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

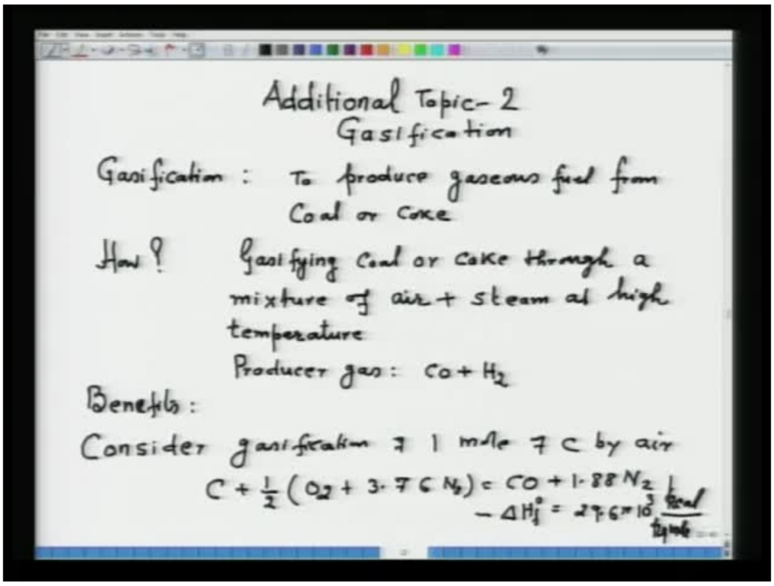
Lecture No. # 36

Additional Topics - II

Gasification.

Today, I will be discussing another important topic which I put under the category- Additional Topic - 2, that is on gasification.

(Refer Slide Time: 00:26).



Now, gasification is in fact a unit process which is employed to produce gaseous fuel. So, gasification is a unit process which is used or which is employed to produce gaseous fuel from coal or coke because of obvious reason - because gaseous fuels are easy to handle. Mind you, the gaseous fuels that are produced by gasification are not classed as fossil fuel; they are the synthetically prepared fuel. The fossil fuel is natural gas which you can class as a fossil fuel; that natural gas is a fossil fuel. Whereas, any gaseous fuel that you are producing by way of gasification, that you can call as a secondary fuel.

Now, the question is how is it done? This gaseous fuel is produced by gasifying coal or coke through a mixture of air plus steam at high temperature.

So, you can imagine, you have a reactor which is filled with the coke or coke bed in which mixture of air and steam is passing, and in a control and by controlling the reactions, one is able to gasify coal into a gaseous fuel. Now, commonly, the gaseous fuel which is produced by way of gasification is known as producer gas. Now, since the gasification is done by steam also, the producer gas, in addition to other components, will have CO plus Hydrogen.

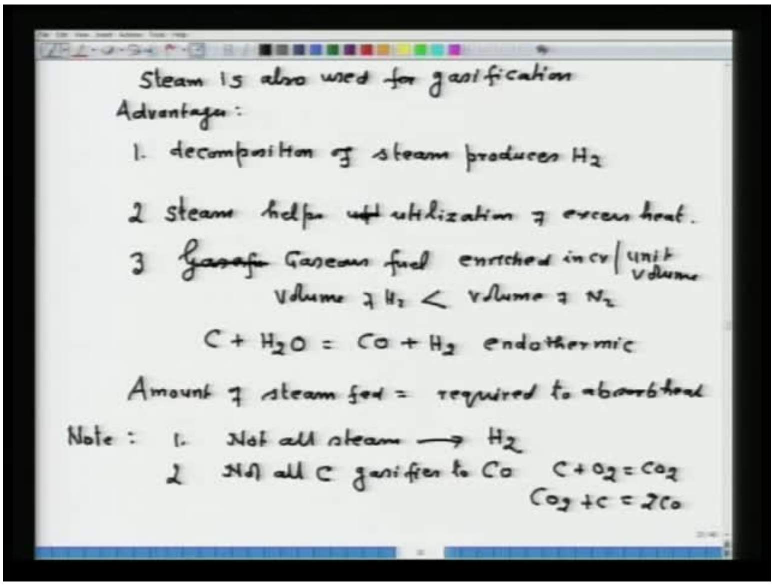
Now, what are the benefits? One has to look the high temperature furnaces, where fuel oil is used as a source of energy. Now, fuel oil on combustion gives thermal energy as well as it discharges Carbon dioxide in the atmosphere. Now, any amount of fuel oil that is being saved by some mechanism will reduce the consumption of fuel oil; it will also reduce the Carbon emission into the environment.

Now, here is the opportunity of using producer gas which contains Hydrogen. So, in proportion to Hydrogen, whatever amount of fuel oil that is being replaced in the actual process, that much amount of Carbon emission will be reduced. So, that is the biggest benefit of employing producer gas. Now, in various high temperature furnaces, gasification is one of the units that is added in order to decrease the fuel oil consumption and also decrease the Carbon emission into the environment, in proportion to the Hydrogen content of the producer gas; so, that is a benefit.

Now, let us consider say, gasification of 1 mole of Carbon by air. So, straightaway, we can write down the gasification reaction - C plus half O 2 plus 3.76 N 2; that is equal to CO plus 1.88 N 2; here, the amount of heat which is produced is delta H naught f; that is equal to 29.6 into 10 to the power 3 kilocalorie per kg mole.

Now, what happens? As a result of exothermic reaction, the heat which is produced also increases the temperature of the reactor. So, in order to decrease a temperature, what is being done? Steam is also used for gasification.

(Refer Slide Time: 06:11).



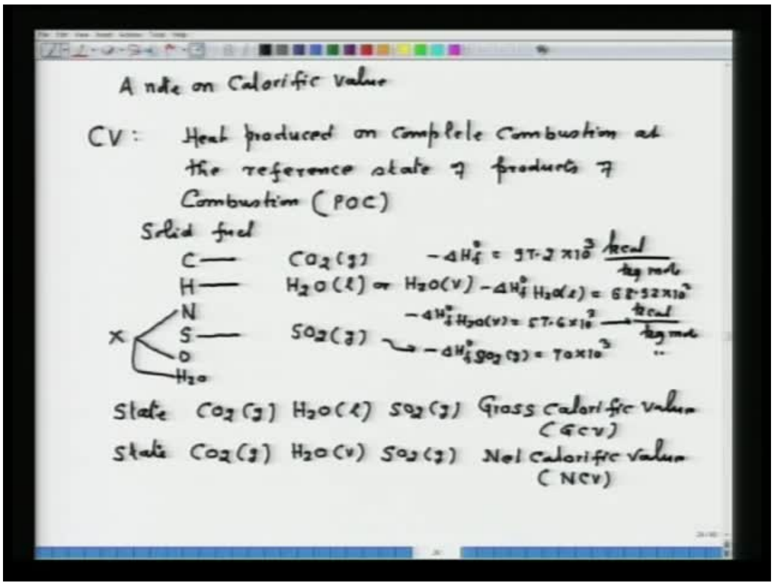
Now, what does the steam do? It utilizes the heat which is produced by gasification reaction. The advantages of addition of steam are as follows: so, the advantages of adding steam: first, decomposition of steam; it produces Hydrogen. Since Hydrogen is being produced, the fuel is enriched by the calorific value without Carbon; that is an important thing.

So, you are now producing a gaseous fuel which has Hydrogen also. On its use in proportion to Hydrogen, the Carbon emission to the environment will be decreased because combustion of Hydrogen will produce H 2 O and there are no emissions. Second - steam helps utilization of excess heat. Third - gaseous fuel. As I have said already, gaseous fuel is enriched in calorific value per unit volume. How? Volume of Hydrogen is less than volume of Nitrogen.

I will show in this course of lecture, how the calorific value is enriched. So, the reaction, which occurs in presence of steam C plus H 2 O - that is equal to CO plus H 2 ; this reaction is highly endothermic. So, that means what is important in carrying out gasification is that, if we do not want to supply any fuel for heating purposes from outside, then amount of steam fed must be equal to the amount that is required to absorb heat. That means one has to calculate, how amount of steam can be used so that whatever the desired temperature that remains.

Now, here, we will do some calculation. Now, note few important things over here. First - not all steam decomposes to Hydrogen, and second - not all Carbon gasifies to CO because the formation of CO consists of two reactions: one - C plus O 2 forms CO 2 and CO 2 in presence of excess Carbon forms 2 CO; so, that is the important thing to note.

(Refer Slide Time: 10:40)



Now, before I proceed to calculation, I will like to make some note on calorific value because we will be doing some heat balance. So, a note on calorific value: It is important to know what calorific value is - a note on calorific value and the listeners of this video, for the details, one can see the video lectures on fuel furnace and refectory where, a calorific value is dealt with in detail over there. Here, I will be presenting whatever is important.

Now, first of all, what is the calorific value? Calorific value is the amount of heat produced on complete combustion of the fuel, now, the important thing is coming at the reference state of product of combustion.

Now, this is important - the products of combustion. What is the reference state at which we are reporting the calorific value? So, here after, I will write products of combustion in short form - POC. Now by that, I mean for example, let us consider a solid fuel. Now, Solid fuel contains: Carbon, Hydrogen, Nitrogen, Sulphur, Oxygen, and H 2 O; out of these three, on combustion, only combustible component will take part and rest will be diluents.

So, Carbon is a combustible component; Hydrogen is combustible component and Sulphur is the combustible component; as regard Nitrogen, Oxygen and Hydrogen - they do not take part in the combustion. So, the product of complete combustion of Carbon is CO_2. Hydrogen - It is important that you can have H_2O liquid or H_2O vapor. Sulphur - The product of complete combustion is SO_2 gas; here also CO_2 gas.

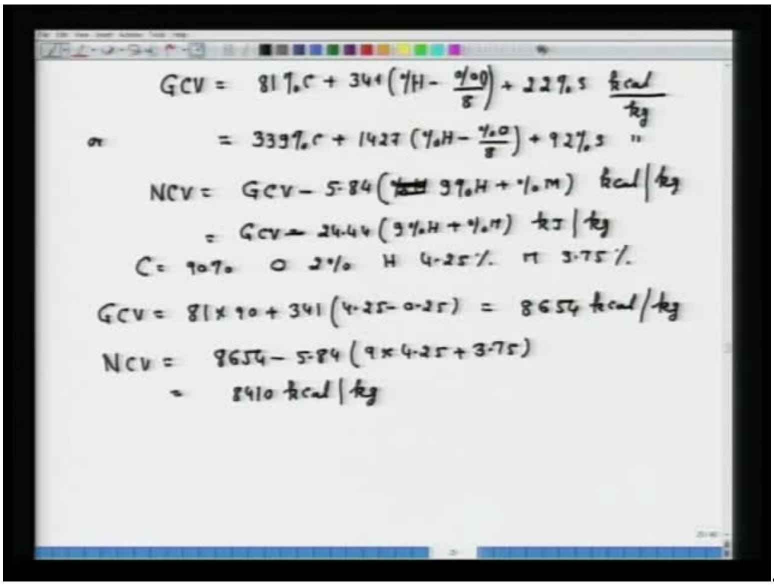
So, on complete combustion means C to CO_2 minus delta H naught f that is equal to 97.2 into 10 to the power 3 kilocalorie per kg mole. Similarly, minus delta H naught f, H_2O liquid that is equal to 68.32 into 10 to the power 3 kilocalorie per kg mole. Now, minus delta H naught f H_2O vapor - this value is 57.6 into 10 to the power 3. Please, read also kilocalorie per kg mole. For S to SO_2 minus delta H naught f H_2SO_2 gas - this value is approximately 70 into 10 to the power 3 kilocalories per kg mole. So, these are the calorific value, or you can also say here, they are the heat of formation of the respective products of combustion.

Now, the reference state say, state if we take: CO_2 gaseous, H_2O liquid, SO_2 gaseous then what calorific value calculate, it is called gross calorific value. Gross calorific value, here after, I will call GCV. Similarly, if the state of POC - CO_2 g, H_2O vapor and SO_2 g, if we report this, it is called net calorific value. Net calorific value - in short, I will call NCV.

Now, product of combustion: Where there is no liquid, then GCV is equal to NCV. For example, there could be only carbonaceous fuel; then, the products of combustion is CO_2; there GCV and NCV will be equal. The difference is coming because of the two states of H_2O, which is liquid at 25 degree Celsius and vapor at 100 degree Celsius; so, that point is important.

Now, one can calculate the calorific value by adding the heat of combustion value of all the combustible components of the fuel and bringing them on to a flat form because you know C to CO_2 - that much amount of heat, H to H_2O and S to SO_2.

(Refer Slide Time: 16:10)



We all know this value if we convert these values on kg basis, If we take 1 kg of the fuel and we try to calculate, then we can calculate gross calorific value, that is equal to 81 into percent Carbon plus 341 percent H minus percent O upon 8 plus 22 into percent Sulphur and its unit is kilocalorie per kg.

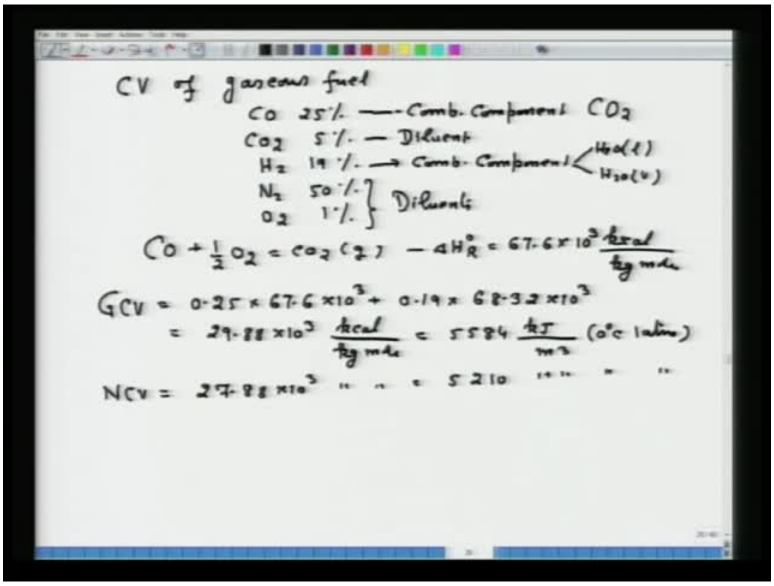
Similarly, we can also calculate in kilojoule per kg; so, that will be equal to 339 percent Carbon plus 1427 percent Hydrogen minus percent Oxygen upon 8 plus 92 percent Sulphur kilocalorie per kg. Now, NCV will be equal to GCV minus 5.84 into percent Hydrogen, sorry, into 9 percent Hydrogen plus percent moisture that is in kilocalorie per kg. Now, this 5.84 picture is coming from the latent heat of condensation or we can also calculate GCV; that is GCV minus 24.44 into 9 percent H plus percent M - that is kilojoule per kg of the fuel.

Now, just an example: suppose if Carbon is 90 percent, Oxygen is 2 percent, Hydrogen 4.25 percent, moisture let us take 3.75 percent and then we have to introduce directly the value of percentage in this formula. So, if you do that, then gross calorific value will be 81 into 90 plus 341, 4.25 minus 0.25. There is no Sulphur; so, that will be 0. So, this value is equal to 8654 kilocalorie per kg.

That is how you can calculate the calorific value. Similarly, one can calculate NCV, if you substitute the value of percent Hydrogen, percent moisture; so, GCV is 8654 minus

5.84 9 into 4.25 plus moisture that is 3.75 and NCV is equal to 8410 kilocalorie per kg. That is how you can calculate the calorific value for example, solid fuel.

(Refer Slide Time: 19:35)



Now, similarly, an example can be given. So, one wants to calculate calorific value of gaseous fuel; CV stands for calorific value; CV of gaseous fuel, the definition remains same - gross or net calorific value. Now, suppose, let us say CO is equal to 25 percent, CO 2 let us take 5 percent, Hydrogen let us take 19 percent, Nitrogen let us take 50 percent and Oxygen let us take 1 percent.

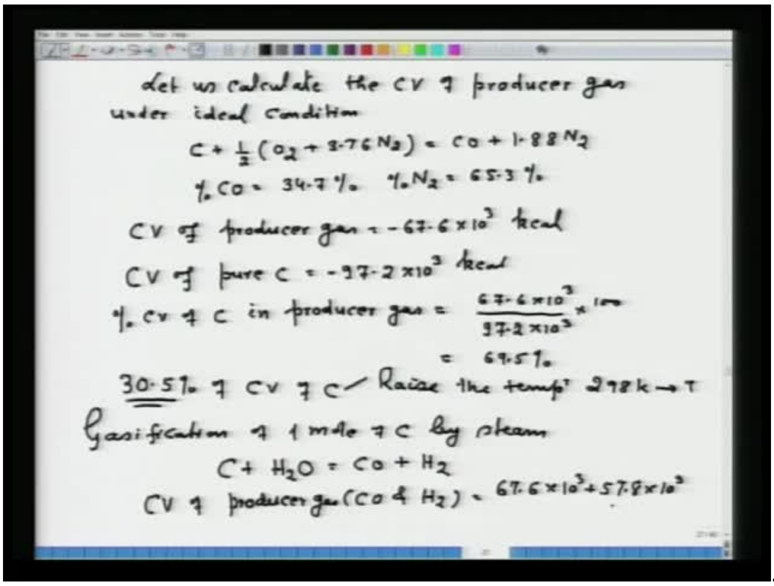
Now, in the gaseous fuel also, this is a combustible component and product of complete combustion is CO 2. The definition remains same; CO 2 is called diluents because it does not take part in the combustion. Hydrogen is also a combustible component and accordingly, one can have either H 2 O liquid or H 2 O vapor; rest both are diluents because they do not combust.

The definition of calorific value remains the same. If you have to calculate, what you have to do? You have to again add the calorific value corresponding to complete combustion of the component of the fuel, add them together, use a reference state and report. Now, the reactions for example, now here CO plus half O 2 that is equal to CO 2 gaseous; now here, you have to calculate heat of reaction that is minus delta H naught R that is equal to 67.6 into 10 to the power 3 kg mole kilocalorie per kg mole.

As regards, H combustion of H 2 to H 2 O liquid, H 2 to H 2 O vapor are values I gave already. So, if I want to calculate, GCV, GCV will be equal to 0.25 into 67.6 into 10 to the power 3 plus 0.19 into 68.32 into 10 to the power 3; that is the GCV and this value will be equal to 29.88 into 10 to the power 3, kilocalorie per kg mole.

Many times you require calculating per meter cube; 5584 that is kilojoule per meter cube. Now, express at 0 degree Celsius and 1 atmospheric pressure. Similarly, one can say you can calculate NCV. So, NCV I am writing - 27.88 into 10 to the power 3 kilocalorie per kg mole; that is also equal to 5210 kilojoule per meter cube 0 degree Celsius at 1 atmosphere. Now, you are also noting that NCV is lesser than GCV by an amount which is equal to the latent heat of condensation.

(Refer Slide Time: 23:18)



Now, let us calculate the calorific value of a producer gas under ideal condition. So, let us calculate the calorific value of producer gas under ideal condition, by ideal conditions; I mean, you are gasifying pure Carbon with air.

So, C plus half O 2 plus 3.76 N 2 - that is equal to CO plus 1.88 N 2. Now, we can calculate here, percentage CO; that will be equal to 34.7 percent. Percent Nitrogen will be equal to 65.3 percent. Now caloric value will be only that of combustion of CO. So, one can calculate the calorific value of producer gas; now, mind you, here the producer gas consists of 34.7 percent CO and 65.3 percent of Nitrogen.

So, if I want to calculate the calorific value of producer gas, I have to consider only the combustible component and the combustible component is Carbon monoxide and nothing else. So, calorific value of producer gas will be equal to, on 1 mole basis, 1 mole Carbon and 1 mole CO; so, it will be straightway 67.6 into 10 to the power 3; of course, it is exothermic reaction. If you wish, you can put minus sign over, here. So, it is an exothermic reaction; that means that much amount of heat will be produced in kilocalorie.

Now, it is interesting to know what section of the calorific value of Carbon is available to you in the producer gas because initially you have used 1 kg mole of Carbon, you know the calorific value. Now, it is interesting to know, what section of the calorific value on gasification is available to you. If you do the calorific value balance, then it is interesting thing.

For example, since we are implying pure Carbon, calorific value of pure Carbon - CV of pure Carbon in kg mole, the product combustion is CO 2. So, that is equal to 97.2 into 10 to the power 3. Of course, this is also an exothermic reaction; so, you can put the minus. It means that it is an exothermic reaction.

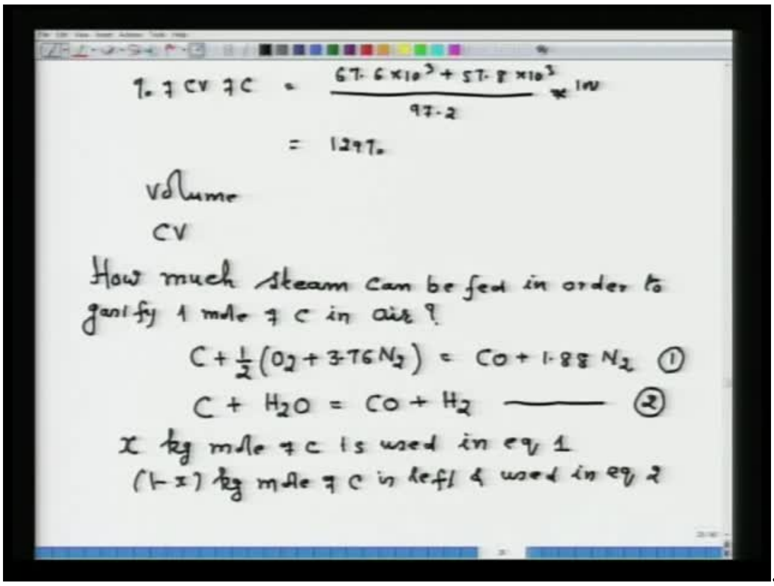
So, now, we calculate percentage of calorific value of Carbon in producer gas; that will be equal to 67.6 into 10 to the power 3 upon 97.2 into 10 to the power 3. You have to multiply by 100; so, that brings 69.5 percent. Now, my dear friend, what this value means? This means that only 69.5 percent of the calorific value of the pure Carbon is available in the producer gas. What happens to 30.5 percent? So, where does 30.5 percent of calorific value of Carbon go?

Energy can neither be created nor destroyed; where does it go? So, it goes, first of all, to raise the temperature from 298 Kelvin to temperature T at which the reactions are being carried out, and second - the Nitrogen which carries the sensible heat; Carbon monoxide - that also carries the sensible heat. So, around 30.5 percent of the calorific value of the Carbon is available over there, but as regards, if you talk of the calorific value of the fuel, its only 69.5 percent; that means if you use this producer gas in an actual process, then 69.5 percent of the calorific value of Carbon will be available to you.

Now, let us consider gasification of 1 mole of Carbon by steam. Let us see, C plus H 2 O that is equal to CO plus H 2. Now, we can calculate calorific value of this producer gas;

producer gas or fuel gas - all things are same. Calorific value of of this producer gas, I mean, which contains CO and Hydrogen - it contains both CO and Hydrogen; that will be equal to 1 mole of Carbon. So, you have 67.6 into 10 to the power 3 plus 57.8 into 10 to the power 3; this is kilocalorie per kg mole, sorry, kilocalorie.

(Refer Slide Time: 29:25)



So, percentage of calorific value of Carbon that is available in a fuel gas, which you have obtained by gasifying in a steam will be equal to 67.6 into 10 to the power 3 plus 57.8 into 10 to the power 3 divided by 97.2 that into 100; that becomes 129 percent. It is not surprising; it has become more than 100 percent; that means what? That means, if you gasify with steam, you are enriching the calorific value of producer gas. There is no surprise because decomposition of H 2 O to Hydrogen is bringing an additional calorific value to your gas. It is enriching the gas. So, that is where you are having a figure 129 percent.

So, gasification with a steam enriches producer gas, both in volume as well as in calorific value because volume of Hydrogen is far less than Nitrogen. So, per unit volume you will be having larger calorific value when the producer gas contains Hydrogen, in comparison to when the producer gas contains Carbon monoxide. So, that is the advantage of using steam as a gasifying medium; rather, when you gasify coal or coke by a mixture of air plus steam. So, the advantages are obvious; that is the per unit volume, you will be having larger calorific value why because steam decomposition is adding Hydrogen to the fuel and Hydrogen is contributing to the calorific value.

Now, let me illustrate the amount of a steam that will be required. Because, in the beginning of my lecture, I have said that the amount of a steam has to be calculated. What you want to do, gasification of Carbon alone; it is an exothermic reaction; if the gasifier is of larger size, heat loss will be less and temperature will rise; you want to use that temperature and how can you use it?

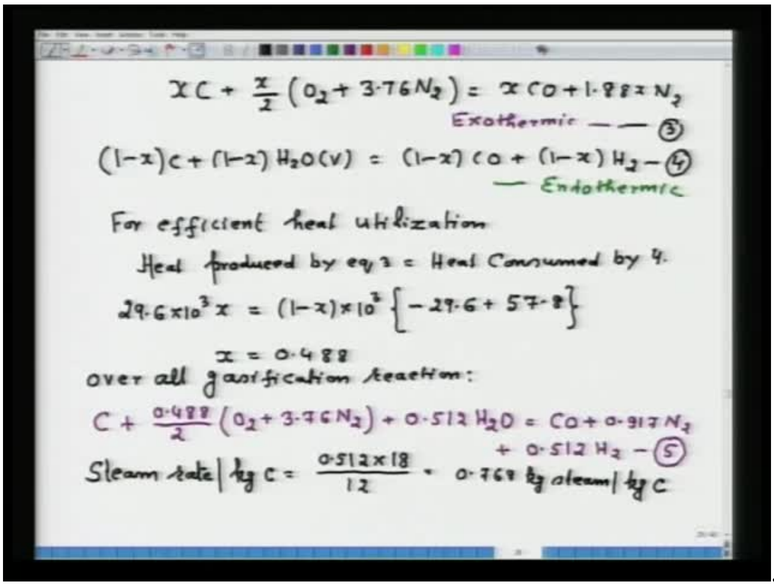
In that, you introduce steam; so, you have dual advantage; by addition of a steam, you can control the temperature as well as you can enrich the calorific value of producer gas. You have two advantages simultaneously, but then, you have to see for a particular gasifier, how much amount of steam can be fed? For that calculation, what you have to do? One - you have to do the heat balance.

So, let me illustrate how much steam; the question is how much steam can be fed in order to gasify 1 mole of Carbon? Let me take an example in air, before we ask the question, how much steam can be fed in a gasifier in order to gasify 1 mole of Carbon in air? Now, what we have to do? We have to do the heat balance.

So, the reaction C plus half O 2 plus 3.76 into…. Now, why I am writing always because you are using air and air comprises O 2 plus 3.76 N 2 , 1 mole of Oxygen, 4.76 moles of air. So, that will be equal to CO plus 1.88 N 2 - that is reaction number 1. Now, we have C plus H 2 ; that is equal to CO plus Hydrogen - that is our reaction number 2. Now, we have 1 kg mole of Carbon - the source of Carbon for reaction 1 and 2 is only 1 kg mole.

If we consider, let us consider x kg mole of Carbon. We consider x kg mole of Carbon is used in equation 1. Then 1 minus x kg mole of Carbon is left and used in equation 2 or reaction 2.

(Refer Slide Time: 34:52)



.

So, now, one can write down the chemical reactions as follows: so, I take x mole of Carbon plus x by 2 moles of O 2 plus 3.76 N 2; that is equal to x mole of CO plus 1.88 x into Nitrogen. Let me take this as my equation number 3. Then, I can write down 1 minus x moles Carbon plus 1 minus x H 2 O; let me consider vapor because we are supplying steam; that is equal to 1 minus x moles of Carbon monoxide plus 1 minus x moles of Hydrogen; this is my equation number 4.

So, I mean, just put reaction 3 is exothermic. Now, reaction 4 is endothermic; so, what we have to do? If you want to calculate how much amount of a steam can be fed, the condition is for efficient heat utilization which is produced by reaction number 3.

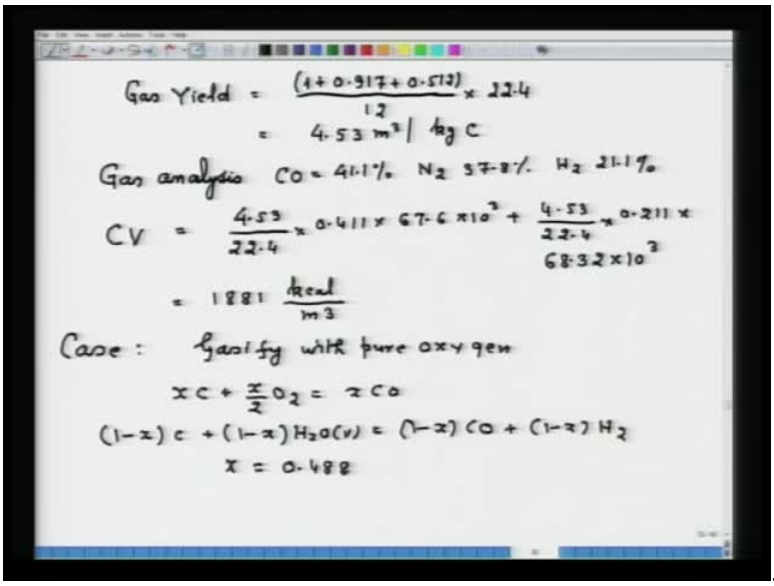
So, we can write down what is the condition for efficient heat utilization; that is, required heat produced by equation 3 must be equal to heat consumed by equation 4. So, I have already given you the various heat of formation values; I am straightaway using.

So, these values 29.6 into 10 to the power 3 x should be equal to 1 minus x into 10 to the power 3, minus 29.6 plus 57.8. So, if I solve, then the value of x is equal to 0.488. Now, I can write the overall gasification reaction. Now, I know the value of x from the heat balance. It can be written as C plus 0.488 upon 2 O 2 plus 3.76 N 2 plus 0.512 H 2 O; that is equal to CO plus 0.917 N 2 plus 0.512 H 2 and this is my equation number 5.

Now, this is the overall reaction that we have found after doing the heat balance. By using x equal to 0.488, one will balance the heat produced that is equal to heat consumed. So, once this is known to us, we can get various information; first of all, steam rate per kg of Carbon. How much will require steam rate per kg Carbon?

You know, steam rate is 0.512 per kg mole. So, that will be equal to 0.512 into 18 upon 12; so that is equal to 0.768 kg steam per kg Carbon; you can use it at this rate of steam supply. You will be able to maintain heat balance condition that is, the heat produced will be equal to heat utilized.

(Refer Slide Time: 40:04)



You can also calculate, gas yield. You can also calculate; that means, how much amount of gas is produced per kg or kg mole of Carbon, whichever way? So, that is, straightaway one can put it say 1 plus 0.917 plus 0.512; that is the right hand side of the equation 5. If we divided by 12, and of course, you have to multiply by 22.4; so, the gas yield would be equal to 4.53 meter cube per kg Carbon.

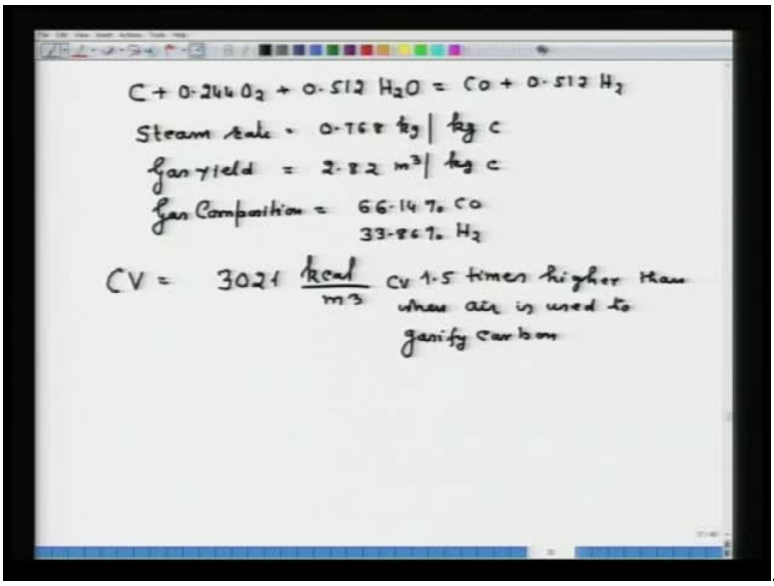
Another important thing is the gas analysis; we can have CO that is equal to 41.1 percent, N 2 - 37.8 percent and Hydrogen - 21.1 percent; that is the gas analysis.

Now, we have to calculate calorific value. Calorific value of the producer gas that will be equal to 4.53 upon 22.4 into 0.411 into 67.6 into 10 to the power 3 plus 4.53 upon 22.4 into 0.211 into 68.32 into 10 to the power 3; so, that is the calorific value of the producer gas, that you obtained after gasification of a mixture of air plus steam. So, you can calculate; so, this value will come out to be equal to 1881 kilocalorie per meter cube; that is how you can calculate the calorific value of the gas which is obtained.

Now, another interesting case would be - let us consider case (b), another interesting case is that, suppose now, we gasify with pure Carbon, sorry the, gasify with pure Oxygen; you cannot gasify with Carbon; you have to gasify with Oxygen.

So, you gasify with pure Carbon, again the same thing, x kg mole of Carbon and so on. So, the reaction is – straightaway, I am writing x C plus x by 2 O 2; that is equal to x CO and 1 minus x C plus 1 minus x H 2 O. Since we are using pure Oxygen, there is no Nitrogen component here; that is equal to 1 minus x CO plus 1 minus x Hydrogen.

(Refer Slide Time: 44:09)



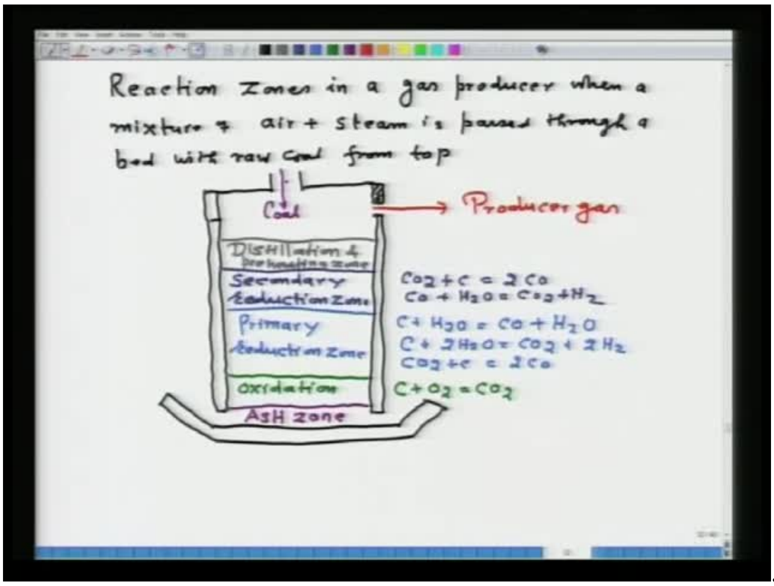
Now, as regards the heat balance, you have to make the heat balance; you can calculate the value of x and that will come up to be same as we calculated earlier - 0.488 as calculated previously. So, our equation would be C plus 0.244 O 2 plus 0.512 H 2 O; that will be equal to CO plus 0.512 H 2 .

So, steam rate will also not change. Steam rate will also be same as the earlier 0.768 kg per kg Carbon; gas yield will change. Why will it change? Now, there is no Nitrogen. So, gas yield is 2.82 meter cube per kg Carbon. Gas composition will also change and gas composition will be 66.14 percent Carbon monoxide and 33.86 percent Hydrogen.

Now, you can calculate the calorific value. Already you know the procedure; I will not repeat the procedure. So, the calorific value will be equal to 3021 kilocalorie per meter cube. So, what do you think? Now, you think that the calorific value is around 1.5 times, say, CV with pure Oxygen is 1.5 times higher than when air is used to gasify Carbon. Second important thing you are noting here is that the gas is around 2.82 meter cube which is half. Then you have calculated earlier, with the air it was 4.8.

You are also reducing the per heat volume that is the gas volume, but the calorific value of the fuel will be high. So, that is the advantage of having gasification in Oxygen. Now, towards the last, let me just give you a brief idea of how a gasifier looks and how the various reactions are taking place in a gasifier.

(Refer Slide Time: 46:57)



Now, let us consider reaction zones in a gas producer, when a mixture of air plus steam is passed through a bed, with raw coal from top. That means you have a reactor; coal is being fed; top up from top, bed is created and air steam is passing; so, it looks something like this (Refer Slide Time: 48:10).

So, this is the kind of a reactor. Now, this is the one, and here you are having a system for the coal which is fed from the top. So, this is a reactor; you are observing when the reactions are taking place; a bed is formed and coal is continuously fed from top, and a mixture of air plus steam is going from the bottom.

So, at the bottom here, somewhere here, you have an Ash zone that is coal after combustion. Ash will be there and a disposal of ash is there at the bottom. Now, next to this, we have a sort of an oxidation zone. You have an oxidation zone; it meets with the mixture of air and steam. So, in the oxidation zone, this reaction takes place - C plus O 2 that is equal to CO 2.

Now, remember when your Carbon at high temperature comes in contact with Oxygen, the first product of CO 2 and CO 2 in presence of Carbon is unstable and reduces to CO; that is an important thing. So, on the top of it, you have a sort of… this is called primary reduction zone. As the zone suggests, you have the reaction C plus H 2 O - that is equal to CO plus H 2; C plus 2H 2 O - that is equal to CO 2 plus 2H 2; finally, you have CO 2 plus C - that is equal to 2 CO.

Now, say on the top of it, you have a secondary reduction zone. Here, there are possibilities that CO 2 gas reduces with Carbon and it gives you 2CO and CO plus H 2 O gas reduces to CO 2 plus Hydrogen, and on the top of it, you have the so called distillation and preheating zone distillation; preheating zone and here you are feeding coal and here you are taking out the producer gas.

So, as the producer gas moves upward, its temperature decreases; as the coal descents, it gets heated up in the distillation; preheating zone distillation means gets orientalized in the secondary reduction zone, primary zone and Oxygen. That is how a sort of a gasifier will look when the coal is gasified with a mixture of air plus steam. Now, if you want to go for further details, then you can look to the book of Metallurgical Engineering Principle by Shumen.

So, that is what, today I thought of to give you the concept of gasification: What does gasification mean? How gasification is done? What are the important things to be calculated in gasification? You are required to calculate how much amount of steam is decomposed. What is the composition of the producer gas? How much amount of producer gas is produced? What is the calorific value of the producer gas and so on and so forth?

So, this aspect of gasification which I call as a material and heat balance, that will constitute the lecture content of the next lecture.