



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

CHARACTERIZATION OF WASTES-2

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CHEMICAL ENGINEERING



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Heating value determination

- **Heating value** (or calorific value) of a substance, is the amount of heat released during the combustion of a specified amount of it. It is measured in units of energy per unit of the substance, usually mass, such as: kJ/kg, kJ/mol, kcal/kg, Btu/lb.
- Heating value unit conversions:
$$\text{kcal/kg} = \text{MJ/kg} \times 238.846$$
- **Higher heating value(HHV) or Gross calorific value (GCV):** is determined by bringing all the products of combustion back to the original pre-combustion temperature, and in particular condensing any vapor produced. Such measurements often use a standard temperature of 15 °C (59 °F; 288 K) .



Lower heating value (LHV or LCV) or Net calorific value (NCV): is determined by subtracting the heat of vaporization of the water vapor from the higher heating value. This treats any H_2O formed as a vapor. The energy required to vaporize the water therefore is not released as heat.

A common method of relating HHV to LHV is:

$$\text{HHV} = \text{LHV} + H_v(n_{\text{H}_2\text{O}, \text{out}} / n, \text{fuel})$$

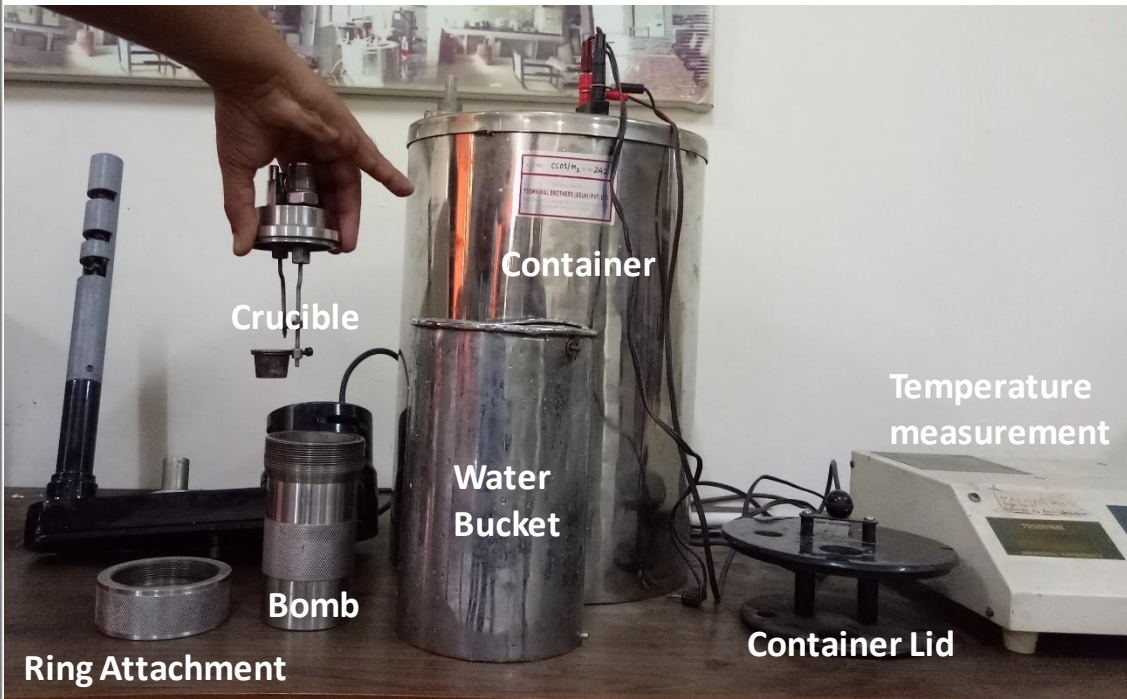
Where

H_v = Heat of vaporization of water

$n_{\text{H}_2\text{O}, \text{out}}$ = moles of water vaporised

n, fuel = number of moles of fuel combusted

Determination of heating value of solid and liquid fuel



Principle:

Known amount of solid fuel is burnt in a bomb. The generated heat is used to raise the temperature of certain volume of water kept in a bucket. Heat accepted by the water is equivalent to the heat released by the fuel.

Operating procedure of calorimeter

- The sample of weight 1-1.5g is charged in bomb and it is pressurized with excess pure oxygen. it is submerged under a known volume of water (2 Kg) before the charge is electrically ignited.
- The weighed reactant put inside the steel container is then ignited. Energy is released by the combustion and heat flow released from this, crosses the stainless steel wall, thus raising the temperature of the steel bomb, its contents, and the surrounding water jacket. The temperature change in the water is then accurately measured with a thermometer.



- When the water temperature reaches equilibrium, the difference in temperature is considered to compute the energy received by the water.
- Bomb factor (which is dependent on the heat capacity of the metal bomb parts), is also added to calculate the energy given out by the sample burnt.
- Some corrections are also made to account for the electrical energy input, the burning fuse, and acid production (by titration of the residual liquid).
- After the temperature rise has been measured, the excess pressure in the bomb is released.

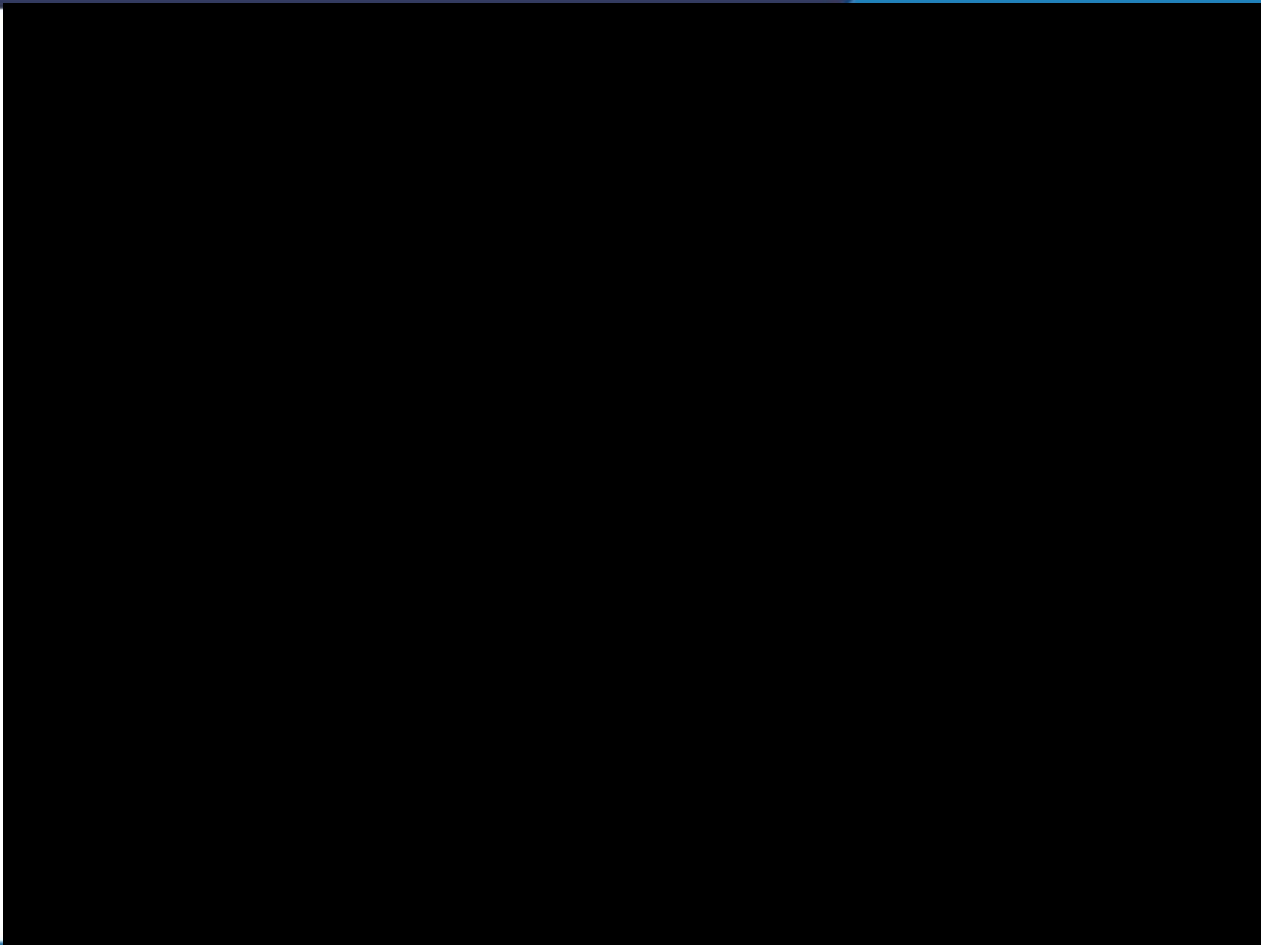
The interior of the bomb is checked for soot or other evidence of incomplete combustion. If such evidence is found, the test is discarded.

All interior surfaces of the bomb is washed with a jet of distilled water and the washings titrated with a standard sodium carbonate solution using methyl orange or red indicator. A 0.0709N sodium carbonate solution is recommended for this titration to the calculation. NaOH or KOH solutions with equivalent strength may be used.

All unburned pieces of fuse wire are collected and straighten; their combined length is subtracted from the initial length of 10 centimeters for correction.

Bomb washings are analysed to determine the sulfur content of the sample if it exceeds 0.1 percent.





Calculating the heat of combustion

The following data should be available at the completion of a test in an adiabatic calorimeter:

- T_a = temperature at time of firing, corrected for thermometer scale error
- T_f = final maximum temperature, corrected for thermometer scale error
- C_1 = millilitres of standard alkali solution used in acid titration
- C_2 = percentage of sulfur in sample
- C_3 = centimetres of fused wire consumed in firing
- M = mass of sample in grams



Temperature rise, compute the net corrected temperature t , by substituting in the following equation:

$$T = T_f - T_a$$

Since the released heat raises the temperature of the water as well as the wall of the calorimeter; to calculate the energy release; energy equivalent of calorimeter (W) is considered

W = energy equivalent of calorimeter in calories per degree Celsius (centigrade)

To get accurate result the following corrections are also considered:

Heat of formation of HNO_3 (E_1)

Heat of formation of H_2SO_4 (E_2)

Heat of combustion of fuse wire (E_3)



Thermochemical corrections :

E_1 = correction in calories for heat of formation of nitric acid (HNO_3)
= C_1 calories, if 0.0709N Sodium carbonate was used for the acid titration

E_2 = correction in calories for heat of formation of sulfuric acid
= $(13.7)(C_2)(M)$ calories

E_3 = correction in calories for heat of combustion of fuse wire
= $(2.3)(C_3)$ when using Parr 45C10 nickel-chromium fuse wire, or
= $(2.7)(C_3)$ when using 34 B. & S. gage iron fuse wire
= 0 when using 34 ga or finer platinum wire

Gross heat of Combustion.

$$H_g = \frac{T * W - E_1 - E_2 - E_3}{M}$$

W can be determined by standardizing the calorimeter using a compound whose heat of combustion is known



Standardization procedure

- The procedure for the standardization test is exactly the same as for testing a fuel sample. A pellet of benzoic acid weighing not less than 0.9 nor more than 1.25 grams is added. The energy equivalent of the calorimeter is determined by:

$$W = \frac{H \cdot M + E_1 + E_3}{T}$$

W = energy equivalent of the calorimeter in calories per degree celsius

H = heat of combustion of the standard benzoic acid sample in calories per gram

M = mass of the standard benzoic acid sample in grams

T = net corrected temperature rise in degree C

E₁ = correction for heat of formation of nitric acid in calories

E₃ = correction for heat of combustion of the firing wire in calories



Net calorific value

The calorific value obtained in a bomb calorimeter test represents the gross heat of combustion for the sample. This is the heat produced when the sample burns. plus the heat given up when the newly formed water vapor condenses and cools to the temperature of the bomb.

In real application this water vapor escapes as steam in the flue gases and the latent heat of vaporization which it contains is not available for useful work.

The net heat of combustion (H_n) is obtained by subtracting the latent heat from the gross calorific value. It depends on the percentage of hydrogen, H, in the sample.

An empirical relationships are:

$$H_n = 1.8H_g - 91.23H \quad (\text{Where } H_n \text{ is in Btu per pound}) = 2.326*[1.8H_g - 91.23H] \text{ in KJ/kg} \\ = 0.555927*[1.8H_g - 91.23H] \text{ in KCal/Kg}$$

$$\text{LHV (MJ/kg)} = \text{HHV} - 0.212*H - 0.0245*M - 0.008*O$$

H, M and O are % of these elements in feed



Empirical relations for heating value calculation based on **proximate and ultimate analysis data**

Name of the author	Correlation (HHV, MJ/kg)
Jimenez and Gonzalez	$\text{HHV} = -10.81408 + 0.3133 (\text{VM} + \text{FC})$
Demirbas	$\text{HHV} = 0.196 \text{ FC} + 14.119$
Demirbas	$\text{HHV} = 0.312 \text{ FC} + 0.1708 \text{ VM}$
Cordero et al.	$\text{HHV} = 0.3543 \text{ FC} + 0.1708$
Tillman	$\text{HHV} = 0.4373 \text{ C} - 1.6701$
Boie	$\text{HHV} = 0.35\text{C} + 1.16\text{H} - 0.11\text{O} + 0.06\text{N} + 0.1\text{S}$
Demirbas	$\text{HHV} = 0.33\text{C} + 1.42\text{H} - 0.15 \text{ O} - 0.14\text{N}$
Jenkins	$\text{HHV} = -0.76 + 0.30\text{C} + 0.525\text{H} + 0.6 \text{ O}$

Where,

VM – Volatile matter

FC – Fixed carbon

C – Carbon

O – Oxygen

N – Nitrogen

S – Sulfur



Example 1

A solid waste with 1.0 % S is combusted in a Bomb calorimeter. The temperature of the bucket water increases from 25°C to 28 °C. The water equivalent of the calorimeter is 2402 cal/°C. One gm sample is used for the test and Parr 45C10 wire is used for ignition. Out of the 10 cm wire 2.6 cm is unused. To titrate the calorimeter washing 24.2 ml of 0.0709N sodium carbonate is required. Calculate the Gross heating value of the waste. Consider the thermometers are working perfectly.

$$Hg = \frac{T \cdot W - E_1 - E_2 - E_3}{M}$$

Solution :

$$T_a = 25\text{ }^\circ\text{C}; T_f = 28\text{ }^\circ\text{C}, T = 28 - 25 = 3\text{ }^\circ\text{C}$$

$$C_1 = 24.2\text{ ml, Thus } E_1 = 24.2\text{ cal}$$

$$C_2 = 1.0\% \text{ S, Thus } E_2 = (13.7)(1.00)(1) = 13.7\text{ cal}$$

$$C_3 = 7.4\text{ cm per Parr 45C10 wire, Thus } E_3 = (2.3)(7.4) = 17.0\text{ cal}$$

$$W = 2402\text{ cal/}^\circ\text{C}; M = 1\text{ g}$$

$$Hg = \frac{(3)(2402) - 24.2 - 13.7 - 17.0}{1} = 7150\text{ Cal/g}$$



Thanks...

