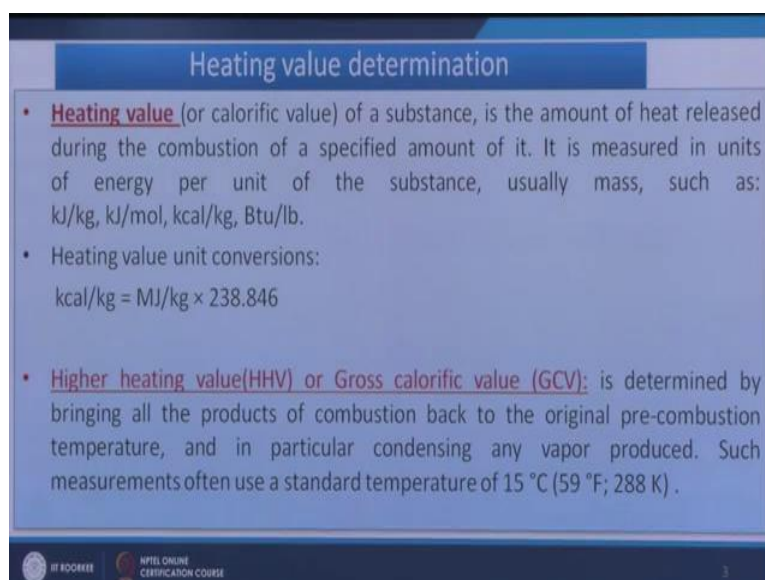


Waste to energy conversion
Dr. Prasenjit Mondal
Department of Chemical Engineering
Indian Institute of Technology, Roorkee

Lecture - 4
Characterization of Wastes -2

Hi friends. Now will start discussion on the second part of the module Characterization of Wastes, and in this module we will concentrate on the determination of heating value of the solid wastes; set first we will see what is heating value.

(Refer Slide Time: 00:39)



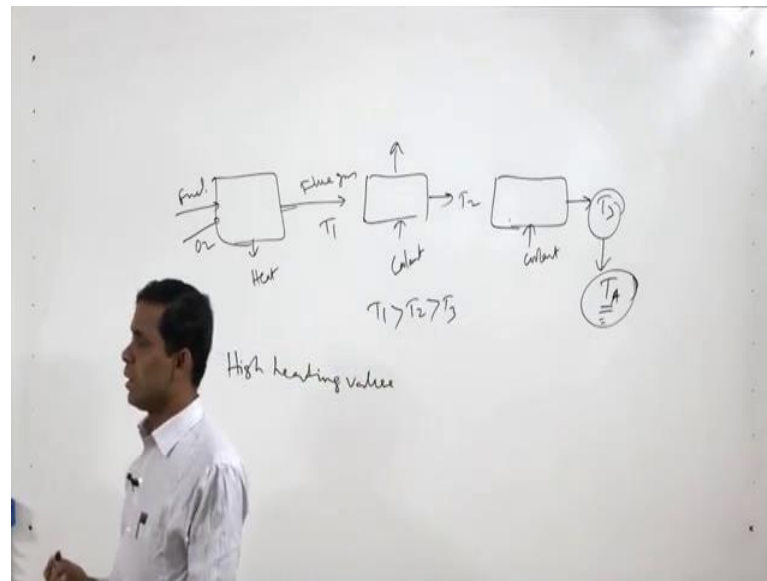
Heating value determination

- **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) .

IIIT Roorkee NPTEL ONLINE CERTIFICATION COURSE 3

If we combust some amount of waste it will generate some amount of heat. So, that heat can be used for different applications.

(Refer Slide Time: 00:56)



So, if we consider say one combustion chamber is there we are putting some fuel say solid waste may be; so that is solid waste we are combusting oxygen is also sent. So, after combustion heat is released. So, heat is released and it is going through the flue gas. So, that flue gas temperature we are reducing set T_1 here. So, we are getting T_2 we are putting some say coolant. So, its temperature will raise rise, but this temperature will fall. Again say another set of we are using so coolant and here we are getting T_3 .

Now, we are T_1 is greater than T_2 is greater than T_3 , and ultimately that T_3 will reach to T_a that is ambient temperature. So, the amount of heat which are releasing which we are getting from the flue gas after combustion that will vary up to which extent we are considering the cooling of the flue gas. So, here find the T_a is the ambient temperature when T_a that is temperature is the ambient temperature in that case you will get the maximum amount of heat for all further application. So, that is called high heating value.

So, high heating value we get when the gas temperature is in ambient condition, normally this is 15 degree centigrade. So, another type of heating value is also there that is called low heating value. So, higher or lower we can say higher and lower somewhere sometimes higher and lower heating value also it is called.

(Refer Slide Time: 02:55)

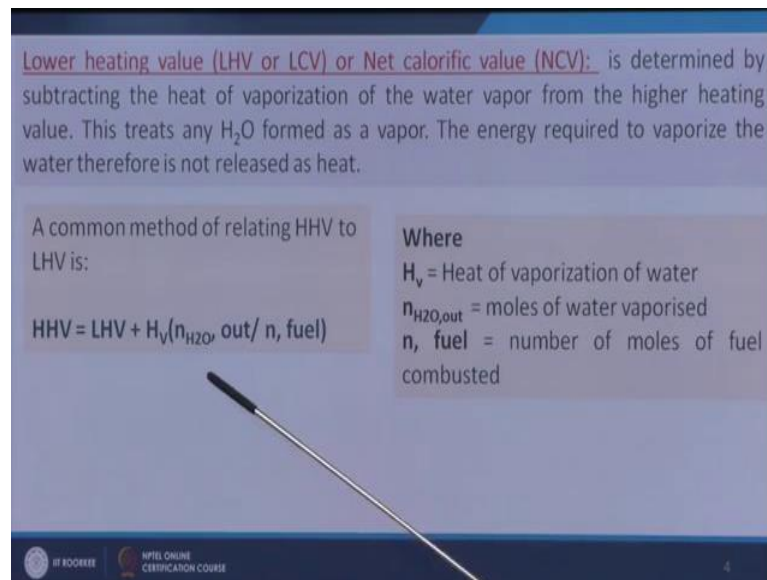
Lower heating value (LHV or LCV) or Net calorific value (NCV): is determined by subtracting the heat of vaporization of the water vapor from the higher heating value. This treats any H_2O formed as a vapor. The energy required to vaporize the water therefore is not released as heat.

A common method of relating HHV to LHV is:

$$HHV = LHV + H_v(n_{H_2O, out} / n, fuel)$$

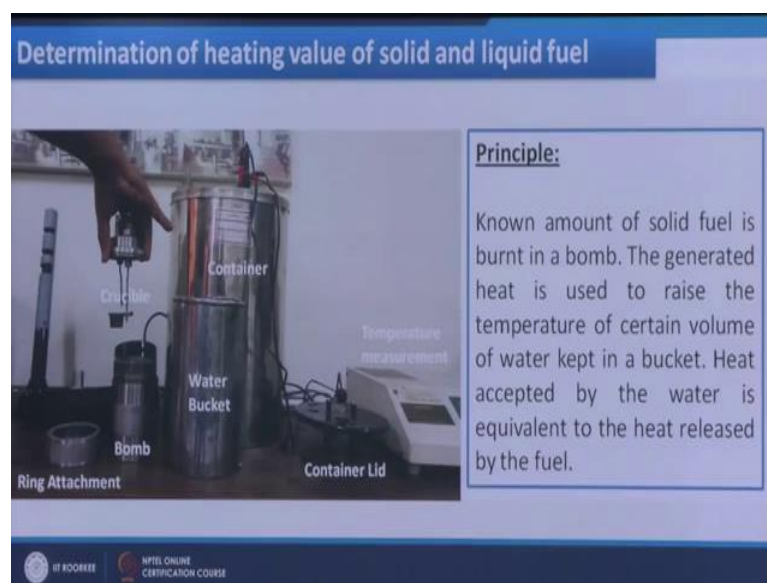
Where

H_v = Heat of vaporization of water
 $n_{H_2O, out}$ = moles of water vaporised
 $n, fuel$ = number of moles of fuel combusted



So, that lower heating value will be lower than the higher heating value and the how much lower it will be, it will depend upon how much water has been produced during combustion and that water molecules has captured some amount of heat for its vaporization. So, the HHV is equal to LHV plus H_v into number of H_2O produced a by number of fuels number of moles of fuels. So, if we take n number of fuels n number of moles of fuels then $n_{H_2O, out}$ number of moles of H_2O produced during combustion divided by number of fuels into heating value for the vaporization of water; so this amount of it if we add with LHV that will be the HHV or high heating value. So, this is the relationship between high heating value and low heating value.

(Refer Slide Time: 04:05)



Now, how can I determine the heating value? The bomb calorimeter is normally used to determine experimentally the heating value of any solid and liquid samples where may be waste also. So, in this case as shown in the figure, so this is our bomb calorimeter. So, this is our bomb. So, in the bomb some amount of solid waste can be put in this crucible and after putting that crucible inside the bomb, the ring attachment help to tighten it and then oxygen will be passed through some nozzles and high purity oxygen will be provided into the bomb. So, that it will ensure the complete combustion of the solid waste or any liquid wastes also are put here.

So, the basic principle of this bomb calorimeter is that the amount of heat which is been released by the material here inside the bomb, that will be transmitted through this wall and will raise the temperature of the water kept in the water bucket. So, ultimately temperature will raise, by this temperature raise should be say 2 3 4 5 degree centigrade like this. So, amount of materials will be selected in that way and normally that is around one gram not much more amount of solid or liquid waste is added here.

So, then one equilibrium temperature will raise then that at after at that time, what is the difference in temperature initial and final that will be the temperature raise. So, $M C P \Delta T$ will be the total amount of heat released by the solid present in it. So, this is the mechanism the heat released by the solid or liquid waste it captured by the bomb as well as the water inside the bucket and the temperature raise is measured. So, $M C P \Delta T$

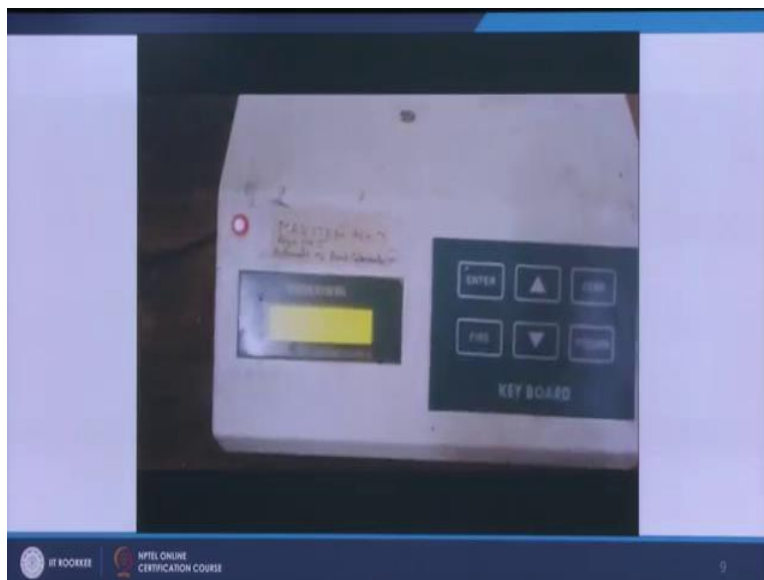
that the amount of it received by the water and the bomb is equal to amount of it released by the solid materials or liquid materials in the bomb.

So, now what is the operating what is the operating procedure? So, you have to take 1 to 1.5 gram of materials that is charged in the bomb and the bomb is highly pressurized with pure oxygen, then when we are putting inside it after fixing this one by ring attachment will supply oxygen, then it will put inside this one and that will be inside this container. Then will ignite the material through this electric circuit there will be some wire will be used fuels wire will be used and or threads, and then the this the temperature measurement instrument some thermocouple will be here water jag water bucket and temperature measurement will be done.

So, these are the steps, but when the equilibrium temperature will reach will reach the equilibrium temperature, then we are our run is almost complete then will release the pressure inside it, then will open it and will find if there is anything inside the bomb or if there is any material unconverted; if it is unconverted the test is discarded. Thereafter will collect the fused wires if any then will straighten it and will get the a length of the wire present, and will get the subtraction within ten centimeter minus the total length of the wire we are getting at the end so that that will be used to determine how much of energy the wire such generated during the combustion method.

So, during combustion if there is sulfur and nitrogen some acid will from. So, acid will be deposited on the surface of it up when the condensation will take place. So, that has to be collected the wash washing liquid has to be collected and tight it against sodium hydroxide or calcium hydroxide or any other alkaline solution standard solution for the collection of those acid sulfur and nitrogen correction, and another correction will be thread correction that is used for ignition. So, these are the corrections required and these are the procedure.

(Refer Slide Time: 09:04)

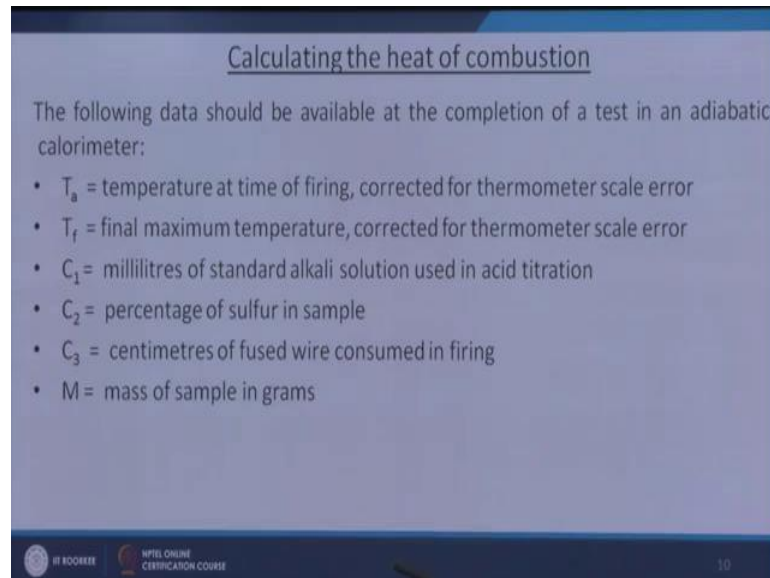


Now, I will show you some video it will explain it is self explanatory and it will explain how this work. So, the material is taken this the crucible the material is taken and it is put inside the bomb now it is tightened.

So, oxygen is sent to this nozzle into the bomb. So, pure oxygen is supplied, you see the pressure here pressure increasing inside the bomb the oxygen pressure is increasing. So, now, supply line is open. So, this is the bucket with water that is 2 liter of water is normally added. So, water added. So, this inside is bucketed water is added now bomb is put in the bucket, and electric circuit is getting ready. Now will cover the led the covering is being done, the container is being covered by led. Now this is the thermocouple, so that is inserted into the water present in the bucket, now these going to be ready for firing. So, now it is running.

So, firing will start now you set 0 that is the initial point. So, set 0 then it is firing fire starts, you see the temperature will increase there is increasing 129.68, 0.683 degree centigrade this differential temperature. So, this will continue we reach the equilibrium temperature.

(Refer Slide Time: 15:51)



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

NPTEL ONLINE CERTIFICATION COURSE 10

So, now we have reached equilibrium temperature and the procedure is like this just explained as well as the video is shown to you for better understanding. Now after that we have got some information and some values; what are those initial temperature, final temperature, and then we have after this test finally, we will be taking the washing of the bomb. So, that wash will tight it and will get the amount of tighter liquid required that is standard sodium dioxide or potassium oxide or any other alkali required for its neutralization. So, that will be C_1 , C_1 millilitres of standard alkali solution required and then we will get C_2 percentage of sulfur in sample that is known to us if we have some C H analysis of the solid waste or any other liquid waste also. So, C_3 is the centimeters of fused wire that was used or consumed in firing so that we can determine; and mass of sample how much we have taken that is known to us. So, these are the parameters know it is known to us.

(Refer Slide Time: 17:09)

Heat released by solid/liq. sample = Heat received by bomb and water

$$H_g M = W \Delta T$$

$$m_b C_{p,b} \Delta T + m_w C_{p,w} \Delta T = \Delta H$$

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

$$H_g M + E_1 + E_2 + E_3 = W \Delta T$$

$$\Delta T = \frac{H_g M + E_1 + E_2 + E_3}{W}$$

Then what is the principle? Heat released by waste sample is equal to heat received by bomb and water, bomb and water in the bucket.

(Refer Slide Time: 17:44)

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)

11

So, how can we measure this? It is equal to $M c_p \Delta T$. Mass $C_p \Delta T$, ΔT can be measured that is T_f minus T_a , final temperature minus initial temperature. We can measure the T equal to that is ΔT equal to T_f minus T_a ; and then what is our C_p , M C_p say we have M_1 of the bomb M of the bomb into C_p of the bomb $M C_p$ into ΔT plus M of the water in the bucket C_p of the water in the bucket into ΔT ; that is equal

So, in this case when (Refer Time: 19:32) acid is used. So, this is our case we can get the value W. So, once we get the value of W then heat released by the solid is equal to how much? H into M , M is the mass of the material we have taken and H is the heat released (Refer Time: 19:54) unit mass. So, H into M that is equal to W into ΔT . So, this is the relationship which can be used to determine the heating value of the material. Now the $W \Delta T$ which were getting that require some correction, that is the total about of heat which is received by the water and the bomb calorimeter, but all that amount of heat is not actually released by the materials some amount of heat as been continuative due to the formation of acid like say HNO_3 and H_2SO_4 due to the presence of nitrogen and due to the presence of sulfur and some amount of heat has been contributed by the fused wire. So, we need to get the correction of E_1 , E_2 , and E_3 .

Thermochemical corrections :

E_1 = correction in calories for heat of formation of nitric acid (HNO_3)
 = C₁ 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

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

Gross heat of Combustion.
$$H_g = \frac{T - W - E_1 - E_2 - E_3}{M}$$

IIT ROORKEE

NPTEL ONLINE
CERTIFICATION COURSE

12

So, ultimately we can calculate H is say here H is equal to W into del T here we are mentioning T, minus some correction what are those E 1, minus E 2, minus E 3 by M. So, this is the relationship for determination of H that H is high heating value higher heating value for gross heating value. So, gross heating value can be determined by this formula. So, now, we have to determine E 1, E 2 and E 3 values E 1, E 2, E 3 values can be determined from the value of C 1, C 2 and C 3 fine C 1 is the amount of m l of standard alkali solution required for the neutralization of the bomb wash, and E 2 can be determined from this 13.7 into C 2 into M; where C 2 is the percentage of sulfur and M is the mass of the solid of the samples taken into the bomb; and E 3 can be calculated depending upon the nature of the wire which have been used.

So, different types of wires it is given and different relationship has been given; obviously, the amount or the length in centimeter of the wire fused during firing that is responsible for determining the E 3 value as per different equations it is given here.



(Refer Slide Time: 22:26)

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

 IIT KHARAGPUR
 NPTEL ONLINE
CERTIFICATION COURSE

13

So, we can get the H g value by using this formula; then what will be the W determination how can we determine W. So, for determination of the W similar test we will do, in that case the heating value of the material is known to us in that case for example, say here benzoic acid is used. So, a pellet of benzoic acid not less than 0.9 or not higher than 1.25 gram is used, and in that case what will get W is equal to H into M plus E 1 plus E 3 by T. So, it same formula if we like this. So, H g into M plus E 1 plus E

2 plus 3 divided by T divided by T. So, this T means del T. So, this T means del T. So, this is the formula by which we can get the value of W, but now in benzoic acid the material is known to us there is no sulfur. So, this component is equal to 0.

So, ultimately we are getting formula W is equal to H into M, E 1 plus E 3 by T. H is known for benzoic acid, M is known that how much we have taken E 1, E 3 is known and T is also W can be calculate it.

(Refer Slide Time: 23:50)

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:

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

$$= 0.555927 * [1.8H_g - 91.23H] \text{ in KCal/Kg}$$

$$LHV \text{ (MJ/kg)} = HHV - 0.212 * H - 0.0245 * M - 0.008 * O \quad H, M \text{ and } O \text{ are \% of these elements in feed}$$

14

Now, what will be the net calorie value? So, determine net calorie value some empirical relationships are given that is H net is equal to 1.8 into H gross higher heating value minus 91.23 into H where H is the hydrogen percentage, but this when H n unit of Btu per pound, but after conversion we get 0.555927 into 1.8 H g minus 91.23 H in kilocalorie per kg unit, and some other expressions are also available that HHV and LHV are related on the basis of hydrogen, oxygen and moisture content in the fixed stocks, because all those three the hydrogen produces H₂O, oxygen produces H₂O.

So that amount of H₂O produce during combustion is responsible for the lower heating value, so that is why this relationship is also used.

(Refer Slide Time: 25:00)

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 :


$T_a = 25^\circ\text{C}$; $T_f = 28^\circ\text{C}$, $T = 28 - 25 = 3^\circ\text{C}$ $Hg = \frac{(3)(2402) - 24.2 - 13.7 - 17.0}{1} = 7150 \text{ Cal/g}$


$C_1 = 24.2 \text{ ml}$, 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 $E_3 = (2.3)(7.4) = 17.0 \text{ cal}$

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

 NPTEL
NATIONAL INSTITUTE OF TECHNOLOGICAL EDUCATION LIBRARY

 NPTEL ONLINE
CERTIFICATION COURSE

Here we will see some empirical relationship purposed by different researchers for the determination of high heating value based proximate analysis on, based on ultimate analysis etc.

Now, we will see one example; a solid waste with one percent sulfur which combusted in bomb calorimeter, the temperature of the bucket water increases from 25 degree centigrade to 28 degree centigrade, the water equivalent of the calorimeter is 2402 calorie per degree centigrade one gram sample is used for the test and parr 45C10 wire is used for ignition. Out of the 10 centimeter wire 2.6 centimeter is unused, titrate to titrate calorimeter the washing 24.2 ml of 0.079 sodium carbonate is required; calculate the gross heating value of the waste consider the thermometers are working perfectly. So, there is no need for thermometer correction. So, we are using it is perfect working.

So, how to calculate the high heating value? We know the formula H_g is equal to W into T minus E_1 minus E_2 minus E_3 by M . So, in this case we can calculate E_1 ; what is E_1 for calculating E_1 we need C_1 , C_1 is equal to how much 24.2 ml of standard sodium carbonate. So, 24.2 into 1 that E_1 is equal to 24.2 calorie, for E_2 it is required sulfur content, 1 percent sulfur. So, E_2 is equal to 13.7 into 1 into mass of it 1 gram. So, that is equal to 13.7 calorie, and for the determination of E_3 we need how much wire has been consumed.

So, out of 10 centimeter 2.6 centimeter remaining, so consumed is equal to 7.4 centimeter. So, as the type is Parr 45C10. So, 2.3 into 7.4 that is equal to 17.0 calorie that is the E 3. So, now, will put the value of E 1, E 2, E 3 W is given 2402 calorie per degree centigrade, T is equal to 28 minus 25 that is equal to 3. So, 3 into 2402 minus 24.2 minus 13.7 minus 17 divided by M, M is equal to one gram. So, you put it here and we were getting 7150 calorie per gram. So, this is the high heating value of the material.

So, after this in this module and in this module we have discussed how to measure the heating value of any solid or liquid waste, so after this in this module.

Thank you very much for your patience.