 0.08 kg of hydrogen needs $(32 / 4) \times 0.08=0.64 \mathrm{~kg}$ of oxygen.

$$
\begin{array}{ll}
\text { SULPHUR } & \mathrm{S}+\mathrm{O}_{2}=\mathrm{SO}_{2} \\
\text { Mass ratio } & 32+32=64
\end{array}
$$

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

TOTAL OXYGEN needed is $2.347+0.64+0.01=2.997 \mathrm{~kg}$
TOTAL AIR needed is $2.997 / 23 \%=13.03 \mathrm{~kg}$
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:

$$
120 \% \times 13.03=15.637 \mathrm{~kg}
$$

Oxygen is also $20 \%$ excess so $0.2 \times 2.997=0.599 \mathrm{~kg}$ is left over.
Nitrogen in the air is $77 \% \times 15.637=12.04 \mathrm{~kg}$
List of products :

| Nitrogen | $12.04 \mathrm{~kg}=75.8 \%$ |
| :--- | :--- |
| Carbon dioxide | $3.227 \mathrm{~kg}=20.3 \%$ |
| Sulphur dioxide | $0.02 \mathrm{~kg}=0.1 \%$ |
| Oxygen | $0.599 \mathrm{~kg}=3.8 \%$ |
| Total dry product | $15.886 \mathrm{~kg}=100 \%$ |

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 $18 \% \mathrm{H}_{2} \quad 2 \% \mathrm{~S}$
$30 \%$ 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 :
$75 \% \mathrm{C} 15 \% \mathrm{H}_{2} \quad 7 \% \mathrm{~S}$ remainder ash
Calculate the \% Carbon Dioxide present in the dry products if $20 \%$ excess air is supplied.
( $16.5 \% \mathrm{CO}_{2}$ )
3. Calculate the $\%$ of each dry product when coal is burned stoichiometrically in air. The analysis of the coal is:
$80 \% \mathrm{C} \quad 10 \% \mathrm{H}_{2} \quad 5 \% \mathrm{~S}$ and $5 \%$ ash.
( $76.7 \% \mathrm{~N}, 22.5 \% \mathrm{CO}_{2} \quad 0.8 \% \mathrm{SO}_{2}$ )

## 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 $\mathrm{O}_{2}$ and 2 kg of $\mathrm{H}_{2}$ and 28 kg of $\mathrm{N}_{2}$.

The molecular mass of a substance is expressed as $\mathrm{kg} / \mathrm{kmol}$ so the molecular mass of $\mathrm{O}_{2}$, for example, is $32 \mathrm{~kg} / \mathrm{kmol}$.

## Avogadro's Law states:

$1 \mathrm{~m}^{3}$ 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:

$$
\mathrm{pA}_{\mathrm{A}} \mathrm{~V}_{\mathrm{A}}=\mathrm{m}_{\mathrm{A}} \mathrm{R}_{\mathrm{O}} \mathrm{~T} / \tilde{\mathrm{N}}_{\mathrm{A}} \quad \mathrm{pB} V_{\mathrm{B}}=\mathrm{m}_{\mathrm{B}} \mathrm{R}_{\mathrm{o}} \mathrm{~T} / \tilde{\mathrm{N}}_{\mathrm{B}}
$$

$\tilde{\mathrm{N}}$ is the relative molecular mass.
$\mathrm{pA} / \mathrm{pB}=\mathrm{m}_{\mathrm{A}} \tilde{\mathrm{N}}_{\mathrm{B}} / \mathrm{m}_{\mathrm{B}} \tilde{\mathrm{N}}_{\mathrm{A}}=$ ratio of the kmol fractions.
pA and pB are the partial pressures.
$\mathrm{V}_{\mathrm{A}}$ and $\mathrm{V}_{\mathrm{B}}$ 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 $\quad \mathrm{VA}_{\mathrm{A}} / \mathrm{VB}_{\mathrm{B}}=\mathrm{pA}^{2} / \mathrm{pB}$


Figure 1

When not mixed the pressure is $p$ and the volumes are $V_{A}$ and $V_{B}$. Hence:
$\mathrm{pV}_{\mathrm{A}} / \mathrm{T}=\mathrm{mR}_{\mathrm{o}} / \tilde{\mathrm{N}}_{\mathrm{A}}$
$\mathrm{p}=\mathrm{m}_{\mathrm{A}} \mathrm{R}_{\mathrm{o}} \mathrm{T} / \tilde{N}_{\mathrm{A}} \mathrm{V}_{\mathrm{A}}$
$\mathrm{p} V_{\mathrm{B}} / \mathrm{T}=\mathrm{mR}_{\mathrm{o}} / \tilde{\mathrm{N}}_{\mathrm{B}}$
$\mathrm{p}=\mathrm{mB}_{\mathrm{B}} \mathrm{R}_{\mathrm{o}} \mathrm{T} / \tilde{N}_{\mathrm{B}} V_{\mathrm{B}}$
Since (1) $=(2)$ then:
$\mathrm{m}_{\mathrm{A}} / \tilde{\mathrm{N}}_{\mathrm{A}} \mathrm{V}_{\mathrm{A}}=\mathrm{mB}_{\mathrm{B}} / \tilde{\mathrm{N}}_{\mathrm{B}} \mathrm{V}_{\mathrm{B}}$ and so $\mathrm{V}_{\mathrm{A}} / \mathrm{V}_{\mathrm{B}}=\left(\mathrm{m}_{\mathrm{A}} / \tilde{\mathrm{N}}_{\mathrm{A}}\right)\left(\mathrm{m}_{\mathrm{B}} / \tilde{\mathrm{N}}_{\mathrm{B}}\right)$ 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:

$$
\begin{align*}
& \mathrm{pA}_{\mathrm{A}}=\mathrm{m}_{\mathrm{A}} \mathrm{R}_{\mathrm{o}} \mathrm{~T} / \tilde{\mathrm{N}}_{\mathrm{A}} \mathrm{~V}_{\ldots} . . . . . .(3)  \tag{4}\\
& \mathrm{pB}=\mathrm{m}_{\mathrm{B}} \mathrm{R}_{\mathrm{o}} \mathrm{~T} / \tilde{\mathrm{N}}_{\mathrm{B}} \mathrm{~V}_{. .} . \ldots \ldots . . .(4)
\end{align*}
$$

(3)/(1) gives $\mathrm{pA}_{\mathrm{A}} / \mathrm{p}=\mathrm{V}_{\mathrm{A}} / \mathrm{V}$ and (4)/(2) gives $\mathrm{pB} / \mathrm{p}=\mathrm{V}_{\mathrm{B}} / \mathrm{V}$

Hence

$$
\mathrm{VA}_{\mathrm{A}} / \mathrm{VB}_{\mathrm{B}}=\mathrm{pA} / \mathrm{pB}
$$

Consider the combustion of Methane. $\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
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 $1 \mathrm{~m}^{3}$ of methane we need $9.52 \mathrm{~m}^{3}$ of air for stoichiometric combustion. If the products are at the same p and $T$ as the original reactants, we would obtain $1 \mathrm{~m}^{3}$ of carbon dioxide and $2 \mathrm{~m}^{3}$ of water vapour which would probably condense and cause a reduction in volume and/or pressure.

## WORKED EXAMPLE No. 4

Calculate the $\% \mathrm{CO}_{2}$ in the dry products when methane is burned with $15 \%$ excess air by volume.

## SOLUTION

$\begin{array}{llllll}\text { Volume ratio } & 1 & 2 & 1 & 2\end{array}$
The stoichiometric air is $2 / 21 \%=9.524 \mathrm{~m}^{3}$
The actual air is $9.524 \times 115 \%=10.95 \mathrm{~m}^{3}$
Analysis of dry products:

| Nitrogen | $79 \% \times 10.95$ |
| :--- | :--- |
| Carbon Dioxide | $8.65 \mathrm{~m}^{3}$ |
| Oxygen $15 \% \times 2$ | $1.00 \mathrm{~m}^{3}$ |
| Total | $0.30 \mathrm{~m}^{3}$ |
|  | $9.95 \mathrm{~m}^{3}$ |

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 $1 \mathrm{~m}^{3}$ 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 $1 \mathrm{~m}^{3}$ of methane is $2 \mathrm{~m}^{3}$.To burn $0.6 \mathrm{~m}^{3}$ needs $1.2 \mathrm{~m}^{3}$ of oxygen. For carbon monoxide we use the combustion equation:

$$
2 \mathrm{CO}+\mathrm{O}_{2}=2 \mathrm{CO}_{2}
$$

Hence to burn $1 \mathrm{~m}^{3}$ of CO need $0.5 \mathrm{~m}^{3}$ of oxygen, so to burn $0.3 \mathrm{~m}^{3}$ needs $0.15 \mathrm{~m}^{3}$ of oxygen.

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

## 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 :
$5 \% \mathrm{CO}_{2}, 40 \% \mathrm{H}_{2}, 40 \% \mathrm{CH}_{4}, 15 \% \mathrm{~N}_{2}$
Determine the stoichiometric air and the \% content of each dry product. ( $4.76 \mathrm{~m}^{3}, 89.7 \%, \mathrm{~N}_{2} 10.3 \% \mathrm{CO}_{2}$ ).

## 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.
$\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O}$
1 vol 2 vol 1 vol 2 vols

## SOLUTION

Let the excess air be x (as a decimal)
The stoichiometric air is 9.52 vols. Actual air is $9.52(1+\mathrm{x})$
Dry Products:

| Nitrogen | $0.79 \times 9.52(1+\mathrm{x})=$ | $7.524 \mathrm{x}+7.524$ |
| :--- | :--- | :--- |
| Oxygen |  | 2.000 x |
| Carbon Dioxide |  | $9.524 \mathrm{x}+8.524$ |

$\%$ Carbon monoxide $=100\{1 /(9.524 \mathrm{x}+8.524)\}$
\% Oxygen $\quad=100\{2 /(9.524 \mathrm{x}+8.524)\}$
For example if the $\% \mathrm{CO}_{2}$ is $10 \%$ then the excess air is found as follows:

$$
\begin{aligned}
& 10 \%=100\{1 /(9.524 \mathrm{x}+8.524)\} \\
& 0.1=1 /(9.524 \mathrm{x}+8.524) \\
& (9.524 \mathrm{x}+8.524)=10 \\
& 9.524 \mathrm{x}=1.476 \\
& \mathbf{x}=\mathbf{0 . 1 5 5} \text { or } \mathbf{1 5 . 5 \%}
\end{aligned}
$$

Similarly if the $\mathrm{O}_{2}$ 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 $90 \% \mathrm{C}$ and $10 \% \mathrm{H}_{2}$ by mass. Assuming complete combustion, determine the air/fuel ratio used.

## SOLUTION

1 kg of fuel contains 0.9 kg of C and 0.1 kg of $\mathrm{H}_{2}$. Converting these into kmol we have $0.9 / 12 \mathrm{kmol}$ of C and $0.1 / 2 \mathrm{kmol}$ of $\mathrm{H}_{2}$. For 1 kmol of dry exhaust gas we have :

> 0.15 kmol of $\mathrm{CO}_{2}$
> Y kmol of excess $\mathrm{O}_{2}$

$$
1-0.15-\mathrm{Y}=0.85-\mathrm{Y} \mathrm{kmol} \text { of } \mathrm{N}_{2}
$$

1 kmol of $\mathrm{CO}_{2}$ is 44 kg
1 kmol of $\mathrm{N}_{2}$ is 28 kg
1 kmol of O is 32 kg
0.15 kmol of $\mathrm{CO}_{2}$ is 0.15 x 44 kg

This contains ( $12 / 44$ ) carbon so the carbon present is $0.15 \times 12 \mathrm{~kg}$
The carbon in the fuel is 0.9 kmol per kmol of fuel. Hence the number of kmols of DEG must be $0.9 /(.15 \times 12)=0.5$

There are 0.5 kmol of DEG for each kmol of fuel burned.
The Nitrogen present in the DEG is $0.85-\mathrm{Y}$ 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 :
$(23.3 / 76.7) \times 28 \times(0.85-\mathrm{Y})=7.24-8.5 \mathrm{Y} \mathrm{kg}$ per kmol of DEG.
(using precise proportions of air for accuracy).
The oxygen contained within the carbon dioxide is:
$(32 / 44) \times 0.15 \times 44=4.8 \mathrm{~kg}$ per kmol DEG
1 kmol of $\mathrm{CO}_{2}$ contains 44 kg and $32 / 44$ of this is oxygen. The oxygen in the $\mathrm{CO}_{2}$ is hence $32 \times 0.15 \mathrm{~kg}$ per kmol DEG.

The excess oxygen is
32 Y kg per kmol DEG

Total oxygen in the products excluding that used to make $\mathrm{H}_{2} \mathrm{O}$ is :

$$
32 \times 0.15+32 Y
$$

The oxygen used to burn hydrogen is hence :

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

$\mathrm{O}_{2}$ used to burn $\mathrm{H}_{2}$ is

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

For 0.5 kmol this is

$$
1.22-20.25 \mathrm{Y} \mathrm{~kg}
$$

To burn hydrogen requires oxygen in a ratio of $8 / 1$. There is 0.1 kg of $\mathrm{H}_{2}$ in each kmol of fuel so 0.8 kg of $\mathrm{O}_{2}$ is needed. Hence :

$$
\begin{aligned}
& 0.8=1.22-20.25 \mathrm{Y} \\
& \mathrm{Y}=0.208 \mathrm{kmol} \text { per } \mathrm{kmol} \mathrm{DEG}
\end{aligned}
$$

The nitrogen in the DEG is $0.85-\mathrm{Y}=0.642 \mathrm{kmol}$ per kmol DEG
The actual Nitrogen $=0.642 \times 0.5 \times 28=11.61 \mathrm{~kg}$
The air supplied must be $11.61 / .767=15.14 \mathrm{~kg}$ 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 $86.2 \% \mathrm{C}, 12.8 \% \mathrm{H}_{2}$ and $0.9 \% \mathrm{~S}$ by mass. The dry exhaust gas contains $9 \% \mathrm{CO}_{2}$ by volume. Calculate the excess air by mass.

## SOLUTION

| CARBON | $\mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$ |
| :--- | :--- |
| Mass ratio | $12+32 \rightarrow 44$ |
|  | $0.862+2.299 \rightarrow 3.16$ |
| HYDROGEN | $2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ |
| Mass ratio | $4+32 \rightarrow 36$ |
|  | $0.128+1.024 \rightarrow 1.152$ |
| SULPHUR | $\mathrm{S}+\mathrm{O}_{2} \rightarrow \mathrm{SO}_{2}$ |
| Mass ratio | $32+32 \rightarrow 64$ |
|  | $0.09+0.09 \rightarrow 0.18$ |

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

|  |  | \% of total |
| :--- | :--- | :--- |
| $\mathrm{CO}_{2}$ | 3.16 kg | $316 / \mathrm{T}$ |
| $\mathrm{O}_{2}$ | 3.413 xkg | $341.3 \mathrm{x} / \mathrm{T}$ |
| $\mathrm{SO}_{2}$ | 0.18 | $18 / \mathrm{T}$ |
| $\mathrm{N}_{2}$ | $11.23(1+\mathrm{x})$ | $1123(1+\mathrm{x}) / \mathrm{T}$ |
| $\mathrm{Total}=\mathrm{T}=3.34+3.413 \mathrm{x}+11.23(1+\mathrm{x})$ |  |  |

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

```
CO2 316/44T = 7.18/T
O2
    341.3x/32T = 10.67x/T
SO2
    18/64T = 0.56/T
N2
    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)
%CO2 = 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
50.78x=79.78-47.85=31.92
x = 0.63
```

Answer the \% excess air is $63 \%$

## SELF ASSESSMENT EXERCISE No. 3 - EXCESS AIR.

1. $\mathrm{C}_{2} \mathrm{H}_{6}$ is burned in a boiler and the dry products are found to contain $8 \% \mathrm{CO}_{2}$ 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 $85 \% \mathrm{C}$ and $15 \% \mathrm{H}_{2}$ ( $21.5 \mathrm{~kg}, 44.5 \%$ )
3. A fuel oil contains by mass $85 \% \mathrm{C}$ and $15 \% \mathrm{H}_{2}$. The dry exhaust gas contains $11 \%$ $\mathrm{CO}_{2}$ 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 $\Delta \mathrm{h}$

In simple terms we may say: $h($ reactants $)=h($ products $)+\Delta h_{o}$
Since $h($ products $)>h($ reactants $)$ it follows that $\Delta h_{0}$ 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 $\Delta h_{o}$ for various reactants may be found in standard tables. These are normally stated for 1 kmol of substance at $25^{\circ} \mathrm{C}$. We will be more practical here and quote values for 1 kg (solid and liquid fuels) and $1 \mathrm{~m}^{3}$ 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 $25^{\circ} \mathrm{C}$. If this energy is added we get the Higher Calorific Value (H.C.V.). Typical L.C.V.s are as follows.

$$
\begin{array}{ll}
\text { Coal } & 30-36 \mathrm{MJ} / \mathrm{kg} \\
\text { Fuel Oils } & 43-46 \mathrm{MJ} / \mathrm{kg} \\
\text { Natural Gas } & 38 \mathrm{MJ} / \mathrm{m}^{3}
\end{array}
$$

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 $\Delta h_{o}$ (energy released) when a particular chemical reaction takes place. The law states "if a reaction is carried out in a series of steps, $\Delta \mathrm{h}_{\mathrm{o}}$ 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 $\mathrm{CH}_{4}$ in its gaseous form is completely burned to form $\mathrm{CO}_{2}$ and $\mathrm{H}_{2} \mathrm{O}$ (both in the gaseous form) the enthalpy of reaction is $-802.3 \mathrm{~kJ} / \mathrm{kmol}$. When vapour is condensed to water at standard conditions the energy released is $87.98 \mathrm{~kJ} / \mathrm{kmol}$. Determine the H.C.V. for methane gas.

## SOLUTION

$\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O}$ (vapour) all gas $\Delta \mathrm{h}_{\mathrm{o}}=-802.3 \mathrm{MJ} / \mathrm{kmol}$. (L.C.V.)
$\mathrm{H}_{2} \mathrm{O}$ (Vapour) $\rightarrow \mathrm{H}_{2} \mathrm{O}$ (liquid) $\quad \Delta \mathrm{h}_{\mathrm{o}}=-43.99 \mathrm{MJ} / \mathrm{kmol}$.
We need the figure for two atoms of water.

$$
\begin{array}{ll}
2 \mathrm{H}_{2} \mathrm{O} \text { (Vapour) } \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \text { (liquid) } & \Delta \mathrm{h}=2 \times(-43.99)=-87.98 \mathrm{MJ} / \mathrm{kmol} . \\
\mathrm{CH}_{4}+2 \mathrm{O}_{2}=\mathrm{CO}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \text { (liquid) } & \Delta \mathrm{h}_{\mathrm{o}}=-802.3+(-87.98) \\
& \Delta \mathrm{h}_{\mathrm{o}}=-890.28 \mathrm{MJ} / \mathrm{kmol} \text {. (H.C.V.) }
\end{array}
$$

## PARTIAL COMBUSTION

If a substance is partially burned, energy E1 is released.
If the partially burned substance is then completely burned the energy released is E2.
If the substance is completely burned in one step, the energy released is $\mathrm{E}=\mathrm{E} 1+\mathrm{E} 2$.

## WORKED EXAMPLE No. 10

The enthalpy of reaction for solid carbon being burned to form carbon monoxide gas is $-110 \mathrm{~kJ} / \mathrm{kmol}$.

The enthalpy of reaction for solid carbon into carbon dioxide gas is $-393 \mathrm{~kJ} / \mathrm{mol}$.
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.
$\mathrm{C}+\mathrm{O} \rightarrow \mathrm{CO}$
$\Delta \mathrm{h}_{\mathrm{o}}=-110 \mathrm{~kJ} / \mathrm{kmol}$. (E1)
$\mathrm{C}+\mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$
$\Delta \mathrm{h}_{\mathrm{o}}=-393 \mathrm{~kJ} / \mathrm{kmol}$. (E3)
$\mathrm{CO}+1 / 2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}$
$\Delta h_{0}=-393-(-110)=-283 \mathrm{~kJ} / \mathrm{kmol}$. (E2) (Answer)

## 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 though 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 $\Delta \mathrm{T}$.


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 $\mathrm{H}_{2} \mathrm{O}$ is condensed to water.
$\mathrm{M}_{\mathrm{f}}=$ mass of fuel.
$\mathrm{M}_{\mathrm{w}}=$ total effective mass of water.
$\mathrm{c}=$ specific heat capacity of water.
Higher Calorific value $=\mathrm{M}_{\mathrm{w}} \mathrm{C} \Delta \mathrm{T} / \mathrm{m}_{\mathrm{f}}$

## 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 1.32 kg . The increase in temperature after ignition is 7.8 K . Calculate the higher calorific value. The specific heat of water is $4.186 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$.

## SOLUTION

H.C.V $=\mathrm{M}_{\mathrm{w}} \mathrm{C} \Delta \mathrm{T} / \mathrm{m}_{\mathrm{f}}=1.32 \mathrm{X} 4.186 \times 7.8 / 0.00101=42672 \mathrm{~kJ} / \mathrm{kg}$ or $42.672 \mathrm{MJ} / \mathrm{kg}$

## 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 $=\mathrm{M}_{\mathrm{w}} \mathrm{c} \Delta \mathrm{T}$
Assuming $100 \%$ efficiency we may equate and get H.C.V. $=\left(\mathrm{M}_{\mathrm{w}} \mathrm{c} \Delta \mathrm{T}\right) / \mathrm{Volume}$ 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) $=0.004 \mathrm{~m}^{3}$
Volume of water heated in the same time $=1.8 \mathrm{~kg}$
Temperature rise of the water $=20.17 \mathrm{~K}$
Specific heat of water $=4.186 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$
Calculate the Higher calorific value.

## SOLUTION

H.C.V. $=\left(\mathrm{M}_{\mathrm{w}} \mathrm{c} \Delta \mathrm{T}\right) /$ Volume of gas $=(1.8 \times 4.186 \times 20.17) / 0.004=38000 \mathrm{~kJ} / \mathrm{m}^{3}$

## COMBUSTION EFFICIENCY

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

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

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 $0.24 \mathrm{~kg} / \mathrm{s}$ of hot water at $80^{\circ} \mathrm{C}$ from cold water at $18^{\circ} \mathrm{C}$. The boiler burns fuel oil at a rate of $1.6 \mathrm{~g} / \mathrm{s}$ with a calorific value of $44 \mathrm{MJ} / \mathrm{kg}$. 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 $4.186 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$.
$\Phi=\mathrm{mc} \Delta \theta=0.24 \times 4.186 \mathrm{x}(80-18)=62.29 \mathrm{~kW}$
Heat released by combustion $=m_{f} \times$ C.V.
$=1.6 \times 10^{-3}(\mathrm{~kg} / \mathrm{s}) \times 44000(\mathrm{~kJ} / \mathrm{kg})=70.4 \mathrm{~kW}$
$\eta_{\text {th }}=(62.29 / 70.4) \times 100=88.5 \%$

## WORKED EXAMPLE No. 14

A steam boiler produces $0.2 \mathrm{~kg} / \mathrm{s}$ at 50 bar and $400^{\circ} \mathrm{C}$ from water at 50 bar and $100^{\circ} \mathrm{C}$. The boiler burns $5.3 \mathrm{~m}^{3} / \mathrm{min}$ of natural gas with a calorific value of $38 \mathrm{MJ} /$ $\mathrm{m}^{3}$. Calculate the thermal efficiency of the boiler.

## SOLUTION

The enthalpy of the steam produced is found in tables at 50 bar and $400^{\circ} \mathrm{C}$.
$\mathrm{h}_{2}=3196 \mathrm{~kJ} / \mathrm{kg}$
The enthalpy of the water is found as follows.
$\mathrm{h}_{1}=$ Flow energy + internal energy
$\mathrm{h}_{1}=($ pressure x volume $)+4186 \mathrm{x}$ temp. ${ }^{\circ} \mathrm{C}$.
The volume of water is about $0.001 \mathrm{~m}^{3}$ per kg .
$\mathrm{h}_{1}=50 \times 10^{5} \times 0.001+4186 \times 100=423600 \mathrm{~J} / \mathrm{kg}$ or $423.6 \mathrm{~kJ} / \mathrm{kg}$
Energy given to the water and steam $=m\left(h_{2}-h_{1}\right)=0.2(3196-423.6)=3111.3 \mathrm{~kW}$
Energy from burning the fuel $=\mathrm{Vol} / \mathrm{s} \times \mathrm{C} . \mathrm{V}$.
$=(5.3 / 60)\left(\mathrm{m}^{3} / \mathrm{s}\right) \times 38000\left(\mathrm{~kJ} / \mathrm{m}^{3}\right)=3356.7 \mathrm{~kW}$
$\eta_{\text {th }}=(3111.3 / 3356.7) \times 100=92.7 \%$

## SELF ASSESSMENT EXERCISE No. 4 - ENERGY OF COMBUSTION

1. When solid sulphur is burned to form sulphur dioxide gas $\left(\mathrm{SO}_{2}\right)$, the enthalpy of reaction is $-297 \mathrm{~kJ} / \mathrm{kmol}$. When burned to form sulphur trioxide gas $\left(\mathrm{SO}_{3}\right)$ it is -396 $\mathrm{kJ} / \mathrm{kmol}$. Determine the enthalpy of reaction when $\mathrm{SO}_{2}$ gas is burned to form $\mathrm{SO}_{3}$ 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. ( $32.14 \mathrm{MJ} / \mathrm{kg}$ )
3. A Boy's calorimeter gave the following results.

Volume of gas burned (at standard conditions) $=0.004 \mathrm{~m}^{3}$
Volume of water heated in the same time $=1.9 \mathrm{~kg}$
Temperature rise of the water $=18.6 \mathrm{~K}$
Specific heat of water $=4.186 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$
Calculate the Higher calorific value. ( $36.98 \mathrm{MJ} / \mathrm{m}^{3}$ )
4. A hot water boiler produces $0.4 \mathrm{~kg} / \mathrm{s}$ of hot water at $70^{\circ} \mathrm{C}$ from cold water at $10^{\circ} \mathrm{C}$. The boiler burns fuel oil at a rate of $3.2 \mathrm{~g} / \mathrm{s}$ with a calorific value of $44 \mathrm{MJ} / \mathrm{kg}$. The specific heat of water is $4.186 \mathrm{~kJ} / \mathrm{kg} \mathrm{K}$.
Calculate the thermal efficiency of the boiler. (71.4 \%)
5. A steam boiler produces $3 \mathrm{~kg} / \mathrm{s}$ at 70 bar and $500^{\circ} \mathrm{C}$ from water at 70 bar and $120^{\circ} \mathrm{C}$. The boiler burns $17 \mathrm{~m}^{3} / \mathrm{min}$ of natural gas with a calorific value of $38 \mathrm{MJ} /$ $\mathrm{m}^{3}$. Calculate the thermal efficiency of the boiler. (80.8\%)

