Materials and Energy Balance in Metallurgical Processes

Prof. S. C. Koria

Department of Materials Science and Engineering

Indian Institute of Technology, Kanpur

Module No. # 01

Lecture No. # 26

Introduction to Ironmaking

Today, I will be discussing another example for the application of the concept of reduction smelting in the production of pig iron in blast furnace. So, the title of the lecture is Ironmaking.

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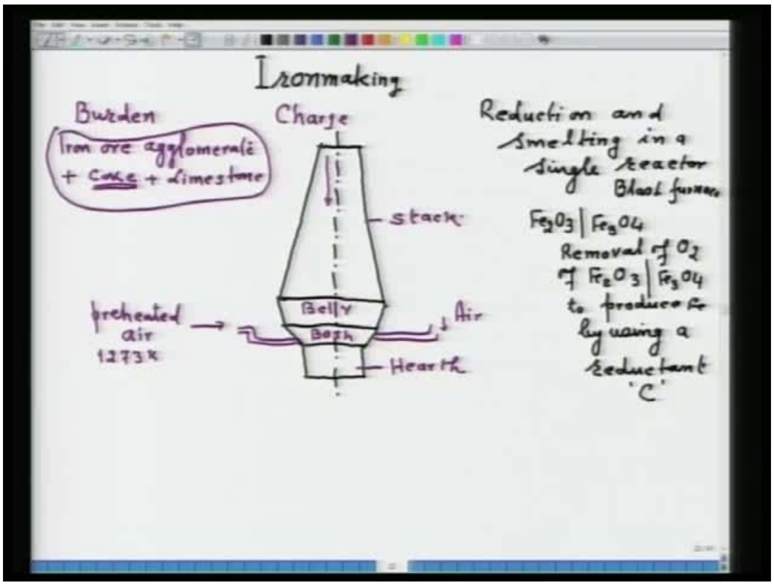

Now, the sketch, which I have drawn, is a blast furnace and it is used for ironmaking. Before I describe the sketch, I would like to say that the blast furnace ironmaking typically implies a reduction and smelting in a single reactor. The sketch before you is called a blast furnace and I hope all of you must be aware of it.

Reduction involves removal of oxygen from metallic mineral. By metallic mineral, I mean that in the ore concentrate, metallic mineral is Fe2O3 or Fe3O4 and removal of oxygen from Fe2O3, if the ore is hematite or from Fe3O4, if the ore is magnetite. To produce iron using a reductant and typically, the reductant used is carbon. This is followed by smelting in a single reactor and the objective of smelting is to separate gangue mineral in the form of slag and to produce pig iron. In fact, we call ironmaking, but the output of blast furnace is pig iron. It means we produce iron, which contains carbon, silicon, manganese, phosphorus and sulphur. In fact, what is the output of blast furnace ironmaking? You may call as hot metal or you may call pig iron and both convey the same meaning. The output is pig iron oblique hot metal or slag.

In this particular process, the charge descent in the downward direction and charge is typically called as burden. The burden consists of iron ore agglomerate; it could be sinter or palate plus coke and limestone. I will come back again to the coke. This is typically called a burden of the blast furnace and the burden is introduced from the top by bell arrangement that I have not shown over here. The burden descents and what is done? A hot blast air is injected through the tuyere somewhere at this (Refer Slide Time: 04:23) particular location. This air is pre-heated to 1273 kelvin or even higher depending upon the operation of the process and this is also called as air blast.

Now, (Refer Slide Time: 04:56) this particular portion is called hearth, this is called belly, this is called bosh and this is called stack. The burden descents and the hot gasses, which are formed by the combustion of coke at the tuyere level descents upward.

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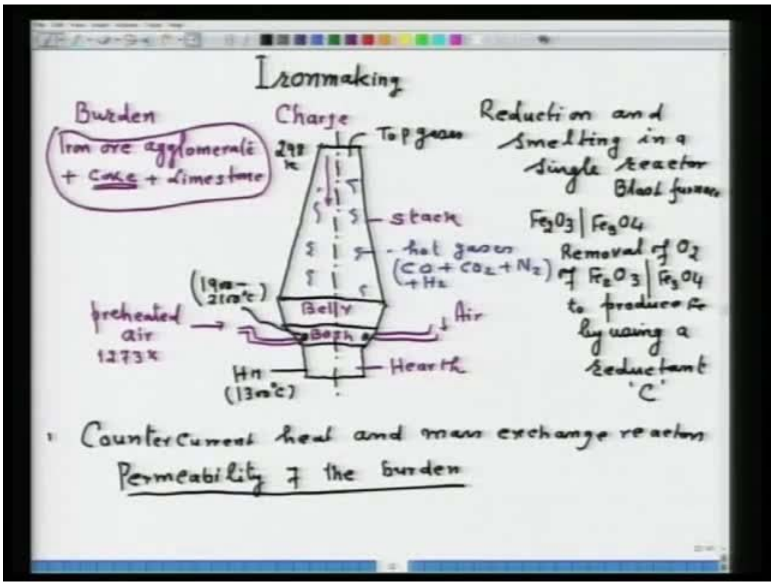

So, the hot gasses comprises of CO plus CO2 plus N2 plus H2O. They travel upward that means this blast furnace is essentially a counter current heat and mass exchange reactor. These are some of the important thing that we must know: first thing that a blast furnace is a counter current heat and mass exchange reactor. In this counter current, the heat and mass are exchange is between the burdens or between the descending burdens with the ascending gasses.

If it is a counter current heat and mass exchange reactor, then the most important thing or the basic of trouble free operation of a heat and mass exchange reactor comprising of gas and solid is the permeability of the burden. The burden is charged at 298 kelvin from top. Here, hot metal is discharged around 1300 degree celsius. At the point when air is injected, there is a reaction occurring between carbon of coke and oxygen of air, a temperature of the order of 1900 to 2100 degree celsius is created and you can add 273 to get in kelvin .

So, when these hot gases raise upward, the bad or the burden, which is falling should provide sufficient permeability, so that the gases can escape unhindered through the burden. Ultimately at the top, you have the top gasses that are at no portion, the flow of the upward raising of the gasses should be hindered. Therefore, the permeability of the burden is a very important issue. I will come back to this aspect again. Before I address this permeability of the burden, I would like to say that the height of this reactor is approximately 25 to 30 meter height. Out of that total height, around 70 percent of the height of the reactor is utilized to reduce Fe2O3 to FeO. Rest of the 25 percent of the height approximately is used to reduce FeO to iron melt; formation of hot metal that is dissolution of carbon, silicon, manganese, phosphorus and sulphur and removal of gangue mineral.

Now, the question always comes why we require so much height, around 25 to 30 meter height. It is essential because we start at the reduction of Fe2O3 and the reduction of Fe 2O3 to FeO. It is quite fast, but from FeO to Fe, the reduction is very sluggish. It requires a very high reducing condition of the order of around 7 equilibrium conditions, around 900 degree celsius. It dictates that if you want to reduce FeO to Fe, you require at least 70 percent of CO in the gases, which are coming in contact with the Fe2O3 of the burden. So, these gases are formed only at the bottom part of the furnace, where oxygen is injected in the bosh region and carbon reacts. You get a very high temperature and you get a CO. So, this height happens at that much of height.

When the burden falls from the top of the stack to the belly portion, which is around 70 to 75 percent of the height burden. It should remain intact every time and every moment, it should provide sufficient permeability to the upward raising of the gases. Since you have solid burden, when it falls into the furnace, it forms a bed. This bed provides the porosity or permeability to the upward raising of the flow gases. Now, what component of the burden or what component of the bed provides porosity.

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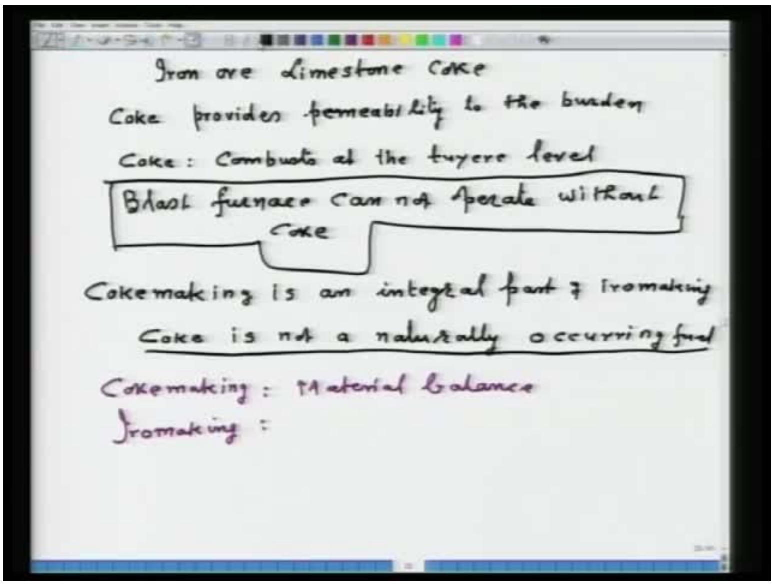

Now, we are charging iron ore, we are charging limestone and we are charging coke. All these three fall into blast furnace. They form a bed consisting of iron ore, limestone and coke. So, the gases raise to the permeability of this particular bed. When these thing falls from the top, since the upward raising gas has enough reduction potential, it will try to reduce Fe2O3 of the ore to decompose calcium carbonate to CaO and CO2. As a result of which, the size and shape of iron ore and limestone will change. So, this will affect the permeability of the burden, but the coke of the burden or coke of the bed is the only component, which reacts at the tuyere level.

Coke provides permeability to the burden. Coke provides permeability to the burden; the reason is very clear that coke of the burden reacts only at the tuyere level. That means the coke maintains its size and shape until it reaches the tuyere level. It requires oxygen to combust and nothing happens to the coke until it arrives at the tuyere level. Of course, little bit shattering may occur, but that is very minimum.

First thing is that coke because combustion at the tuyere level. Therefore, coke provides the permeability of the burden. Therefore, I can make this statement that blast furnace cannot operate without ore. A single reason for this is that coke provides the permeability to the burden. The concept of an efficient heat and mass exchange reactor dictates that at every time during the upward rising of the gases, the gases should flow unhindered. Otherwise, it will create a backpressure, so that is where the blast furnace cannot operate.

Without coke, you can reduce the amount of coke, but at zero coke level, it is not possible to operate the blast furnace.

With the modern technology, by the introduction of pulverized coal injection through the tuyere or height of pressure or high temperature, you may cut down the coke requirement. Certain minimum coke has to be charged into the furnace because this is the only component of the burden, which maintains permeability into the bed of the blast furnace. Therefore, coke making is an integral part of iron making. If a plant is producing, for example, 10000 tons of hot metal per day, you require 500 to 600 kg of coke per ton of hot metal. You can imagine how much amount of coke you will be requiring on a day basis.

To meet this requirement, the coke making has to be an integral part of the ironmaking. Therefore, what I want to say is that while dealing further with the ironmaking, I will first address the issue of coke or the production of coke because coke is not a naturally occurring fuel. Remember, coke does not occur in the nature and also remember, coke is not a fossil fuel. In the nature, you get coals of different varieties. Now, a detailed description of this is addressed in my detailed lecture course on Fuel furnace and Refractory. You can also refer to this lecture.

What will I do now to organize these lectures? First, I will go with the coke making as it has so much of importance. I will also go to material balance in coke making, after giving you a little bit of concept. We will go to iron making concept and material balance. So that is how I will be organizing my lecture.

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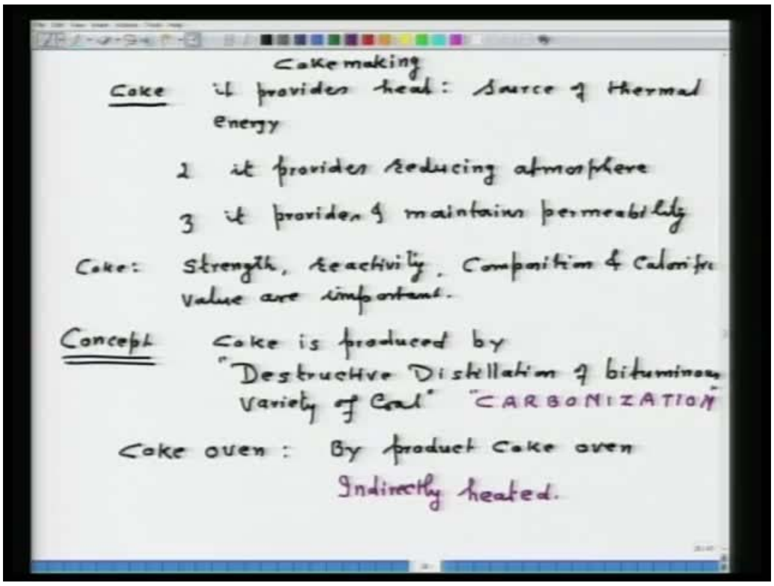

Immediately, I will proceed to the coke making. There are certain important things about the coke. First, it provides heat as a source of thermal energy because you have noticed that a burden is charged at 298 kelvin . The hot metal and slag are discharged at 1300 celsius. The top gases are discharged at 200 or 250 celsius and everywhere heat is to be provided. The heat is only provided by the combustion of coke or I will again repeat that. Many students sometimes do the mistake; coke is not a naturally occurring fuel. Please remember coke has to be produced and therefore, much importance is attached to coke making, when we talk about the blast furnace ironmaking because of certain quality in the coke, we require an ironmaking student to know what is involved in coke making.

Second function: coke provides reducing atmosphere. I mean, it acts on the carbon of the coke as the reducing agent that is the chemical energy, which is required to remove oxygen of Fe_2O_3 comes from coke. Third of course is important, I am taking a separate lecture on coke making. It provides and maintains permeability in the blast furnace. So, this is the importance attached and we are also convinced that coke has to be produced.

What is important is that strength is important. Otherwise, it has to fall to a height of 0 to 20 meter. Before 25 meter, it reacts with the oxygen of the blast, so that height requires strength. It should also have reactivity. Besides strength and reactivity, the composition and calorific value are important. Composition is important because you require carbon and normally, coke is produced from naturally occurring fuel that is called coal.

According to its composition with reference to carbon, hydrogen, nitrogen, oxygen, sulphur and ash. Calorific value is important and how much amount of heat is available, we will take this aspect now. So, the concept of coke making, coke is produced by destructive distillation of bituminous variety of coal. Now, those who are interested in learning more, they should see my video lecture on fuel furnace in refractory. There, I have given the details of coke making, although I will not be giving that much of details. I am giving coke making, so that I can go to the material balance in coke making. So, a brief destructive distillation of bituminous variety of coal - It means, coal is heated out of contact with air. It means destructive distillation of coal and this process it is also called carbonization.

You can say coal is carbonized to coke or coal is destructively distilled to form coke or coal is heated out of contact with air. So that you get coke and the temperature is around 1000 degree celsius. The coal is carbonized in the unit and which is called coke oven. All integrated steel plants of the world use the byproduct of called coke oven. All the byproducts in coke ovens are heated indirectly because you cannot heat coke oven from inside by charging fuel. You have to heat the coke oven indirectly that is the walls are being heated up. Through the heat transfer, the temperature in the coal, which is contained in the coke oven is maintained in order to carry out carbonization.

So, the byproduct coke ovens are indirectly heated. Imagine, you know the composition of the coal. It has organic matter and inorganic matter. When it is heated out of contact with air, what will happen? Coal will disrupt on its own. So, all the bonds will be broken. You have organic coal CHONS, all the bonds will be broken the bonds will reunite. H will combine with N to form NH3, C may form hydrocarbon with C and H, H may combine with S to form H2S and N may react with hydrogen to form NH3.

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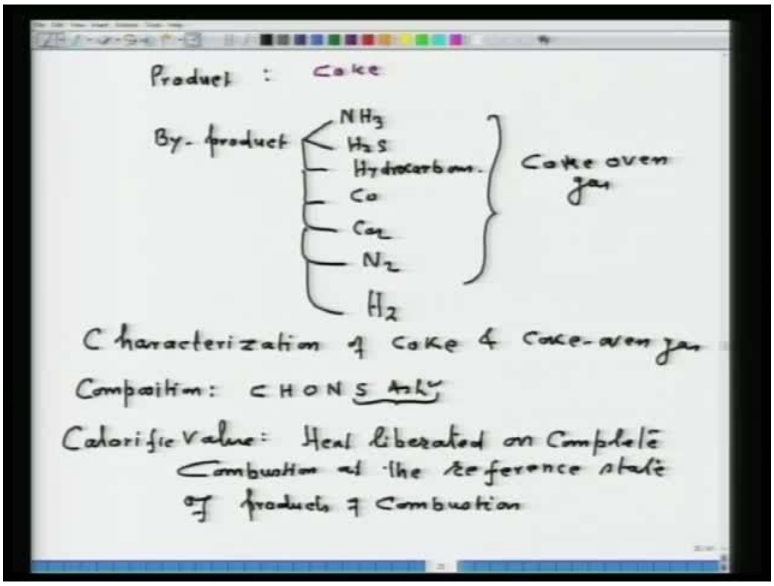

When coal is destructively distilled or coal is carbonized, we get the product and byproducts. I will be writing only the product because my objective of using coal and coke oven is to produce coke and so the product is only coke. Whereas, the byproducts could be NH3, H2S, hydrocarbons like C2H4, CO2, nitrogen and all these are called coke oven gases.

From the coke oven gas, you can produce NH3, NH2 as ammonium sulphate. Similarly, form benzene, you can produce other products also. It may have hydrogen and the coke oven gas is also an important byproduct over here. Why this is important? Because, you are not producing few tons of coal, you are producing 10000 tons of hot metal and 500 kg per ton of hot metal is the consumption of coke. You yourself can calculate how much amount of coal you will be converting to coke on a day basis and how much amount of coke oven gas will be liberated. We will see this in the material balance also. So, in nutshell, this is how the coal is converted to coke.

Now, from our material balance point of view, the importance is the characterization of coke and coke oven gas because you will be using coke in the blast furnace, you have to characterize it. We want to see what the coke oven gas consists of because if it is a gas, it has a calorific value and it is very useful. You are reproducing few hundreds of meter cube of coke oven gas on daily basis. That weight will go for the material balance. If you talk about characterization of coke, then the composition is important.

Composition means, it has carbon, hydrogen, oxygen, nitrogen, sulphur, ash. Ash should be minimum because higher the percentage of ash, same amount of ash will be released when it is charged into blast furnace into coke burns into tuyere level. Accordingly, the high amount of ash has to be removed and so there is low amount of ash.

About sulphur - more amount of sulphur have to be removed during the ironmaking in the blast furnace because all sulphur will enter into hot metal. That is the composition point of view and ash is the most important. You should have minimum ash. Another important thing is - its calorific value, calorific value is the heat liberated on complete combustion at the reference state of products of combustion.

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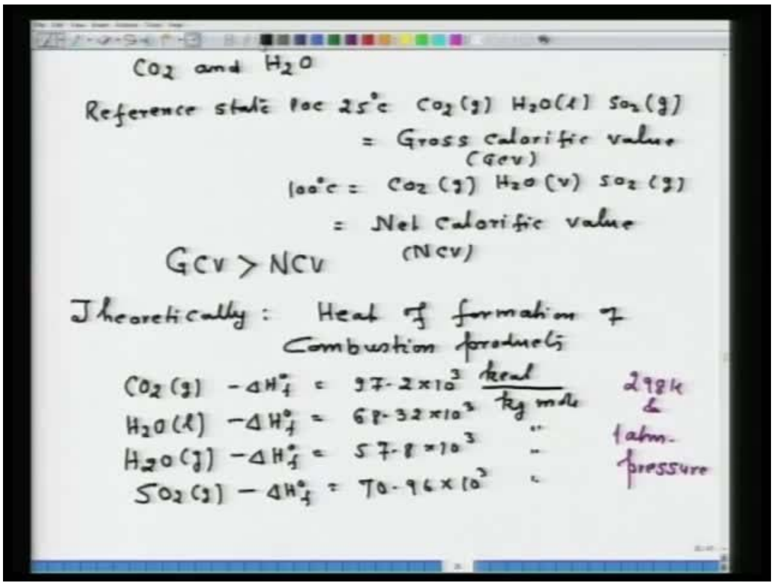

Now, if you see the composition, it has carbon, hydrogen, oxygen, nitrogen and sulphur is very minimum. So, the combustible components are carbon and hydrogen, CO2 and H2O are mainly the products of complete combustion of the coke. For example, let us take the reference state, if we take Poc reference state at 25 degree celsius, then CO2 is in the gaseous state, H2O as liquid and SO2 in the gaseous state. What do we determine? We have gross calorific value.

Now, if the reference state of Poc is 100 degree celsius and in that case, we have CO2 in gaseous state, H2O as vapor state, SO2 in gaseous state. The value determined is called net calorific value. We also called as NCV and this we can also call as GCV. Of course, GCV is greater than NCV. Why can you guess it? Because, in determining gross calorific value, you are adding the latent heat of condensation, which you will be gaining by bringing H_2O vapor from 100 degree to H_2O liquid at 25 degree celsius. This is why gross calorific value is greater net calorific value.

Now, how to determine this calorific value? When you want to do all heat balance calculation in the case of ironmaking, you must know how much amount of heat is being produced by the combustion of coke at the tuyere level. For that you must know what the calorific value of the coal is, what is the calorific value of coke. You must be able to determinate it. Well, you can determine from the experiments by using calorie meter. Again, you can see the details in my video lecture on fuel refractory on furnaces. One can also determine theoretically and theoretically it is determined from the heat of formation values, from heat of formation of combustion product. When we determine from the heat of formation, we always mean a complete combustion.

Complete combustion of carbon gives CO_2. There is no doubt that complete combustion of hydrogen gives H_2O. Absolutely, no doubt in this case and remember that is the important thing. So, I will give you certain heat of formation value for CO_2 gas minus delta H naught f 97.2 into 10 to the power 3 kilocalorie per kg mole. I am giving all the values in kilocalorie per kg mole. H_2O liquid minus delta H naught f is equal to 68.32 into 10 to the power 3. H_2O gas minus delta H naught f is equal to 57.8 into 10 to the power 3. SO_2 gas minus delta H naught f is equal to 70.96 into 10 to the power 3. All these values are on kilocalorie per kg mole. These values are at 298 kelvin , 1 atmospheric pressure and this point is remembered. From this heat of formation values of the products on combustion, one can determine theoretically on the assumption that the products of combustion of coke are CO_2, H_2O and SO_2.

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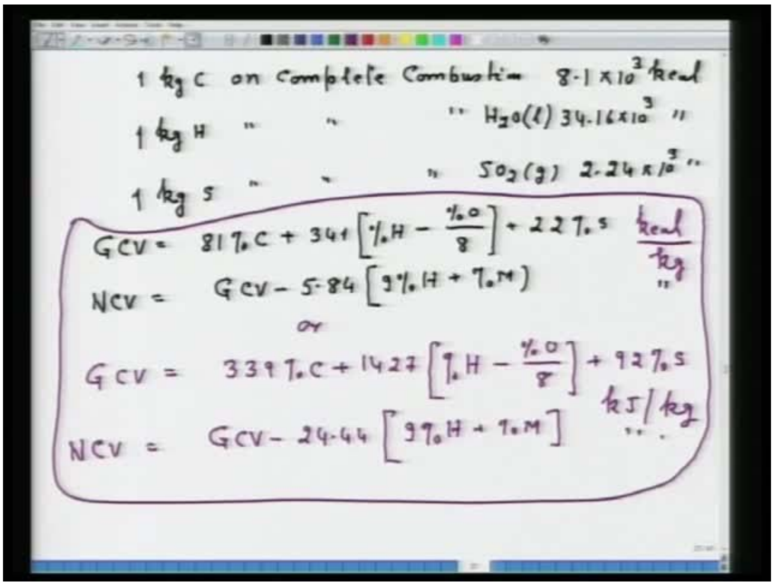

How to determine for 1 kg carbon? On complete combustion gives 8.1 into 10 to the power 3 kilocalorie. Similarly, 1 kg hydrogen on complete combustion to H2O liquid it gives 34.16 into 2 to the power 3 kilocalorie. What you can do? 1 kg carbon on complete combustion is 97.2 divided by 12 and you will get 8.5 per kg. 1 kg sulphur on complete combustion to SO2 gas will produce 2.24 into 10 to the power 3 calorie. Now, if I express carbon, hydrogen, sulphur on percentage basis as percent carbon, percent hydrogen. I can determine gross calorific value equal to 81 percent carbon plus 341 into percent hydrogen minus percent oxygen upon 8 plus 22 percent sulphur and this is in kilocalorie per kg.

Similarly, we can determine NCV equal to GCV minus 5.84. 9 percent H plus percent moisture in kilocalorie. Now, 9 percentage is coming because hydrogen in the coke, on combustion will also give H2O. From there, 18 by 9, 18 H2O divided by 2 and there comes 9 percent H. Now, in GCV, you are finding percent H minus percent O by 8 and percent O is coming because the coke also contains oxygen in it. I can also put it GCV equal to 339 percent carbon plus 1427 into percent hydrogen minus percent oxygen upon 8 plus 92 percent S in kilo joule per kg.

NCV is equal to GCV minus 24.44. 9 percent hydrogen plus percent M 9, I mean 9 into percent hydrogen. This formula is also in kilo joule per kg. In this formula that I have given over is called Dulong petit formula. Here, percent carbon means- the composition of coke in terms of percent carbon, percent hydrogen. You can directly substitute in order to calculate the calorific value.

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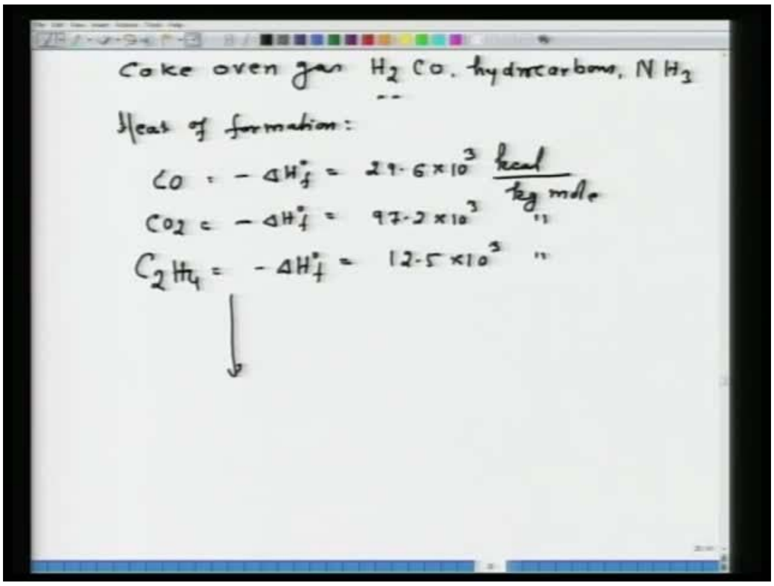

Now, think of the coke oven gas. Coke oven gas contains hydrogen, carbon monoxide, hydrocarbons, it may contain NH3 and these are all combustible components. So, in order to find out the calorific value of coke oven gas… We can also find out the calorific value of coke oven gas by the heat of formation value. So, I am giving heat of formation, for example, CO is minus delta H naught f equal to 29.6 into 10 to the power 3 kilocalorie per kg mole.

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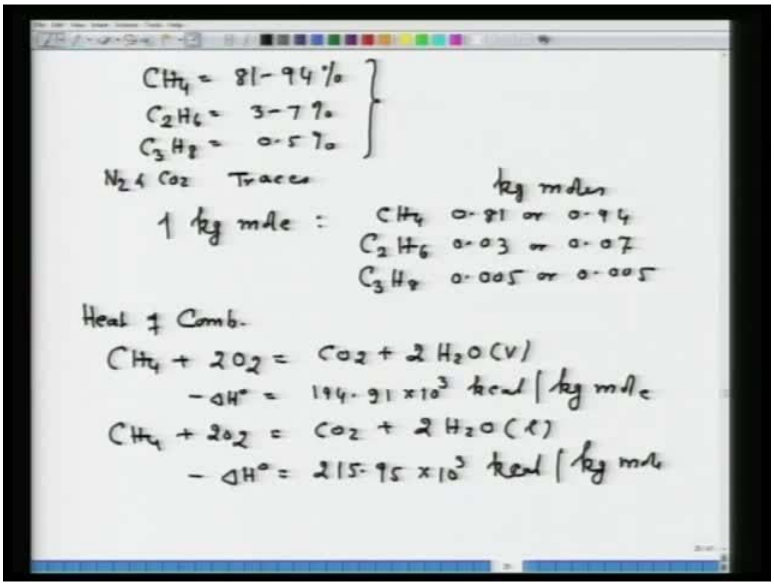

Although, I have given the heat of formation of CO2 earlier, it is minus delta H naught f equal to 97.2 into 10 to the power 3 kilocalorie. Some heat of formation value, for example, C2H4 is equal to minus delta H naught f and that is equal to 12.5 into 10 to the power 3 kilocalorie. Similarly, one can see all the heat of formation values for all other hydrocarbons. Let me illustrate by an example, CH4 is equal to 81 to 94 percent, C2H6 is equal to 3 to 7 percent, C3H8 is equal to 0.5 percent and N 2 and CO2 in traces.

We are required to find the calorific value of this gas. So, for example, if you consider 1 kg mole of gas, it will have CH4 equal to 0.81 or 0.94, C2S6 in 0.03 or 0.07, C3H8 in 0.005. Now, we have to write down these complete combustion reaction. For example, if you want to calculate CH4, then we have to find out heat of combustion value and I have given the heat of formation value.

So, if you want to find out heat of combustion, CH4 plus 2O2 is equal to CO2 plus 2H2O vapor. You know how to calculate the heat of combustion value. It is product minus reactant. If I do that then I will be getting minus delta H naught equal to 194.91 into 10 to the power 3 kilocalorie per kg mole that is product minus reactant. Now, I take CH4 plus 2O2, I have put it as CO2 plus 2H2O liquid. Now, I can calculate as minus delta H naught will be equal to 215.95 into 10 to the power 3 kilocalorie per kg mole. Now, I have explained this in my thermo chemistry lecture. If you want to find out heat of combustion, it is heat of formation of product minus heat of formation of reactant.

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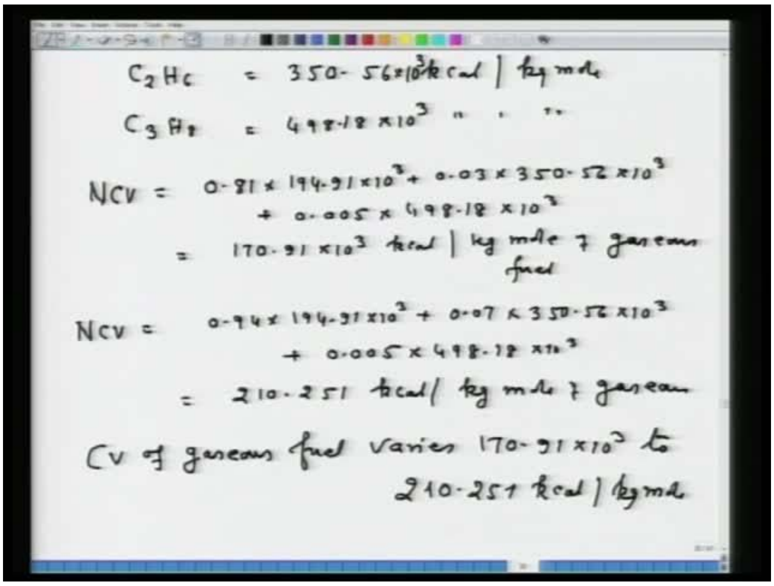

Similarly, I have to find out for C2H6, C3H8. For C2H6, value is 350.56 kilocalorie per kg mole and of course, you have to multiply by 10 to the power 3. For C3H8, the value is 498.8 into 10 to the power 3 kilocalorie per kg mole. Once I know all the heat of combustion value, what I have to do. I am calculating net calorific value, when H2O is in the vapor state. It will be 0.81into 194.91 into 10 to the power 3 plus 0.03 into 350.56 into 10 to the power 3 plus 0.005 into 498.18 into 10 to the power 3.

If you total it, this value will be equal to 170.91 into 10 to the power 3. This will be kilocalorie per kg mole of gaseous fuel, whose analysis was given in the beginning. Now, another composition, I have given the range as 0.1 to 0.81 to 0.94. Now, instead of 0.81, I substitute 0.94. If I take another extreme composition, it will be 0.94 into 194.91 into 10 to the power 2 plus 0.07 into 350.56 into 10 to the power of 3 plus 0.005 into 498.8 into 10 to the power 3.

If I substitute these values, then I will be getting the calorific value equal to 210.251 kilocalorie per kg mole of gaseous fuel. It means, you can say from here that the calorific value of gaseous fuel varies between 170.91 into 10 to the power 3 to 210.251 kilocalorie per kg mole.

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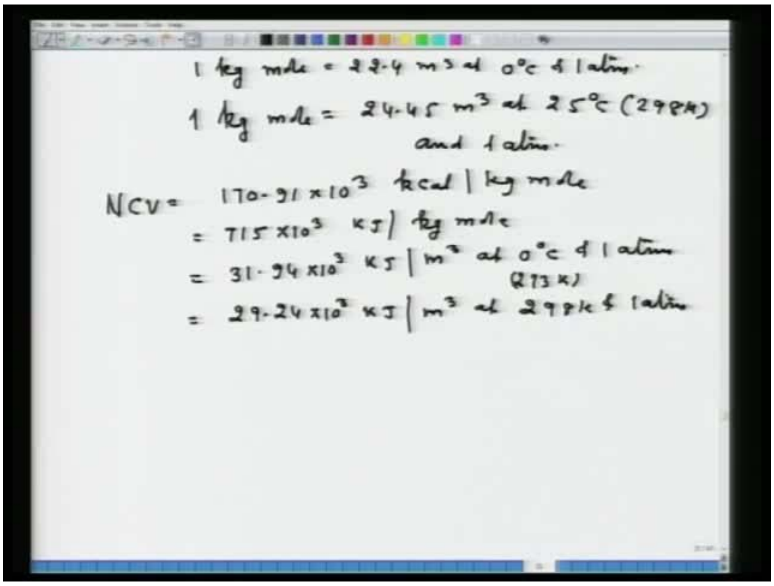

Now, if you want to calculate it in terms of meter cube, then you have to be careful because 1 kg mole is equal 22.4 meter cube at 0 degree celsius and 1 atmospheric pressure. If you want to calculate 1 kg mole at 22.4 meter cube at 0 degree celsius, at 1 atmosphere and 1 kg mole, it is equal to 24.45 meter cube at 25 degree celsius or you may write it as 298 kelvin and 1 atmospheric pressure. By utilizing these values or this conversion of kg mole to meter cube, you can express the calorific value in terms of kilocalorie per meter cube or kilo joule per meter cube, whichever way you want to express it.

Now, for example, we have determined NCV as 170.91 into 10 to the power 3. It is in kilocalorie per kg mole and it will be equal to 715 into 10 to the power 3 kilojoules per kg mole and 1 kilocalorie is 4.1 x 6 kilo joule. It will also be equal to 31.94 into 10 to the power 3 kilojoules per meter cube at 0 degree celsius and 1 atmospheric pressure or you can also put it as 273 kelvin if you wish. So, this will also be equal to 29.24 into 10 to the power 3 kilojoules per meter cube at 298 kelvin and 1 atmospheric pressure. Now, why I am telling? Because, many times you require to express the value in kilocalorie per meter cube or per kg mole. You should know the conversion and the most important thing is to remember that 1 kg mole of gas occupies 22.4 meter cube volume at 273 kelvin and 1 atmospheric pressure.

1 kg mole of gas at 298 kelvin and 1 atmosphere occupies 24.45 meter cube of gas. By utilizing these conversions, one can convert kg mole into meter cube or meter cube into kg mole, whichever is require depending on the type of problem. Many problems are given in kilocalorie per meter cube and you have to calculate in kg mole. So, these inter conversions are also important. Now, you try to learn how to calculate the calorific values that is heating values in order to have calculations on material and heat balance in coke making.

For calculation of the heat balance, you must know what are the sources of heat input, what are the sources of heat output. If the heat output is gas, then you must know what is the potential energy of this gas and that is the combustion value of this gas. In this perspective, these calculations give you a concept to calculate the calorific value of the gaseous fuel as well as the solid fuel.