Chemical Process Utilities
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Lecture – 4
Fuel Analysis

Welcome to the fuel analysis concept of chemical process utilities. Before we go into the detail of the different aspects of fuel analysis, which we have partially discussed in the previous lecture, let us look at what we covered previously.

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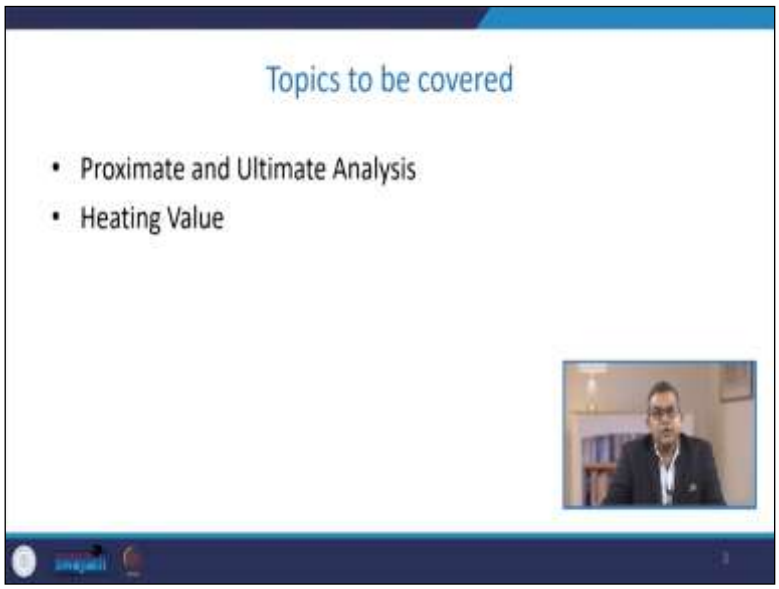

Previously, we have covered the various thermodynamic aspects of power generation and refrigeration in which we have discussed the various concept of different cycles vapor power cycles, Carnot cycle, Rankine cycle etc. In this particular lecture, we will cover the approximate and ultimate analysis. Apart from this, we will discuss the concept of heating value.

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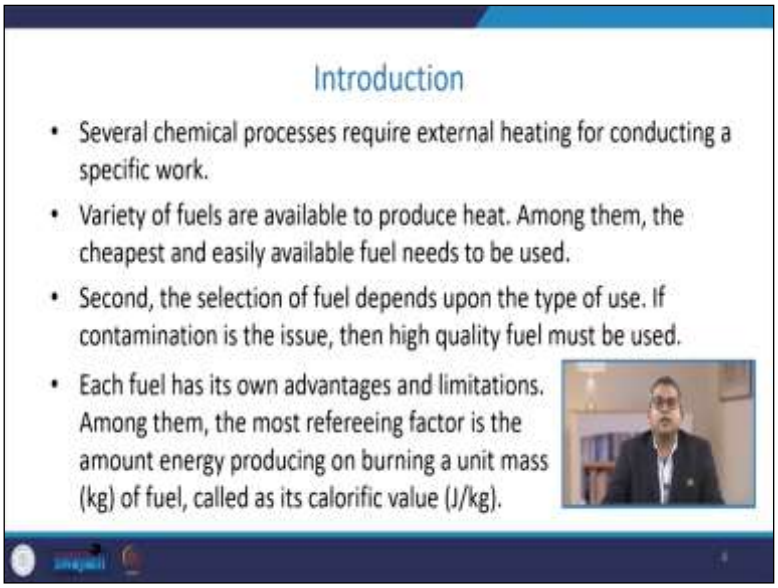

Before we go into the detail, as you know, there are various chemical processes requiring external heating for conducting a specific work. Whenever there is a requirement for external heating, we have to look into several different parameters. The one parameter or one aspect is the fuel as we discussed in the previous lecture; there is a variety of fuels available as of date but based on our requirement based on other issues like environment calorific value, n number of choices available.

So, we can say the variety of fuels is available to produce heat that is the most generic term. Among them, the cheapest and easiest available fuel needs to be used. The reason is that whenever we are discussing any process or our ultimate aspect is to have a useful product from the raw material in that case if we are overlooking such kind of a concept like cheapest or easily available fuel.

In that case, our product cost will be on the higher side. So, we have to look into this particular aspect. Now the second aspect is the selection of fuel. This usually depends on the type of use. If contamination is the issue, high-quality fuel must be used. Like, see the cheap quality fuel having high contamination may be available at a very low cost, but ultimately whenever we go for the process which is attributed to the environmental issues calorific value efficiency of the system then definitely the cost plays a very vital role.

So, we have to optimize the thing. So, based on this thing, we need to choose the fuel. Now each fuel has its own advantage and limitation. Among them, the most referring factor is the amount of energy produced on burning a unit mass of fuel called the calorific

value, and it is measured in joules per kilogram. This is the foremost requirement as far as the engineering perspective is in question because, ultimately, we have to supply the heat to the target.

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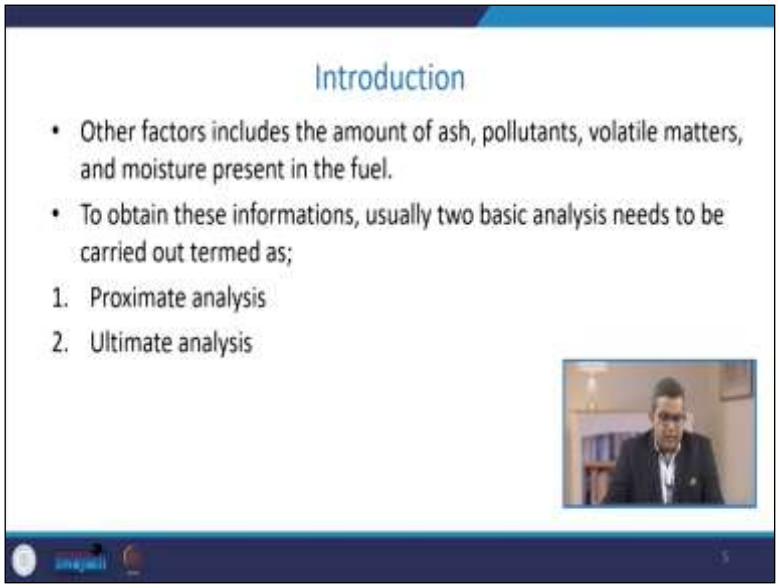

Other factors include the amount of ash pollutants because of environmental issues. When we talk about energy simultaneously, we cannot overlook the importance of the environment. So, pollutants, volatile matters, other impurities, moisture etc. All these things need to be addressed when we are going for the choice of fuel. Two basic analyses need to be carried out to obtain this information, basically, ash calorific value etc. One is the proximate analysis another one is the ultimate analysis.

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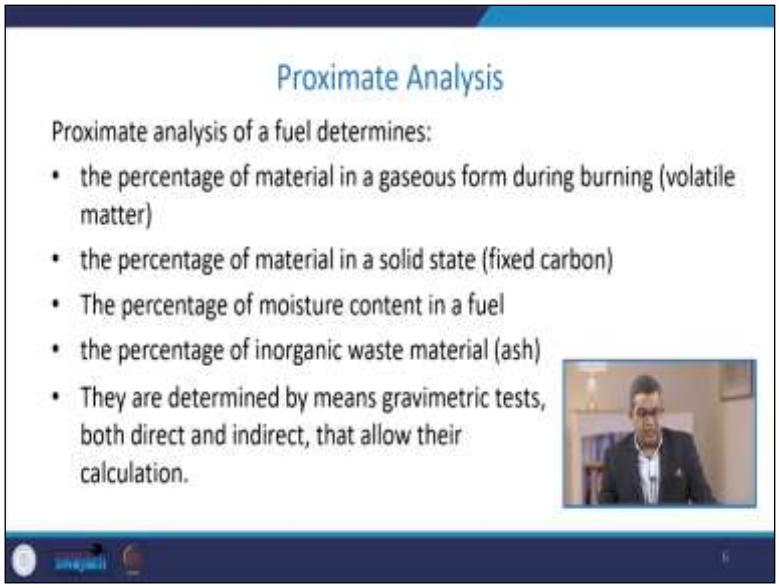

Now let us have a look at the proximate analysis. The proximate analysis of fuel determines how much percentage of material in the gas was formed during burning, reflecting the quantity of volatile matter. The percentage of material in solid-state i.e., fixed carbon, the percentage of moisture in fuel, the percentage of inorganic waste material, ash. They are determined by direct and indirect gravimetric tests that allow their calculation.

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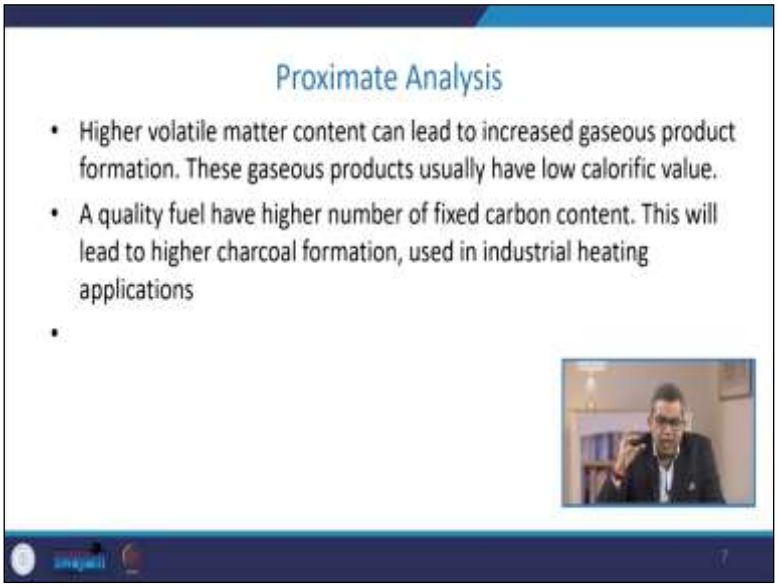

Higher volatile matter content can lead to increased gaseous product formation, and these gaseous products usually have a very low calorific value. So, the quality of fuel must be addressed. Now usually, the quality fuel has a higher fixed carbon content. This sometimes leads to higher charcoal formation used in the industrial heating application. So, this thing has advantages or disadvantages both ways.

Now let us have a brief discussion about the proximate analysis. Now usually, when we go for the determination of moisture content, it reflects in terms of percentage. First, we must know how we can measure this. We require a crucible, and at the outset, you need to weigh the dry crucible

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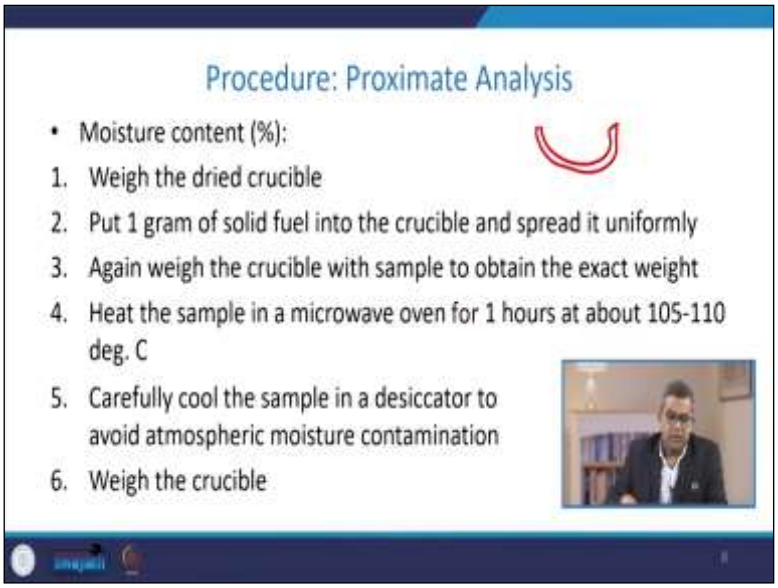

So, when you have weighed the dry crucible, put one gram of solid fuel into the crucible, and you need to spread it uniformly so that the layers and other things or stagnant zone cannot form. Again weigh the crucible with the sample to obtain the exact weight. Heat the sample in a microwave oven for one hour about 105 to 110 degrees Celsius or any oven. Now carefully cool the sample in a desiccator to avoid any moisture contamination because the atmospheric moisture may again re-enter the sample, and whatever results you get may be erroneous. Weigh the crucible.

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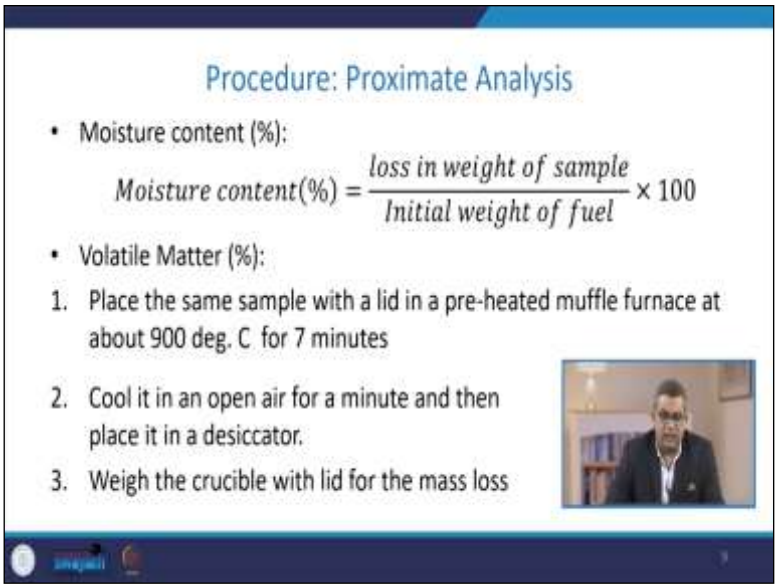

Through this mathematical equation you can find out that what is the moisture content that is

$$Moisture\ content(\%) = \frac{loss\ in\ weight\ of\ sample}{Initial\ weight\ of\ fuel} \times 100$$

So, by this way, you can calculate the moisture content.

Steps to determine the volatile matter:

Place the same sample with a lid in a preheated muffled furnace at around 900 degrees Celsius for 7 minutes.

Cool it in an open-air for a minute, place it in a desiccator, and weigh the crucible with lead to determine the mass loss.

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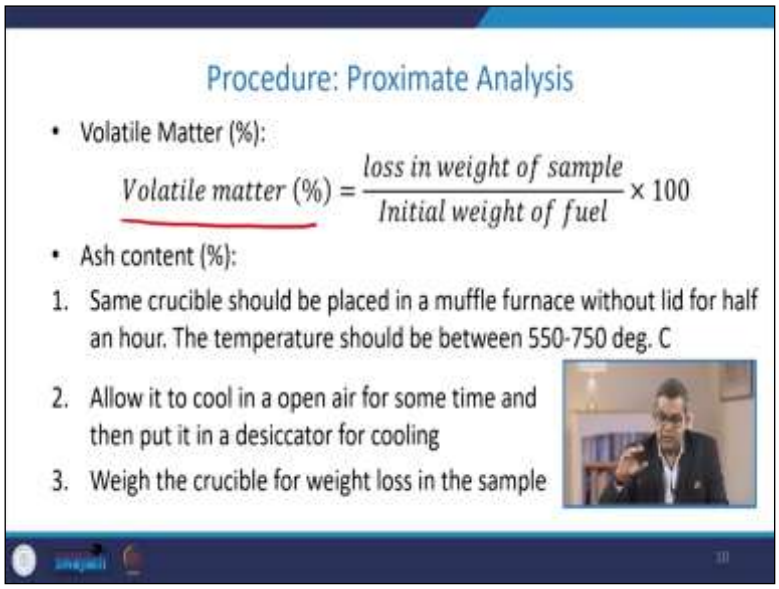

There is a mathematical relationship through which you can calculate the volatile matter

$$Volatile\ matter\ (\%) = \frac{loss\ in\ weight\ of\ sample}{Initial\ weight\ of\ fuel} \times 100$$

So, in this way, you can calculate the volatile matter.

Then coming to the ash content. It requires the same crucible, which should be placed in a muffled furnace without a lid for half an hour, and you have to maintain the temperature between 500 to 750 degrees Celsius.

You need to allow it to cool in the open air for some time and then put it in a desiccator for cooling. Perform the weighing operation for the crucible to determine the weight loss of the sample.

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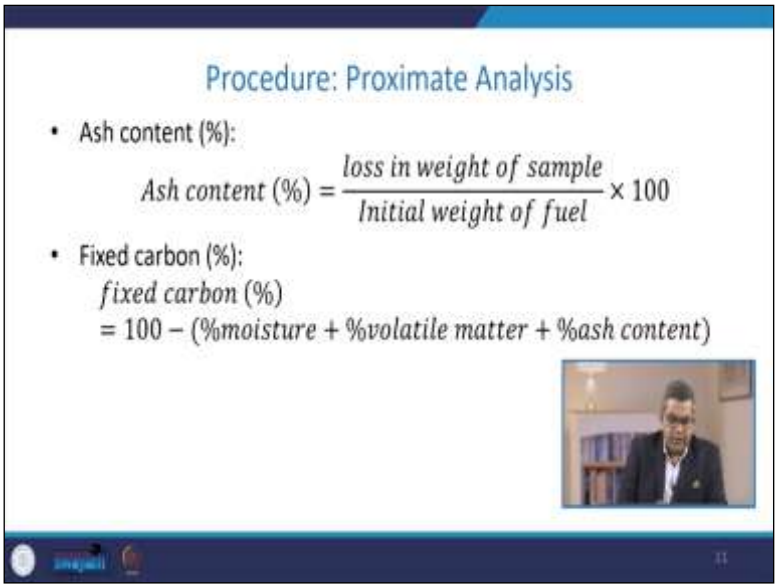

Now ash content again you can calculate through this mathematical relationship that is

$$Ash\ content\ (\%) = \frac{loss\ in\ weight\ of\ sample}{Initial\ weight\ of\ fuel} \times 100$$

This will give you the ash content in percentage.

So, as far as we need to determine the fixed carbon percent, there is a simple mathematical relationship to assess the fixed carbon percentage in the sample.

$$fixed\ carbon\ (\%) = 100 - (\%moisture + \%volatile\ matter + \%ash\ content)$$

So, by this way, you can find out how much percentage of fixed carbon is present in the sample in question.

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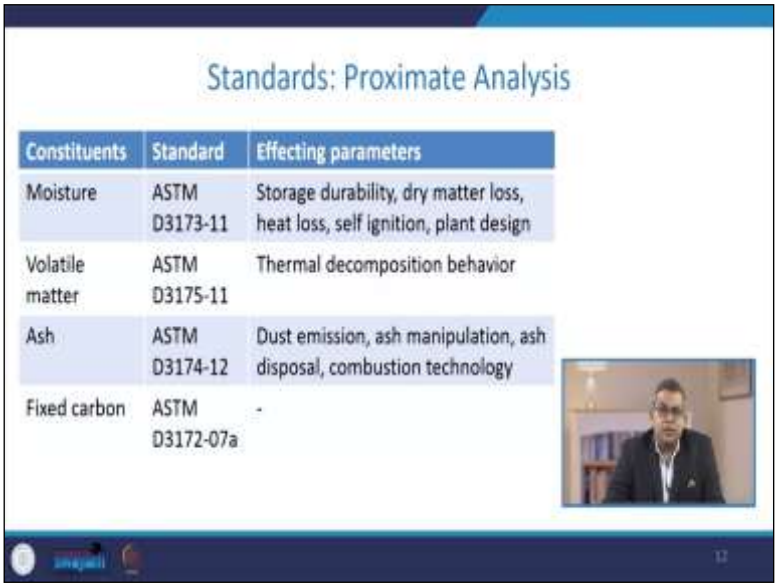

There are various standards as applicable by the ASTM American Society for Testing of Materials. They put forward certain procedures or certain methods and standards for the proximate analysis. As for moisture, the ASTM standard is D3173-11, where the affecting parameters are storage durability, dry matter loss, heat loss, self-ignition, plant design.

Similarly, for volatile matter, ASTM D3175-11, reflects the thermal decomposition behavior of the sample in question. For ash ASTM D3174-12, the effecting parameter are dust emission, ash manipulation, ash disposal, combustion technology etc. For the fixed carbon, the prevailing ASTM standard is D3172-07a.

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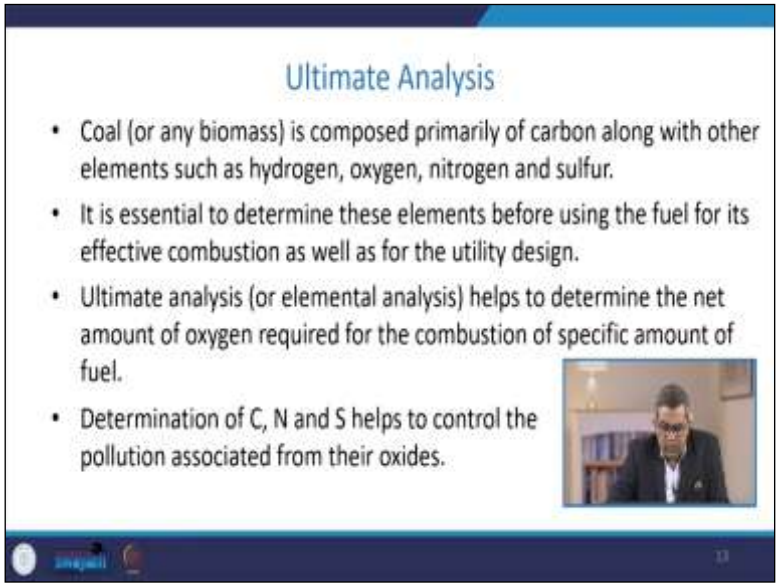

Now coming to the ultimate analysis, we usually know that coal or any other biomass (it is very applicable to biomass) is composed primarily of carbon and other elements like hydrogen, oxygen, nitrogen, sulfur. Now it is quite essential to determine these elements before using the fuel for its effective combustion and utility design.

Now why I am talking about this utility design or effective combustion because whenever we are using it as fuel, all these things may either hinder or may create a problem because sometimes sulfur is present then definitely it may corrode the system, or it may impart the hydrogen sulfide or any of gas which may create an environmental issue. Similarly, other nitrogen, oxygen, etc., like nitrogen, will not impart calorific value in the system.

So, before taking or designing our utility system, we should know the nature of the fuel. Now ultimate analysis sometimes carries the information relevant to the elemental

analysis, or sometimes it is referred to as elemental analysis. This helps to determine the net amount of oxygen required for the combustion of a specific amount of fuel.

Whenever we perform the combustion reaction, we definitely need to know how much oxygen is required. So, unless otherwise, we do not have any clue about the combustible material present in that particular sample, we do not have any information, or we do not have any knowledge about the oxygen requirement in this quiz. So, therefore this particular information is quite essential for assessing the exact requirement of oxygen.

So, the determination of carbon, nitrogen, and sulfur helps to control the pollution associated with their oxides, as this may pose a serious environmental problem. Now let us discuss the procedure through which we can carry out the ultimate analysis. So, first have a look at the carbon and hydrogen.

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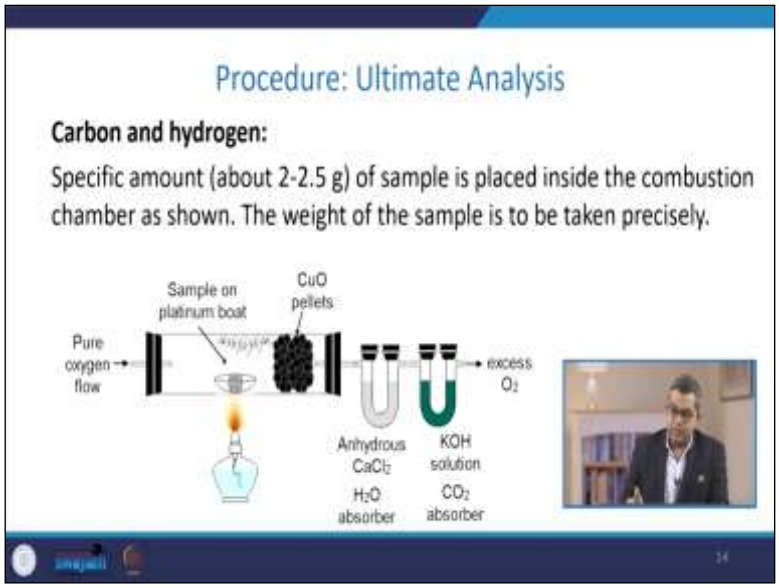

You must have a specific amount of sample, maybe 2 to 2.5 grams of the sample placed inside the combustion chamber, which is here in the figure. Now the weight of the sample is to be taken very precisely because, ultimately, it will give you proper information.

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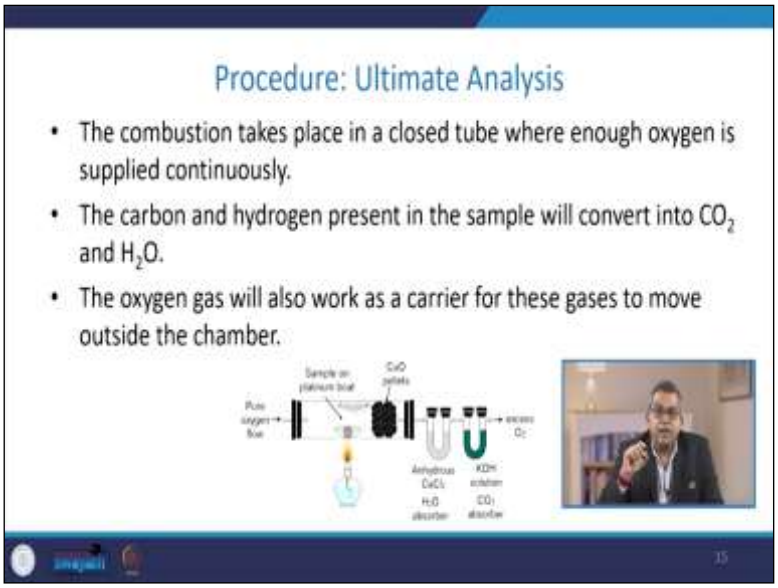

Then the combustion takes place in this closed tube where enough oxygen is supplied continuously for the combustion purpose. So, here we are supplying the pure oxygen from here and the carbon and hydrogen present in the sample they invariably will convert into carbon dioxide and water or H_2O. The oxygen gas will also work as a carrier of these gases to move outside the chamber. So, you have the sample ports over here.

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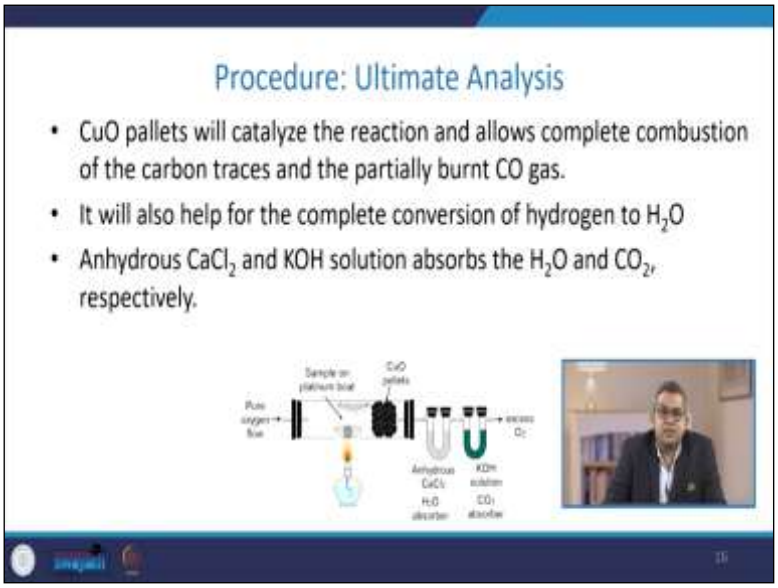

Now, CuO pallets will catalyze the reaction and allow the complete combustion of the carbon traces and partially burnt CO gas. So, it will help for the complete conversion of hydrogen to water. Now, anhydrous $CaCl_2$ and KOH solution absorbs the H_2O and CO_2, respectively. So, in this way, you can assess because you have a pre-knowledge about these solutions. So, you can easily carry out how much carbon and hydrogen are present.

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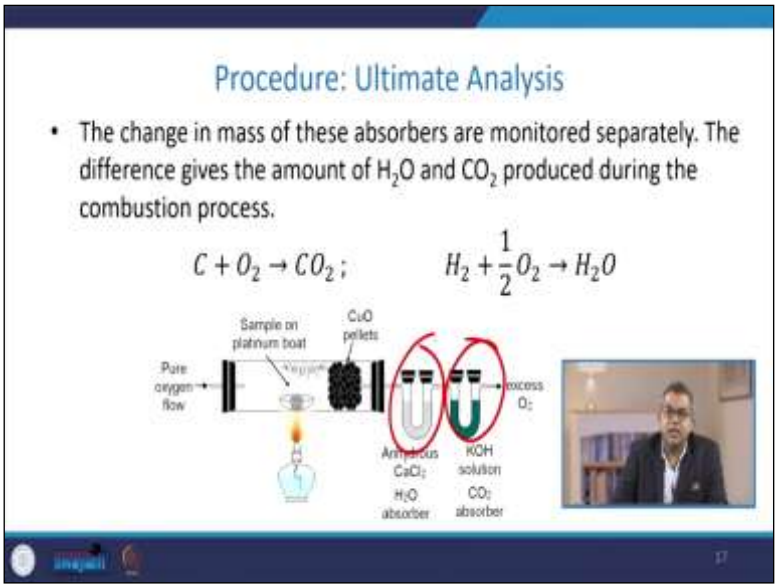

The change in mass of these absorbers is monitored separately. So, whatever difference occurred gives the amount of H_2O and CO_2 produced during the combustion process. So, you can take the cognitions of these two reactions, that is

$$C + O_2 \rightarrow CO_2 \; ; \qquad H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$

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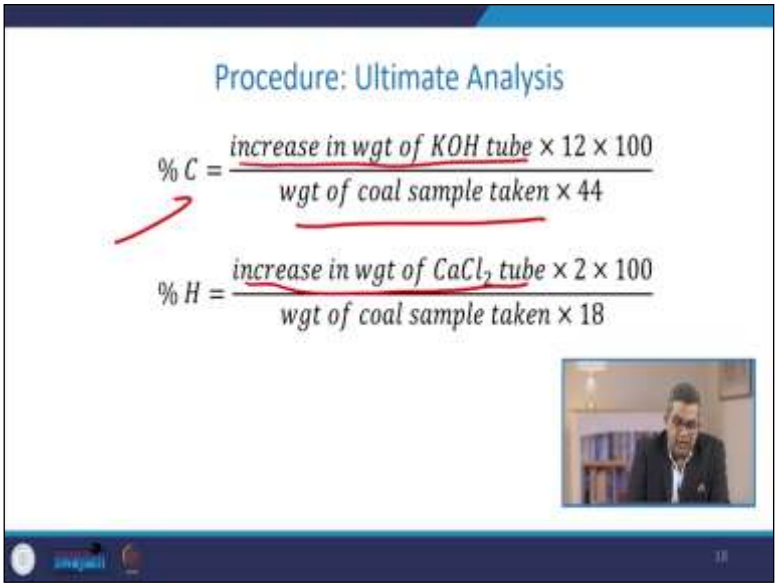

You can find out how much percentage of carbon is present in the sample by this mathematical relationship that is

$$\%\, C = \frac{increase\ in\ wgt\ of\ KOH\ tube \times 12 \times 100}{wgt\ of\ coal\ sample\ taken \times 44}$$

12 and 44 are the molecular weight of C and CO_2, respectively. Similarly if we need to find out the percentage of hydrogen present in the sample

$$\% H = \frac{increase\ in\ wgt\ of\ CaCl_2\ tube \times 2 \times 100}{wgt\ of\ coal\ sample\ taken \times 18}$$

18 is the molecular weight of H_2O.

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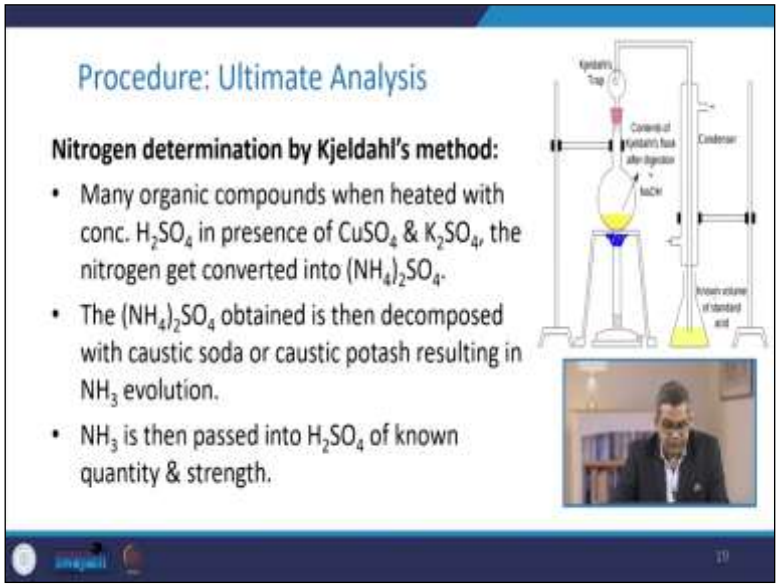

Next is how we can determine the nitrogen percentage. So, the determination of nitrogen is being carried out by Kjeldahl's method. For many organic compounds, when heated with concentrated H_2SO_4 in the presence of $COSO_4$ and K_2SO_4, the nitrogen gets converted into $(NH_4)_2SO_4$. Ammonium sulfate obtained is then decomposed with the cause caustic soda or caustic potash resulting in ammonia evolution. The ammonia is then passed into the H_2SO_4 of known quantity and strength.

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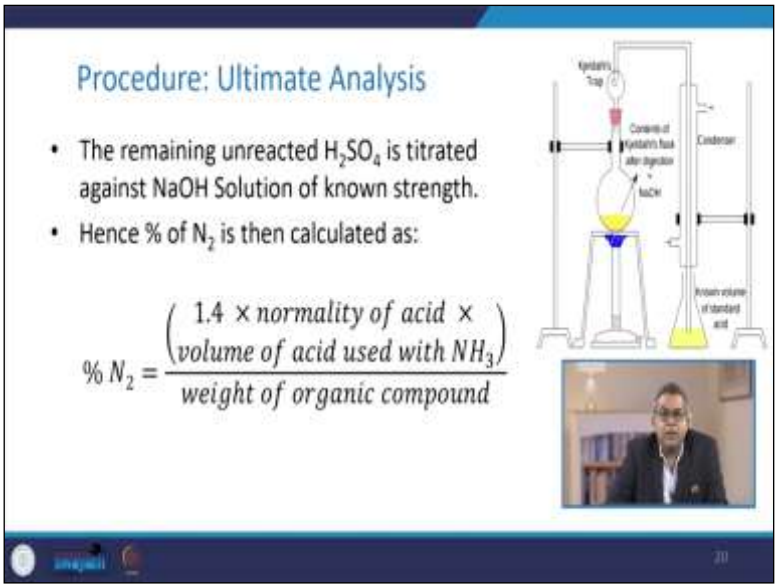

So, the remaining unreacted H_2SO_4 is then titrated against the sodium hydroxide solution of known strength. So, in this way, you can calculate the percentage of nitrogen present in the sample.

Now this is a simple mathematical formula that is

$$\%\ N2 = \frac{\left(1.4\ \times normality\ of\ acid\ \times volume\ of\ acid\ used\ with\ NH_3\right)}{weight\ of\ organic\ compound}$$

This is Kjeldalh's setup, very common and frequently used in the determination of nitrogen content.

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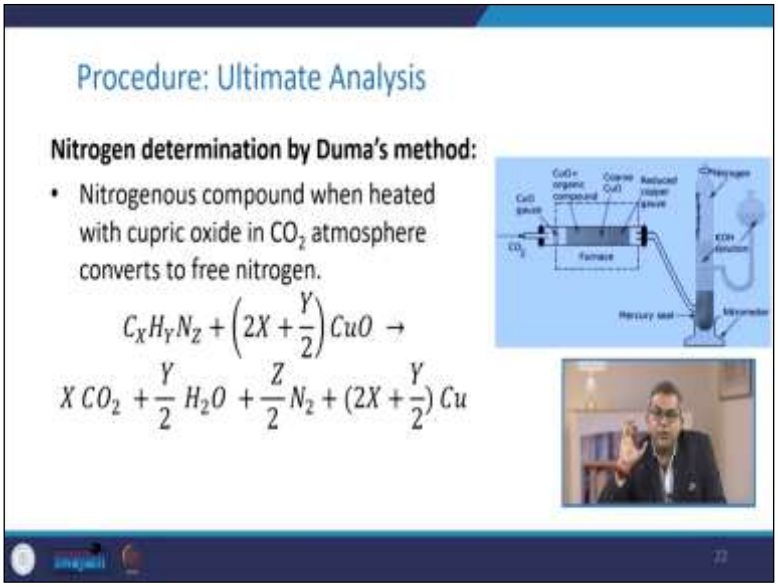

Now another method for determining ultimate analysis under this nitrogen determination is the Duma's method. In Duma's method, the nitrogenous compound, when heated with

the cupric oxide in a carbon dioxide atmosphere, converts into free nitrogen, and the simplified formula is

$$C_X H_Y N_Z + \left(2X + \frac{Y}{2}\right) CuO \rightarrow$$

$$X\ CO_2 + \frac{Y}{2}\ H_2O + \frac{Z}{2} N_2 + (2X + \frac{Y}{2})\ Cu$$

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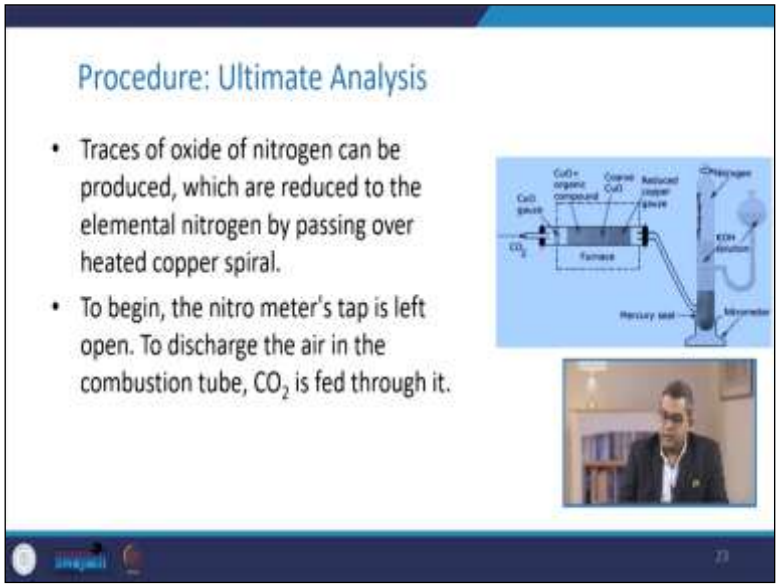

This is the typical diagram of Duma's method. There is a capric oxide gauge, and this cupric oxide and organic compound are placed over here under the edges of coarse cupric oxide, and the reduced copper gauge and continuous supply of CO_2 enters into this one, and this is typical anatomy of the furnace and this it is subjected to this mercury chamber where nitrogen is get collected with the help of displacement of KOH solution and by this way you can find out the volume of nitrogen.

Now traces of oxide of nitrogen it can also be produced, which are reduced to the elemental nitrogen by passing over the heated copper spiral-like here. To begin, the nitrometer strap is left open to discharge the air in the combustion tubes, and CO_2 is fed through it.

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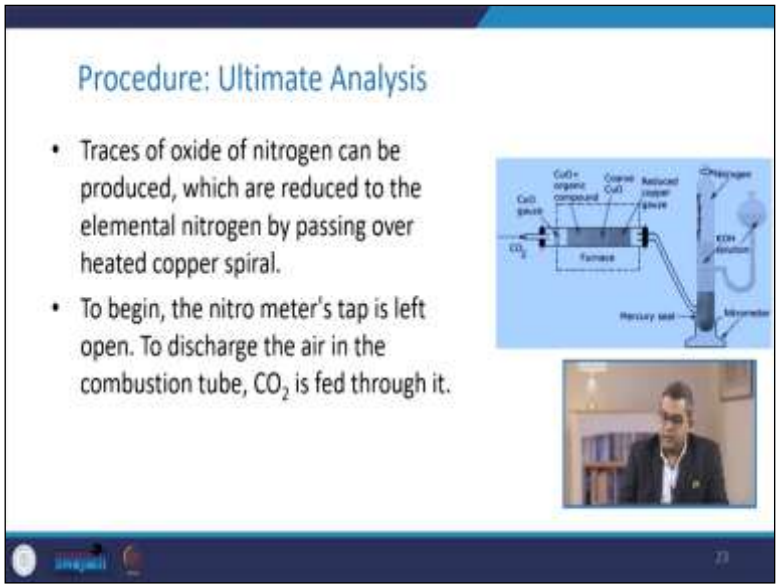

So, when potash solution fails to reach the top and is fully absorbed by rising gas bubbles, it indicates that only CO_2 is arriving and that all air has been evacuated from the combustion tube. After that, the nitrometer is filled with the potash solution by lowering the reservoir and closing the trap.

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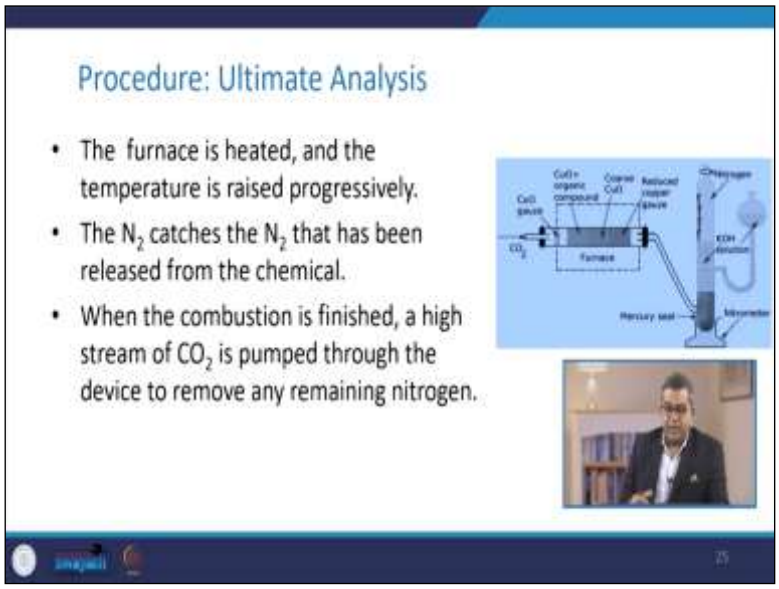

After this, we can heat the furnace, raising the temperature progressively. The nitrogen catches the nitrogen that has been released from the chemical. When the combustion is completed, a high stream of CO_2 is pumped through the device to remove any remaining nitrogen, called nitrogen flushing. So, you can flush it out so that any nitrogen can be collected and measured.

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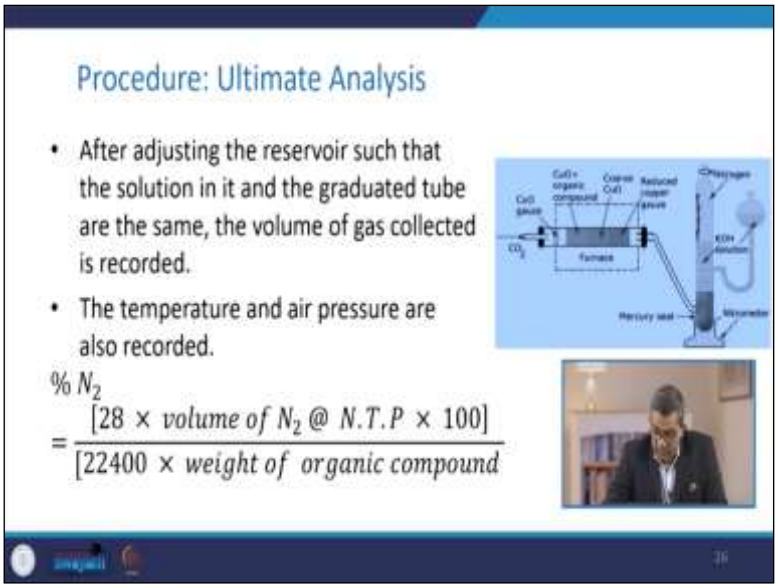

After adjusting the reservoir such that the solution in it and the graduated tube are the same, the volume of the gas collected recorded, and the temperature and air pressure are also being recorded because it carries valuable information and with respect to the mathematical formula.

Now the percentage of nitrogen easily we can calculate with the help of this mathematical relationship

$$\% N_2 = \frac{[28 \times volume\ of\ N_2 @\ N.T.P \times 100]}{[22400 \times weight\ of\ organic\ compound}$$

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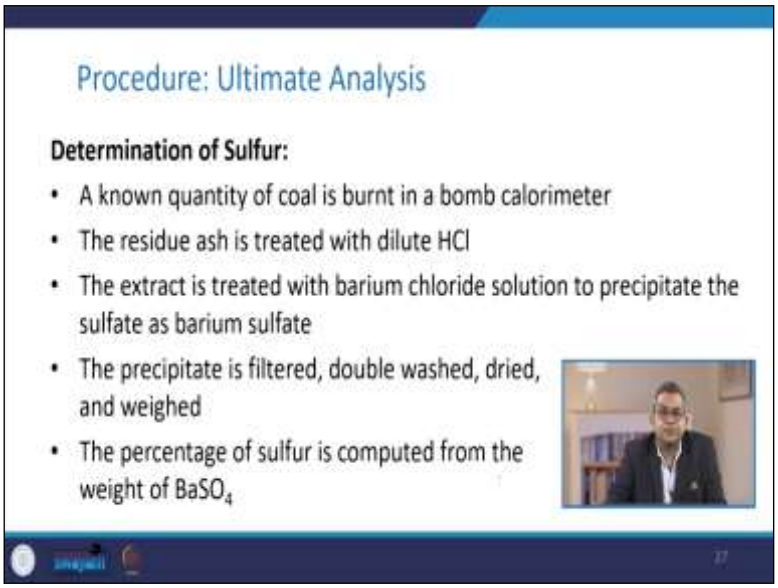

Now at the outset, let us discuss how we can determine the sulfur. Sulfur, among all, is an extremely non-eco-friendly element under the ultimate analysis. So, for this, we require a bomb calorimeter. So, the unknown quantity of coal is burnt in the bomb calorie meter.

Whatever residue remains in the bomb calorimeter is supposed to be treated with dilute HCL. The extract is treated with barium chloride solution to precipitate the sulfate as barium sulfate. Now whatever precipitate is generated in due course of time is filtered, double washed, dried, and weight and a percentage of sulfur are computed from the weight of barium sulfate.

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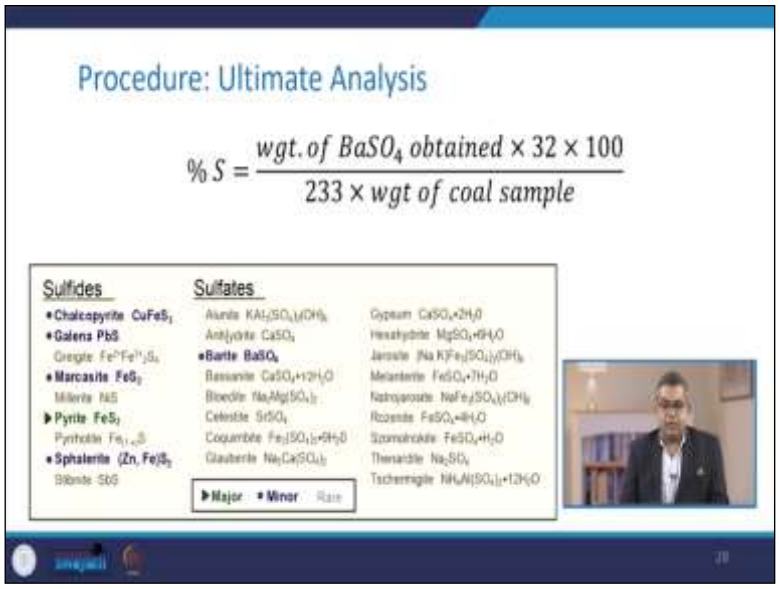

This is the standard formula through which we can calculate the percentage of that is

$$\% S = \frac{wgt.\ of\ BaSO_4\ obtained \times 32 \times 100}{233 \times wgt\ of\ coal\ sample}$$

Some of the sulfides, sulfates etc., are present in the fuel, and some of them are present in the major quantity, and some of them are present in the minor quantity, and some of them are very rare. If you see the major component of pyrites, they are present in most of the fuel. Similarly, barite they are present in the minor quantity yes other they are in the rear one.

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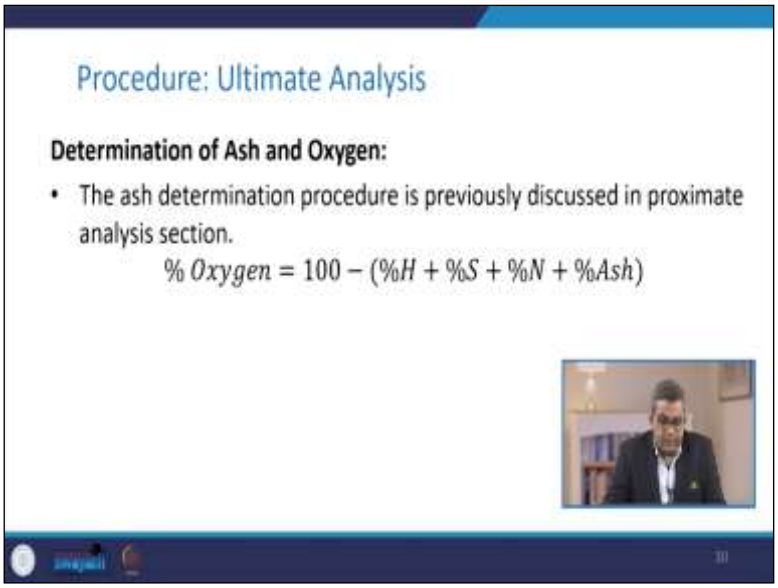

Now under this head, that is a determination of ash and oxygen. So, we have already discussed the ash determination procedure in the proximate analysis. So, we can calculate the percentage of oxygen

$$\% \, Oxygen = 100 - (\%H + \%S + \%N + \%Ash)$$

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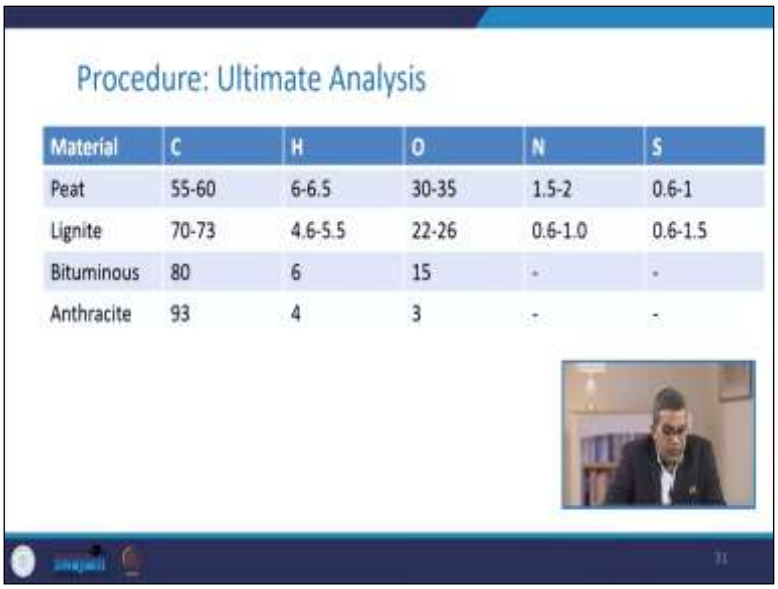

You can see here the percentage of carbon, hydrogen, oxygen, nitrogen, and sulfur in different typese of coal samples. This is for reference, and like peat, it has a carbon content of 55 to 60% hydrogen, 6 to 6.5% oxygen, 30 to 35% nitrogen 1.5 to 2, and sulfur 0.621. Similarly, lignite has 70 to 73%. So, the more carbon, the better will be the calorific value.

Similarly, anthracite and bituminous coal they are having the highest percentage of carbon, like anthracite at 93% and 4% hydrogen, and approximately 3% oxygen. So, it is the purest form you can say of coal. Similarly, bituminous 80% carbon content hydrogen 6% and 15% oxygen. So, this is the thing, and that is why you find that bituminous and anthracite coal has a higher cost than peat lignite.

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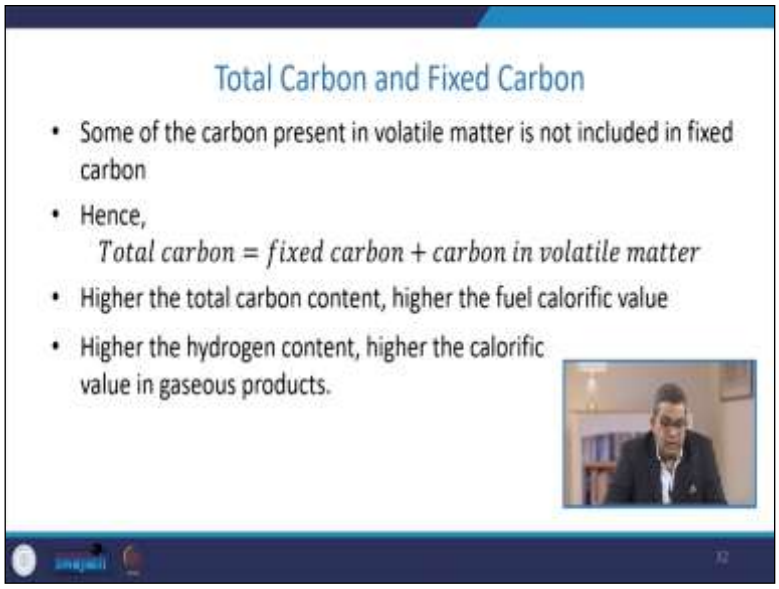

Now let us briefly discuss the total carbon and the fixed carbon. Some of the carbon present in the volatile matter is not included in the fixed carbon. So, therefore we need to find out

$$Total\ carbon = fixed\ carbon + carbon\ in\ volatile\ matter$$

The higher the total carbon content, the calorific fuel value, and the higher the hydrogen content, the higher the calorific value in the gaseous products. So, is by this way we can find out the total carbon.

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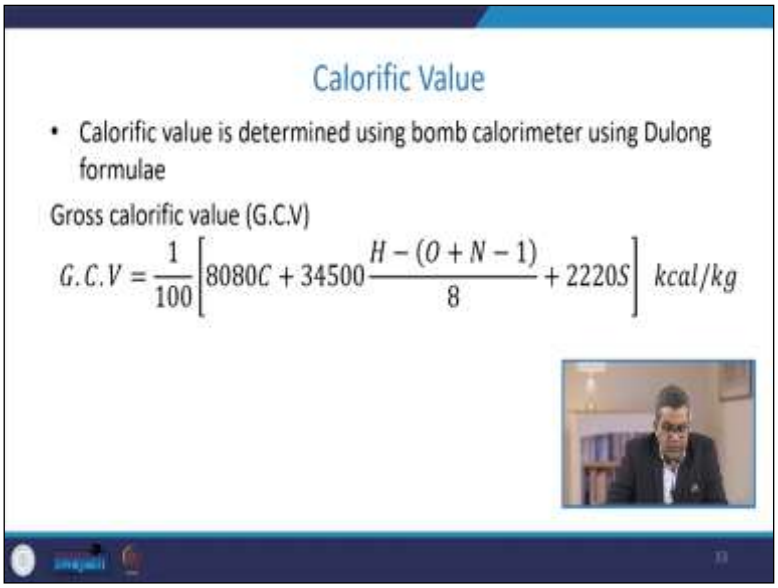

And let us have a brief discussion about the calorific value; this is determined using the bomb calorie meter, which we have already discussed using the Dulong formula equation. So, the gross calorific value that is sometimes referred to as GCV that is

$$G.C.V = \frac{1}{100}\left[8080C + 34500\frac{H-(O+N-1)}{8} + 2220S\right]\ kcal/kg$$

In this chapter, we have discussed the ultimate analysis and proximate analysis. We have already discussed the importance of these two analyses because our ultimate aim is to produce or have fuel for the heating purpose, whatever we are using for the heating purpose. It should give a high calorific value. Apart from this, it should not impart any kind of environmental threats to the environment.

It should not impart any kind of pollutant aspect to any system it should not be a danger to the system in use like sulfur it may corrode like other components. So, we can design our system based on the better choice of fuel cost it should be cost-efficient. So, the ultimate cost of the product should not go on the higher side. Although availability also is very important, we will discuss the availability issue in due course of time in a separate lecture.

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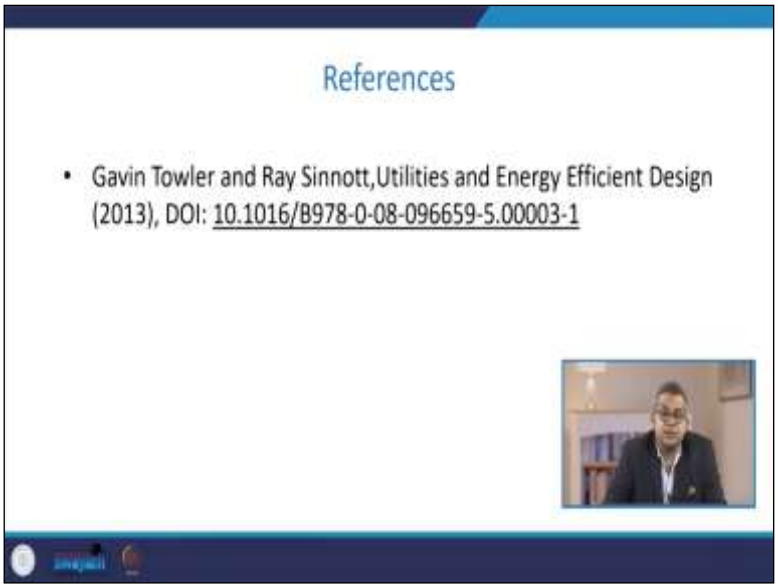

If you like to have some more study or references, I have enlisted one of the references for you, you can have a look at these references for the future course of study, thank you very much.