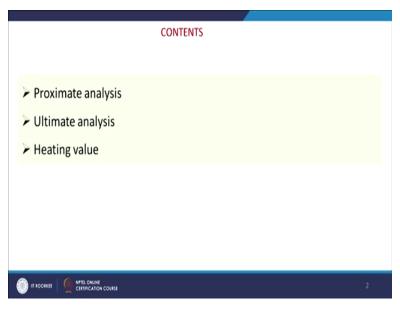
## Technologies for Clean and Renewable Energy Production Prof. Prasenjit Mondal Department of Chemical Engineering Indian Institute of Technology-Roorkee

## Lecture 03 Characterization of Coal

Hi, friends now we will discuss on the topic characterization of coal. In introductory module we have discussed about the different properties of coal and we have seen that some of the properties are very important to fix its price. And as we are interested to use coal as an energy source so heating value is very, very important. And this heating value is dependent on carbon, hydrogen, oxygen, present in it and it also depends upon the ash content, moisture content etc.

So, in this class we will see what are the different methods that can be used to measure the properties of coal like say what is the moisture content what is the fixed carbon? What is the volatile matter content? And what is the carbon hydrogen nitrogen sulphur oxygen present in coal? And ultimately we will see how the heating value is determined.

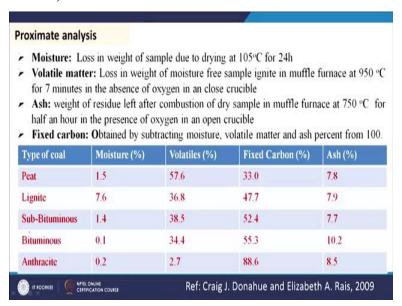
(Refer Slide Time: 01:42)



So, the content of this class is the approximate analysis, ultimate analysis and heating value determination. Now we will see what is proximate analysis? This is a standard method which

gives us the procedure through which we can analyze the moisture content of coal, ash content of coal, volatile matter content and fixed carbon.

(Refer Slide Time: 02:09)



So, these 4 properties moisture, volatile matter, ash and fixed carbon are determined by proximate analysis. So, how it is possible? We have to take small amount of sample and then we will heat it under certain condition that is prescribed in the method, that is 105 degree centigrade for 24 hour, then the mass loss is equivalent to moisture content.

And after the loss of moisture the dry material if we put it in a crucible and cover it with the lead and then put it inside a furnace at high temperature for small period of time then the volatile present in the coal sample goes off and the difference between the initial mass and remaining mass will give us the measure of volatile matter present in the sample. In this case the condition is given as 950 °C for 7 minutes in absence of oxygen that is why we have given the lead on it.

Then we will take this material and heat in presence of oxygen so that the carbon, hydrogen present in it will be converted to CO<sub>2</sub> and H<sub>2</sub>O so that carbon and hydrogen basically is from the volatile matters. During this process in presence of oxygen if we heat for a longer period at moderately lower temperature maybe that it is given here 750 °C and half an hour duration so that all this carbon and hydrogen will be converted to CO<sub>2</sub> and H<sub>2</sub>O and the remaining part which we will get that is nothing but ash content.

So, after that we can determine the fixed carbon by the difference that is 100% minus the

percentage of ash minus percentage of volatile matter and minus percentage of moisture. Now

we will see the volatiles fixed carbon as a moisture content of some materials like peat, lignite

sub-bituminous, bituminous and anthracite. So, from this table we see the volatile matters is

decreasing gradually with the increase of rank.

Fixed carbon is increasing gradually but for moisture and ash there is no such specific trend

because as you know that volatiles and fixed carbon these are the inherent properties, these are

present in the plant biomass and it is converted to coal through coalification process. So, with the

stage of maturity these two are changing, volatiles is reducing and the fixed carbon is increasing

as discussed in the introductory module.

But moisture and ash these two are not the inherent property every time. So, it also depends upon

the exterior external factors like say how we are handling the coal, how we are storing it so all

those things and where from we are getting it so all those factors, that is why there is no specific

trained on it. Now we will see how to determine the elemental composition of coal that is called

ultimate analysis, sometimes it is also called CHNS analysis, C for carbon H is for hydrogen N

for nitrogen S for sulphur.

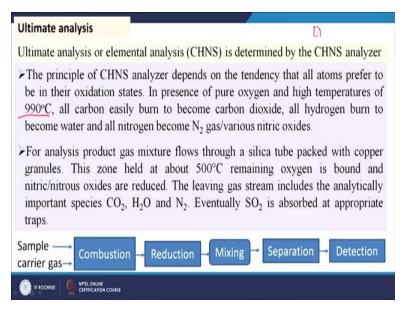
So what is the mechanism for this analysis? What do you do in this case? The full sample is

combusted at higher temperature, the specific temperature is given here that is 990 °C

temperature, when we heat it the carbon is converted to CO<sub>2</sub>, H is converted to H<sub>2</sub>O, N is

converted to NOx, S is converted to SOx. So, now we are getting a mixture of gas components.

(Refer Slide Time: 06:59)

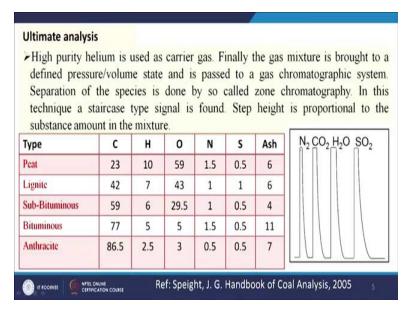


So, if we put the material in small container and then we apply oxygen and heat it here, then the gas will be available in this container. So, now we need one carrier gas so this carrier gas will carry the gas and it will mix well the components and then we will use the methodology for the separation and identification of these gas molecules which is possible by using a gas chromatography.

But in this case we see we have carbon dioxide H<sub>2</sub>O, N<sub>2</sub> and SO<sub>2</sub> so if I want to separate we need the variation in the retention period of the different gas molecules in the GC column that means the interaction of these gas molecules with the stationary phase of GC column should be different that is why NOx is reduced to nitrogen prior to its entry into the GC column. So, one silica tube packed with copper granules is used in the path of this gas.

So, carrier gas along with the components passes through this and NOx is converted to nitrogen by reduction then the mixed gas is going through this separation stage in the GC and detection stage. So, you see here, sample carrier gas, combustion, then reduction for NOx reductions and then mixing, then separation and detection. So, these are the different steps and mechanism for the analysis of carbon, hydrogen, nitrogen, oxygen and Sulphur.

(Refer Slide Time: 08:45)



Now you see this figure is giving us different peak for nitrogen, CO<sub>2</sub>, H<sub>2</sub>O and SO<sub>2</sub> because of the variation of the interaction of these gas molecules with the stationary phase of the GC column. So, retention period is different as nitrogen is inert so its retention time is less then carbon dioxide, then H<sub>2</sub>O, then SO<sub>2</sub>. So, these peaks area gives us the relative concentration of these different gas components.

So, we calculate how much carbon, hydrogen, nitrogen, Sulphur is present in the original sample. Now we will see some example of the ultimate analysis of different types of material including peat, lignite, sub-bituminous, bituminous and anthracite. Here also the hydrogen content is decreasing gradually, oxygen content is decreasing gradually, and carbon content is increasing gradually. But for nitrogen, sulphur there is very less changes, 0.5 to 1.5 so these small changes may be because of the limit of analysis or the instrument error limit.

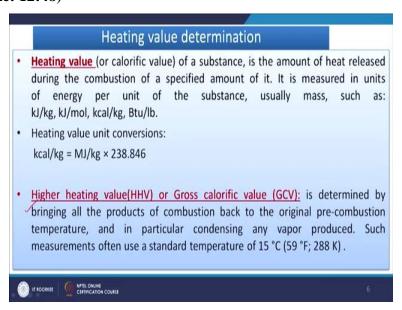
Here we see ash content also does not have any specific trend because it also depends upon the external factors and the handling of the material. Now we are coming to heating value so what is the heating value? That is most desirable parameter of the sample, we need higher heating value so that we can get more heat. So, if we take a coal sample and then combust it in presence of sufficient amount of oxygen then it will release Heat, C+O<sub>2</sub>, CO<sub>2</sub>,

And if hydrogen is available  $H + O_2$  is  $H_2O$  so these are the basic reactions which generates heat and that heat we are interested to get in useable form. So, heating value is obviously the amount of heat energy released per unit amount of sample due to the combustion. Then here we can get two types of heating value as we have discussed in our introductory module also, one is your higher heating value or gross heating value and another is your lower heating value or net heating.

So, what these two are? After combustion we are getting flue gas and during the machine heat is released so flue gas is having high temperature it may be more than 600, 500 like this degree centigrade. That high temperature of flue gas is used to produce steam from the water and then the steam will be available in different temperature as per the need of the application in downstream. So, one possibility is that the steam is condensed, now the flue gas which is produced to the combustion that is cooled down to atmospheric temperature.

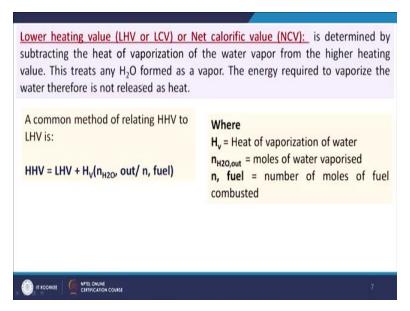
So the heat recovered from this flue gas will be the maximum that is called high heating value and low heating value is the difference of the heat required to vaporize the water available in the flue gas.

(Refer Slide Time: 12:48)



So, low heating high heating value and lower heating value the difference is;

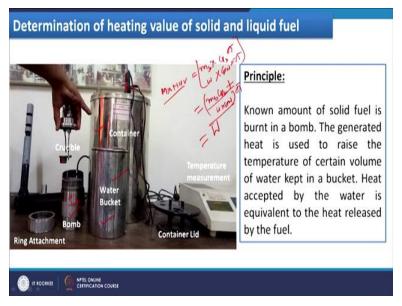
(Refer Slide Time: 12:56)



We have to subtract the energy required to vaporize the water, now how this heating value can be expressed what is the unit of it? Unit may kilo Joule per kg, kilo Joule per mole or kilocalorie per kg, BTU per pound and there are some conversion factors kilocalorie per kg 2 mega Joule per kg if we want to convert this relationship we can use. So, people have tried to find out the relationship between high heating value and lower heating value and it is found that HHV high heating value is equal to low heating value plus H v into number of H<sub>2</sub>O out by number of fuel.

This number of means number of moles of water produced during the combustion and number of moles of fuels so this divided by this n  $H_2O$  per mole of fuel that will be the mole of water produced and if we multiply it with the heat of vaporization of water. So, this amount of heat if we add with the lower heating value then that will give us higher heating value. Now let us see how you can determine it.

(Refer Slide Time: 14:38)



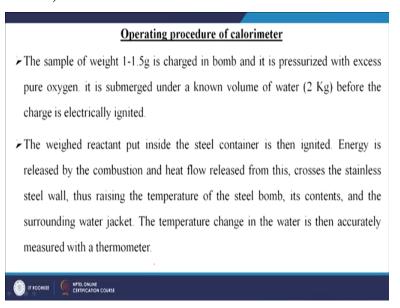
For the determination of higher heating value we use bomb calorimeter and bomb calorimeter has been shown, in this figure you see this is the calorimeter and inside this calorimeter we have water bucket and then in the water bucket we put bomb inside the bomb we put the material in this crucible and then fix it and then with the electric devices we ignite this one, the coal sample, and it combust inside it in presence of excess amount of oxygen.

Then it releases heat during the combustion and that heat is taken up by the water put in this water bucket as well as this bomb of the calorimeter. Now what is the principle? The amount of heat released due to the combustion of the material inside the bomb is taken up by the bomb material as well as the water kept inside the water bucket. So, this is the principle for the determination of heating value in the bomb calorimeter.

Now what type of heating value this is? High heating value or low heating value? Obviously it is high heating value, why? Because inside this bomb we are putting the material and we are putting oxygen inside it in sufficient amount at higher pressure. So, we are assuming that complete combustion is taking place and when the combustion will take place the local heat will be very high. But that heat is being released through this material of the bomb wall the heat will also come to the water inside the water bucket.

And there is some starring arrangement so there is some change in the water temperature. Now if the sample is very small so this variation in temperature may not be very high, it will vary within small range. So, what is happening during combustion? Moisture is formed and again it is cooled down to atmospheric temperature. So, that is why we are able to get complete heat released by the material that is why it is high heating value. So, from bomb calorimeter we can determine high heating value.

(Refer Slide Time: 17:13)



Now I will explain the steps. What we will do at first? We will take 1 to 1.5 gram of material in the crucible and then we will be using some thread or wire to ignite it and after ignition we will be getting the temperature change. How the temperature is changing and what is the equilibrium temperature what is the difference between equilibrium temperature and initial temperature. Then we will do the energy balance. So, how do we do the energy balance?

Here we have heat released by this equal to say we have taken M amount of material. so M into HHV heating value, that amount of heat is released and that is taken up by the calorimeter, that is equal to mass of calorimeter say M bomb mass, MB into CP or bomb MCP $\Delta$ T, this is the heat taken up by the bomb and the heat taken up by the water that is W x CP x w x  $\Delta$ T. so this is the total heat taken up by the system.

And this is the total heat released by the material. So, if we ignore any other type of corrections then this is the basic formula. Now MbCp and this from this relationship we can get Mb Cpb + w x C pw x  $\Delta$ T this whole term is replaced by w that is water equivalent of the calorimeter and this is the property of this material whatever material it is taking and in short the properties of the calorimeter. So, we are getting w into  $\Delta$ T this is the heat gained by the calorimeter bomb as well as the water body.

So this is the basic principle and on basis of which we determine the HHV value excluding the correction factors. But here when you are using the coal and we are using some wire for the ignition, then that will also release some amount of heat so that correction is required. And if the coal contains some sulphur and nitrogen then that  $SO_2$  will be formed and then a  $SO_2$  will be converted to  $H_2$ ,  $SO_4$  or  $NO_2$  can be converted to  $HNO_3$ .

So these acid converts and they will also contribute some amount of heat in this process so that has to be excluded to determine the HHV of this sample. Now I will show you a video which is self explanatory.

## (Video Start: 20:54)

Which explain us how the bomb calorimeter is used to determine the heating value of coal or any other solid sample. So, now you see the crucible part is getting ready, the wire connection is being made. Now the sample is pulled into the crucible and the sample is put inside the bomb and it is present with the lead. Then we will put oxygen inside it the bomb is connected with the oxygen supply line from the oxygen cylinder.

Now oxygen will go, it is started to go and set the bomb and pressure will increase, pressure is increased. So, this high pressure is basically needed to ensure that all the samples will be combusted. Now the bomb will be put inside a bucket and water will be filled in the bucket. This video is made for demonstration purposes only, the water has to fill so that the bomb will be completely immersed in the water.

And then electricity connection is provided and the calorimeter is covered. The temperature measurement device is inserted and studying arrangement is made. Now we have to provide

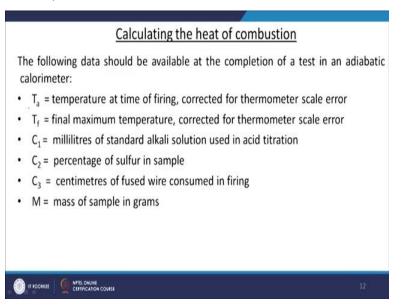
electricity inside it and this is the device which provides electricity and also measures the differential temperature. The temperature difference now I have to put auto zero so difference has to be made zero first, now you see 0, gradually it will reach the equilibrium point.

The temperature difference will be fixed, you see here  $0.683^{\circ}$ C, this is the equilibrium temperature difference that  $t_1$  -  $t_2$  the initial and final temperature difference we are getting point 683 it is now constant it will not change. So, that way we can get the  $\Delta t$  value. Now we are taking the recording, recorded, we are recording the value.

## (Video Ends: 28:17)

So, this is the video for demonstration for the measurement of heating value using bomb calorimeter. So, from this video it is clear to asses, after the process we will be having some parameters or some values.

(Refer Slide Time: 28:37)



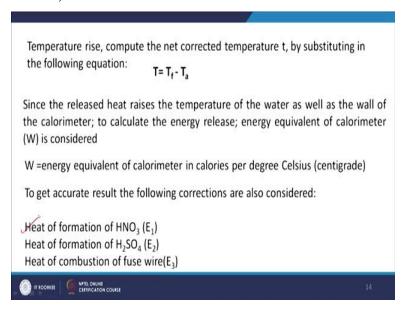
Like say temperature at the temperature at time of firing and final maximum temperature. See in our case we do not have two different but we have  $\Delta$  so you are already getting the difference in the temperature during the process. And then  $C_1$  we get milliliter of standard alkali solution used in acid titration. So, what will be happening after the reaction? After the completion of this will release the oxygen from the bomb and will take the sample out, there will be no sample theoretically.

But in some cases some soots may be available, in that case this run is discarded, not considered. Then it is washed, the wall is washed with water and that is titrated with alkali solution to get the acid deposited on the wall of it and how much acid is formed. That way we get how much how many milliliters of alkali solution is required that we can measure, and then we can get percentage of sulphur in the sample that we should have some idea about the elemental analysis of the sample.

And then what is the length of the wire which was fused during this process that we have to determine initially we take 10 centimeter then after this process how much is left that we measure, the balance is used we assume. So that this value we get and mass of sample how much sample you have taken that also it is known to us. Now, on the basis of this information we can proceed further to determine the heating value of it.

And as I discussed that without incorporation of any error the energy balance formula we have discussed but now there will be some error.

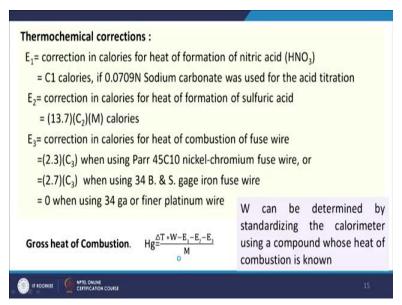
(Refer Slide Time: 30:35)



So, heat of formation of nitric acid heat of formation of sulphuric acid and heat of combustion of fuses so these three correction factors we have to consider and this H<sub>2</sub>SO<sub>4</sub> this is basically we measure from the presence of sulphur in the sample and HNO<sub>3</sub> heat how much can be released that is measured on the basis of acid titration value the titration value how much milliliter NaOH

KOH or Na<sub>2</sub>CO<sub>3</sub> is used. Heat of combustion of fuse wire also is determined. And the supplier of this manufacturer of this instrument they provide the E<sub>3</sub> value or corresponding how to calculate E<sub>3</sub> value.

(Refer Slide Time: 31:25)

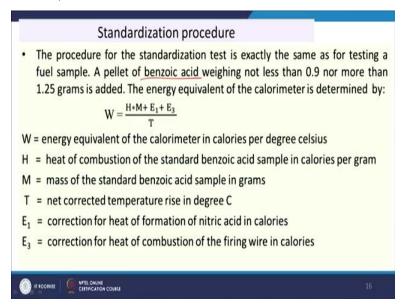


So how can we calculate  $E_1$ ,  $E_2$  and  $E_3$ ?  $E_1$  it is nothing but dependent on the  $C_1$  value, what is  $C_1$ ? That is the milliliter of alkali solution used to get that titrate value of the wall wash of the bomb and then  $E_2$  we can calculate by this formula 13.7 x  $C_2$  x M so  $C_2$  is the percentage concentration of sulphur in the sample and M is the amount of sample I have taken in gram. And  $E_3$  is measured through different equations for different types of fuse wire used. So, nickel chromium if you use then this formula 2.3 x  $C_3$ .

If we use iron 34 B and ash gauge iron then 2.7 x  $C_3$  or if we use 34 gauge platinum wire then is equal to 0. So, these are provided by the manufacturer of the bomb calorimeter. Then how we will get the gross heating value? gross heating value into mass of the material that will be the heat released and that is equal to  $\Delta T$  into W that is equal to water equivalent into the temperature difference minus the amount of energy is released due to the formation of nitric acid that is  $E_1$ . Due to the formation of sulphuric acid  $E_2$  and due to the heat released by the combustion of the fused wire. So, this is the formula through which we can calculate the gross heating value. Then this w value that is the water equivalent value of the bomb calorimeter that is the property of a

calorimeter so we need to determine it. So, the same process is followed but in this case we use a known sample the heating value of the sample is known to us.

(Refer Slide Time: 33:41)



So one such example is benzoic acid, so benzoic acid does not have any sulphur so  $G_2$  component will be 0 so  $E_2$  will also be 0 so in that case we will be getting W x T that is equal to H x M + E  $_1$  + E  $_3$ , E  $_2$  is 0 see if we use this formula so now H is known heating value of the benzoic acid is known, how much benzoic acid you have taken that is known,  $E_1$  we can calculate from the titer value.

And  $E_3$  we can calculate on the basis of the length of wire fuse wire used during the combustion in centimeter unit and we can calculate the W value. Then this way we can calculate gross heating value or high heating value then how can we calculate the net heating value? So, some formula is given H in negative value is equal to 1.8 x Hg that is high heating value and gross heating value minus 91.23 x H where H is the percentage of hydrogen.

So, this formula is in this unit BTU per pound but if we want to get it in kilocalorie per kg we have to convert it and this relationship we can use for the conversion of for the determination of net calorific value. Then people try it to find out some relationship of these two high heating value and low heating value with the amount of hydrogen, oxygen and moisture present in it. So, this is one empirical relationship which is provided.

So, what we have come to know on the basis of this discussion that to measure the heating value we need to perform it limit. So, it requires time and investment of manpower and money also. So, for general purpose for the comparison of different types of coals we may use some empirical relationships which have been reported by different researchers.

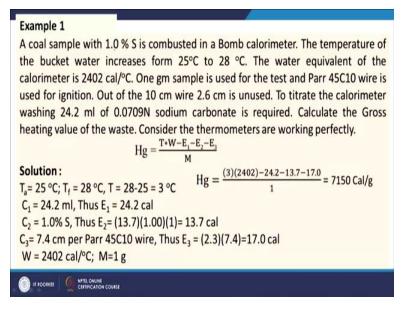
(Refer Slide Time: 35:53)

Name of the author	Correlation (HHV, MJ/kg)	Where, VM – Volatile matter FC – Fixed carbon C – Carbon O – Oxygen N – Nitrogen S – Sulfur
Jimennez and Gonzalez	HHV= -10.81408+ 0.3133 (VM+FC)	
Demirbas /	HHV= 0.196 FC+ 14.119	
Demirbas	HHV= 0.312 FC + 0.1708 VM	
Cordero et al	HHV= 0.3543 FC+ 0.1708	
Tillman	HHV= 0.4373 C-1.6701	
Boie	HHV= 0.35C + 1.16H - 0.11O + 0.06N + 0.1S	
Demirbas	HHV= 0.33C + 1.42H - 0.15 O - 0.14N	
Jenkins	HHV= -0.76+0.30C+ 0.525H + 0.6 O	

And provided in this table different researchers they have provided different empirical relationship for different types of coal and some are based on approximate analysis some are based on ultimate analysis basis. So, these will not be used to determine the actual calorific value of whole sample and to fix its price but it will be useful they will be useful to screen coal samples when it is needed.

If we have number of coal samples we can screen it that can be a suitable one by these applying this formula.

(Refer Slide Time: 36:39)



Then I will give you some example so a coal sample with 1% sulphur is combusted in a bomb calorimeter. The temperature of the bucket water increases from 25 to 28 °C. The water equivalent of the calorimeter is 2402 calorie per °C, 1 gram sample is used for the test and power 45 CT no wire is used for ignition. Out of the 10 centimeter wire 2.6 centimeters are unused. To titrate the calorimeter washing 24.2 ml of 0.0709N sodium carbonate is required this is equivalent to N by 10 NOH.

So, calculate the gross heating value of the waste consider the thermometers are working perfectly. So, here there is no correction for thermocouple or thermometer is required. So, if we want to calculate the gross heating value obviously we will use the formula just we have discussed. So this is the formula Hg equal to  $(T \times W - E_1 - E_2 - E_3)/M$ . Now we will see how can you get the value of  $E_1$ ,  $E_2$  and  $E_3$  in this case.

And what is the M, T and W value. So, here we have W value is given, M value is given that is 1 gram and temperature difference  $T_a$  and  $T_f$  it is also given so difference temperature we are getting now T is 3°C, W is equal to 2402 calorie/°C,  $E_1$  how can you calculate? The value of  $E_1$ ,  $E_1$  is dependent of  $C_1$ , so  $C_1$  is given how much it is given 24.2 ml.

So, this will be  $E_1$  will be 24.2 calorie then what is  $E_2$ ?  $E_2$  dependent sulphur content so we have 1% sulphur so we will use the formula  $E_2$ , 13.7 x 1 into how much sample you have taken 1 gram

so 13.7 calorie is our  $E_2$  value and  $E_3$  value is dependent on the wire which we have used that 7.4 centimeter power 45C10 wire so  $E_3$  will be 2.3 x 7.4 = 17.0 calorie so we have to subtract this with the TW.

S,o Hg is T x 2402 - 24.2 - 13.7 - 17, so we are getting 7150 calorie per gram. So, this way we can measure the heating value. So, in this module we have discussed how to determine the approximate and ultimate analysis. How to determine the concentration of moisture, volatile matter, fixed carbon and ash and also how to measure the heating value of the coal sample, so thank you very much for your patience.