Corrections

Corrections

- For accurate results the following corrections are also incorporated

1. Fuse wire correction
2. Acid correction
3. Cooling correction

1. Fuse wire correction

Fuse wire correction:

Heat liberated during sparking should be subtracted from calorific value

Fuse wire correction:

1) **As Mg wire is used for ignition, the heat generated by burning of Mg wire is also included in the gross calorific value.**

2) **Hence, this amount of heat has to be subtracted from the total value.**

2. Acid correction

Acid correction:

Fuels containing Sulphur and Nitrogen if oxidized, the heats of formation of H_2SO_4 and HNO_3 should be subtracted (as the acid formations are exothermic reactions)

Acid correction:

During combustion, sulphur and nitrogen present in the fuel are oxidized to their corresponding acids under high pressure and temperature condition.

$$S + O_2 \rightarrow SO_2$$

$$2SO_2 + O_2 + 2H_2O \rightarrow 2H_2SO_4 \qquad \Delta H = -144{,}000 \text{ cal}$$

$$2N_2 + 5O_2 + 2H_2O \rightarrow 4HNO_3 \qquad \Delta H = -57{,}160{,}000 \text{ cal}$$

2. Acid correction (Cont.)

- The corrections must be made for the heat liberated in the 'bomb calorimeter' by the formation of H_2SO_4 and HNO_3.
- The amount of H_2SO_4 and HNO_3 is analyzed by washings of the calorimeter.
  - For each mL of 0.1 N H_2SO_4 formed, 3.6 calories should be subtracted.
  - For each mL of 0.01N HNO_3 formed, 1.43 calories should be subtracted.

3. Cooling correction:

Cooling correction:

The rate of cooling of the calorimeter from maximum temperature to room temperature is noted. From this rate of cooling [*i.e.* dt (°C/min)] and the actual time taken for cooling (X min) then correction (dt × X) is called cooling correction and is added to the $(t_2 - t_1)$ term.

If the time taken for the water in the calorimeter to cool down from the maximum temperature attained to the room temperature	**=**	**"X" minutes**
Rate of cooling	**=**	**dt (°C/min)**
Cooling correction	**=**	**X × dt**

This should be added to the observed rise in temperature

Calculation after correction

- **HCV - Before corrections**

$$\text{HCV} = \frac{(W+w)(t_2-t_1)}{m}\ \text{cal/g}$$

- **HCV – After corrections**

$$\text{HCV} = \frac{(W+w)[(t_2-t_1) + \text{Cooling correction}] - (\text{Acid correction} + \text{Fuse correction})}{m}\ \text{cal/g}$$

Numerical - Problem

A sample of coal contains C = 93%; H = 6% and ash = 1%. The following data were obtained when the above coal was tested in bomb calorimeter.

Weight of coal burnt	**=**	**0.92 g**
Weight of water taken	**=**	**550 g**
Water equivalent of calorimeter	**=**	**2,200 g**
Rise in temperature	**=**	**2.42 °C**
Fuse wire correction	**=**	**10.0 cal**
Acid correction	**=**	**50.0 cal**

Calculate gross and net calorific value of the coal, assuming the latent heat of condensation of steam as 580 cal/g.

Numerical - Solution

Weight of coal burnt	=	m	=	0.92 g
Weight of water taken	=	W	=	550 g
Water equivalent of calorimeter	=	w	=	2,200 g
Rise in temperature	=	(t_2-t_1)	=	2.42 °C
Fuse wire correction	=		=	10.0 cal
Acid correction	=		=	50.0 cal
Latent heat of steam	=		=	580 cal
Percentage of hydrogen	=	H	=	6%

Numerical – Solution (Cont.)

(a)

$$\text{GCV} = \frac{(W+w)(t_2-t1) - (\text{Acid correction}+\text{Fuse correction})}{m}\ \text{cal/g}$$

$$= \frac{(550+2{,}200) \times (2.42) - (50+10)}{0.92}\ \text{cal/g}$$

$$= 7{,}168.5\ \text{cal/g}$$

(b)

NCV = [GCV – 0.09 × H × latent heat steam]

= (7168.5 – 0.09 × 6 × 580) cal/g

= 6855.3 cal/g

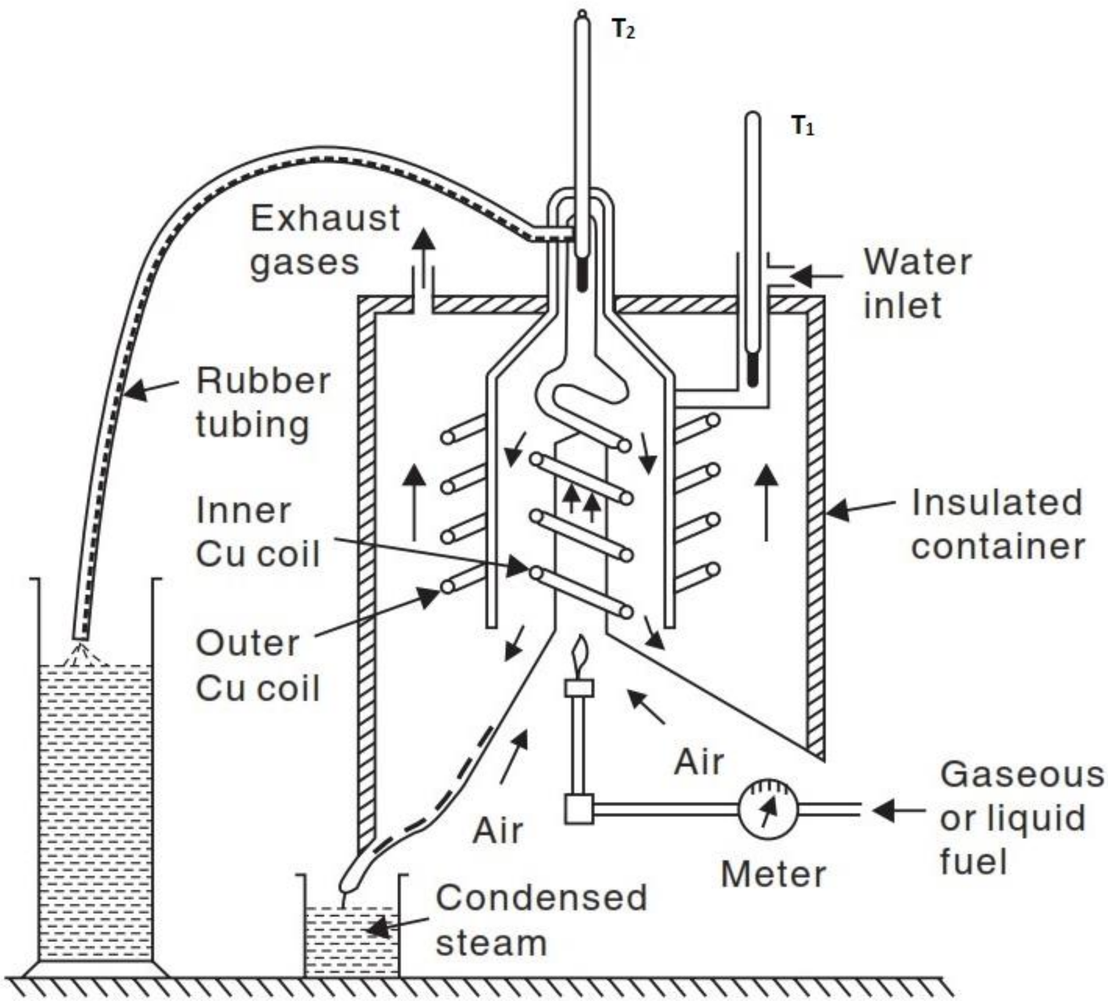
Boy's Calorimeter - Principle

It is used for measuring the calorific value of gaseous (or) liquid fuels.

Principle

- A known volume of gaseous fuel sample is burnt in the combustion chamber of a Boy's calorimeter.
- The released heat is quantitatively absorbed by cooling water, circulated through copper coils surrounding the combustion chamber.
- The mass of cooling water and its rise in temperature are noted.
- The mass of water produced by condensation of steam is calculated.
- The calorific value of the fuel sample is then calculated from these data.

Boy's Calorimeter



Boy's gas calorimeter

Boy's Calorimeter - Construction

Construction

Boy's calorimeter consists of a combustion chamber surrounded by water tube with two thermometers T_1 and T_2 attached. There is a burner in the chamber, which is connected to a gas tube.

Working

- A known volume of water is passed through the tubes.
- The initial temperature is noted when the two thermometers show the same constant temperature.
- A known volume of the gas (measured using a meter) is passed through the tube and burnt in the combustion chamber.
- The heat liberated is absorbed by the water in the tubes.
- The final temperature of water is noted.
- The gaseous products are cooled and condensed into a measuring jar.

Boy's Calorimeter - Calculation

$$\textbf{HCV (or) GCV} = W \times S \times \frac{(T_2 \quad T1)}{V}$$

$$\textbf{LCV (or) NCV} = \left(GCV - \frac{m \times 587}{V} \right)$$

V	=	Volume of the gas burns at STP in certain time (t)
W	=	Mass of the cooling water used in time (t)
T_1	=	Temperature of inlet water
T_2	=	Temperature of outgoing water
m	=	Amount of water collected from condensation in time (t)
S	=	Specific heat of water

Specific heat of water = 1 cal/g °C

Determination of calorific value

Determination of calorific value

- **Experimental methods**
  1. Bomb calorimeter
  2. Boy's calorimeter

- **Theoretical method**
  - Dulong's formula

    (or)
  - I.A. Davies formula

- The calorific value of fuels (e.g. Coal) is determined theoretically by Dulong's formula or I.A. Davies formula

Dulong's Formula

- The approximate calorific value of a fuel can be determined by knowing the amount of constituents present:
- Gross or higher calorific value (HCV) from elemental constituents of a fuel.

  H = 34500 kcal/kg; C = 8080 kcal/kg; S = 2240 kcal/kg

- Oxygen present in the fuel is assumed to be present as water (fixed hydrogen).

  Available Hydrogen = Total hydrogen - Fixed hydrogen

  = Total hydrogen - 1/8 mass of oxygen in fuel

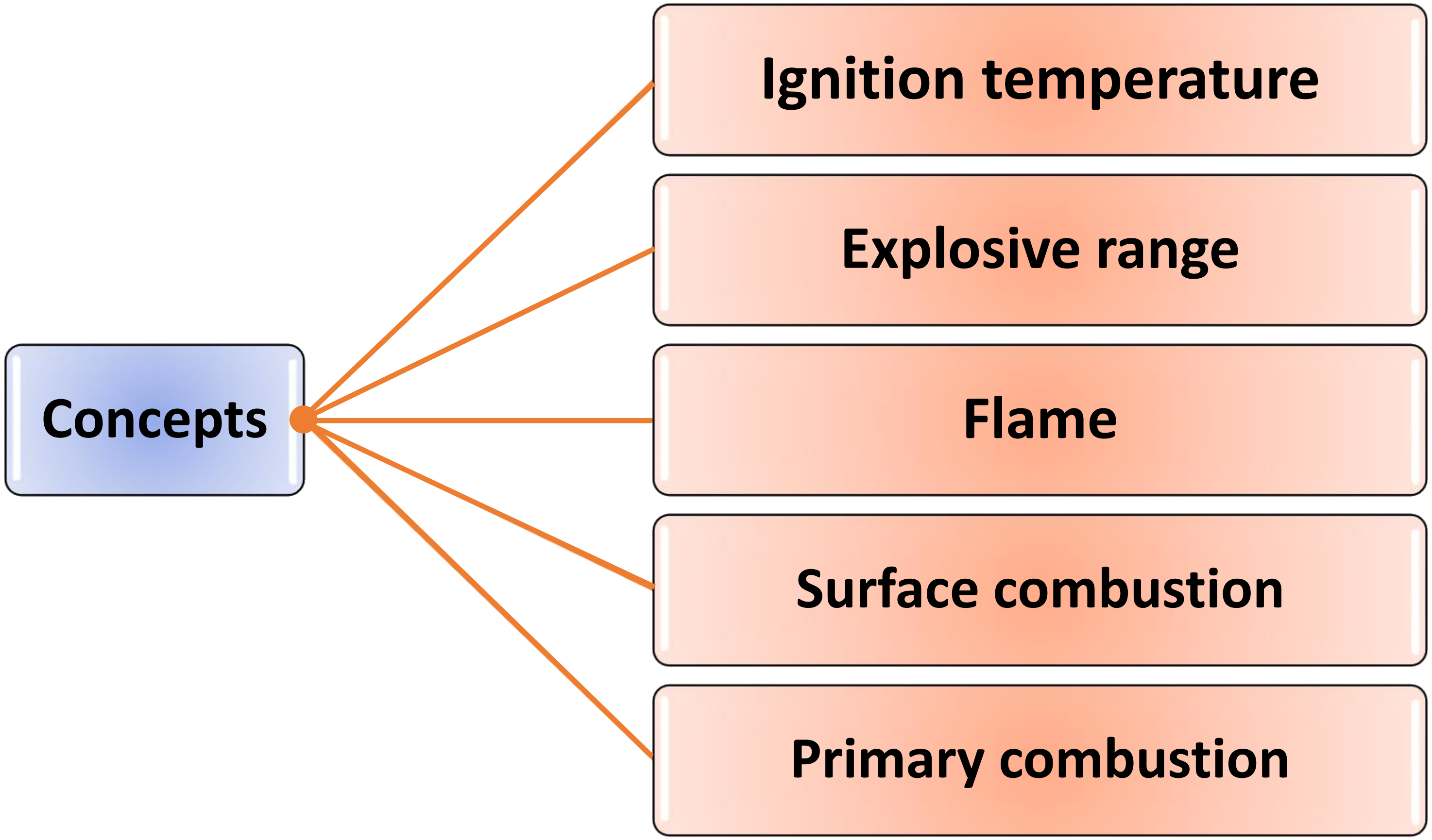
- Dulong's formula for calorific value from the chemical composition of fuel is,

$$\mathrm{HCV} = \frac{1}{100}\left[8080\,\mathrm{C} + 34500\left(\mathrm{H} - \frac{\mathrm{O}}{8}\right) + 2240\,\mathrm{S}\right] \text{ kcal/kg}$$

Combustion of Fuel

Combustion

- **Combustion** is a process in which oxygen from the air reacts with the elements or compounds to give heat.



Combustion

- As the elements or compounds combine in definite proportions with oxygen, we need to calculate what is ***minimum oxygen or air required*** for the complete combustion of compounds.
- The commonly involved combustion reactions are;

i)	C	+	O_2	$\rightarrow$	CO_2
ii)	$2H_2$	+	O_2	$\rightarrow$	$2H_2O$
iii)	S	+	O_2	$\rightarrow$	SO_2
iv)	$2CO$	+	O_2	$\rightarrow$	$2CO_2$
v)	CH_4	+	$2O_2$	$\rightarrow$	$CO_2 + 2H_2O$
vi)	$2C_2H_6$	+	$7O_2$	$\rightarrow$	$4CO_2 + 6H_2O$
vii)	$2C_2H_2$	+	$5O_2$	$\rightarrow$	$4CO_2 + 2H_2O$

Combustion - Calculation of air quantities

✓ Substances always combine in definite proportions.

C (s)	+	O_2 (g)	$\rightarrow$	CO_2 (g)
12		32		44

✓ Air contains 21% of oxygen by volume & 23% of oxygen by mass.

1 kg of oxygen is supplied by $\frac{1 \times 100}{23}$ = 4.35 kg of air

1 m^3 of oxygen is supplied by $\frac{1 \times 100}{21}$ = 4.76 m^3 of air

✓ 28.94 g/mol is taken as the molecular mass of air

- Since air has 23% by weight or 21% by volume of oxygen

- Minimum weight of air needed for complete combustion = Net O_2 x 100/23 g
- Minimum volume of air needed for complete combustion = Net O_2 x 100/21 g

Combustion calculation procedure

Combustion equation	Wt. of Oxygen needed	Vol. Of Oxygen needed
$C + O_2 \rightarrow CO_2$ "x" g or m^3	$x \times 1 \times \frac{32}{12}$	$x \times 1$
$H_2 + 0.5\ O_2 \rightarrow H_2O$ "y" g or m^3	$y \times 0.5 \times \frac{32}{2}$	$y \times 0.5$
$CO + 0.5\ O_2 \rightarrow CO_2$ "z" g or m^3	$z \times 0.5 \times \frac{32}{28}$	$z \times 0.5$
$S + O_2 \rightarrow SO_2$ "p" g or m^3	$p \times 1 \times \frac{32}{32}$	$p \times 1$
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2H_2O$ "q" g or m^3	$q \times 2 \times \frac{32}{16}$	$q \times 2$
$C_2H_6 + 3.5\ O_2 \rightarrow 2CO_2 + 3H_2O$ "r" g or m^3	$r \times 3.5 \times \frac{32}{30}$	$r \times 3.5$

Combustion- Numerical problem

Question: How much air is required to burn 1 kg of pure carbon?

Solution: M. Wt. of O_2 = 32

This reacts with C, M. Wt. = 12

C (s)	**+**	**O_2 (g)**	**$\rightarrow$**	**CO_2 (g)**
12		**32**		**44**
x = 1000 g		**m_{Oxygen} = ?**		

$$\text{Wt. of Oxygen needed} = m_{Oxygen} = x \times 1 \times \frac{32}{12}$$

$$m_{Oxygen} = 1000 \times 1 \times \frac{32}{12}$$

$$= 2667 \text{ g (or) } 2.667 \text{ kg of } O_2$$

But, air contains only 23% of O_2 by weight

Mass of air required to burn 1 kg of pure carbon = $\frac{100 \times 2.667}{23}$ = 11.59 kg