

**Clean Coal Technology**  
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**Lecture-42**

Hi, I am Professor Barun Kumar Nandi, welcoming you to the NPTEL online certification course on clean coal technology. We are in module 9, discussing the fundamentals of coal gasification. So, in this module, I will be discussing the different chemical reactions involved in coal gasification. So, let's start lecture 2 on chemical reactions in coal gasification.

Now, during the gasification of coal, biomass, or similar types of hydrocarbon-rich materials, different chemical reactions occur. Primarily, these chemical reactions involve coal or any carbon feedstock as carbon. So, during this chemical reaction representation, when we write carbon, it actually represents the carbon-rich feedstock. The first reaction that happens in coal gasification or similar gasification reactions is the conversion of carbon-to-carbon monoxide, and the second reaction that occurs is that carbon monoxide reacts again with oxygen to convert it into carbon dioxide. So, overall, if we see this, carbon in the solid phase reacts with one molecule of oxygen to form carbon dioxide. So, overall, this reaction one That is, C plus O<sub>2</sub> yields CO<sub>2</sub>. It is a two-stage reaction, depending on the concentration of carbon dioxide and the concentration of the feedstock, as well as the temperature, pressure, and other conditions.

So, if this reaction happens completely, like C plus O<sub>2</sub> yields CO<sub>2</sub>, it is the complete combustion reaction. So, in this combustion reaction, we can get a total amount of 97,000 kilocalories of heat. That is the delta H value. This is an exothermic reaction. Overall, this exothermic reaction happens in two stages.

In the first reaction, where the carbon monoxide is produced, where the reaction, where the amount of heat released is less, about 26,000 kilocalories. Whereas, the second reaction, where is the carbon monoxide plus oxygen, that reaction, the amount of heat released is 67,000 kilocalories. So, overall if we see that this complete combustion reaction it is a two-stage reaction. At the first reaction involve production of carbon monoxide with release of some amount of heat and in the second stage involve reactions of carbon dioxide with oxygen to produce the carbon dioxide. Overall, by this reaction we will get about 97000 kilocalorie heat.

So, purpose of this gasification reaction is that if we provide less amount of oxygen we can stop the gasification reaction at this first stage. If we stop this reaction at the first reaction here that is this reaction. if we can stop the reaction at here that means if we can control the reactions in such a way that all the feedstock will be converted to carbon monoxide we will be releasing only 25 000 kilocalorie amounts of heat from the chemical reaction and still in the carbon monoxide what happens in the second reaction we can have this amount of heat is available. So, this amount of heat that is 67,000 kilocalories heat we can get it from the gaseous fuel. So, in the coal gasification reaction first we try or our main objective is to stop the chemical reaction at this first reaction itself. So that only 26,000 kilocalorie heat is released during the coal gasification and remaining 67,000 kilocalorie heat will be released during the utilization of the gasification products. So overall the main objective or main focus or all the design equations, they are primary targets to do this gasification reaction where the production of carbon monoxide is the main product. So, in the gasification reactions, we should try to produce as much as carbon monoxide possible, not the carbon dioxide. Because if carbon dioxide is produced, all the energy available in the coal that will be released at the source itself. That's why in the coal gasification; we provide less amount of oxygen. If we provide less amount of oxygen, all the reactions will be favoring to the production of carbon monoxide and this carbon monoxide, along with the other gases, will be used as the feedstock or as the syngas. At the same time, if we do that, we see that some reduction reactions are also possible, which are known as the Boudouard reactions. So, in these reactions, solid carbon also reacts with carbon monoxide. If the concentration of carbon is high, then in such cases, carbon monoxide can also be used to reduce this carbon. for favorable production of carbon monoxide.

So, if this carbon monoxide is produced, in such cases, this reaction is endothermic, which requires an external heat supply of about 38,000 kilocalories. So, if we do this reduction reaction, that means if the carbon concentration in the product or the feedstock is on the higher side, then whatever carbon monoxide can be produced by Reaction 1, as mentioned here. So, this amount of carbon monoxide can also react with residual carbon to facilitate the carbon monoxide production reaction. So, as a result, this Boudouard reaction helps increase the concentration of carbon monoxide in the product as well as reduce the concentration of carbon dioxide in the product.

So, whether this reaction will happen or not—that is, whether these Boudouard reactions will occur—depends on the internal reaction conditions. That means if the carbon is at a high temperature and there is no oxygen available, and the carbon monoxide concentration is

significantly higher, then in such cases, carbon monoxide can reduce it. So, there needs to be some reduction conditions and a reducing environment inside the gasification reactor where carbon monoxide reacts with carbon to increase carbon monoxide production. Overall, if we observe this reaction, this amount of energy is released, or at least if we stop this reaction—if I write here—some amount of heat is released from the coal surface. So, whatever the calorific value of the coal is, about you can say about one-fourth of the energy is released here. About 97,000 kilocalories—26,000 kilocalories—are released in the first reaction. So, this is actually the heat released during the gasification reaction. As this amount of heat is released from the gasification, obviously, the temperature of the reactor will be on the higher side, meaning a type of partial combustion is happening. So, this amount of energy will be released.

So, if we can utilize this energy to conduct reaction 2, which is the Boudouard reaction, whatever heat is released from all these reactions can be absorbed or utilized to carry out reaction 2. If we carry out this reaction based on the concentration of feedstock as well as carbon monoxide, overall, there will not be any excess heat released at the spot itself. The purpose of this coal gasification is to convert coal into a gaseous medium. Not to waste the energy available in the coal; if we waste or release the entire amount of energy available in the coal, the product gases' calorific value will be less. If we look again at the first reaction, what is expected from coal gasification is that during gasification, we will carry out this reaction by releasing about one-fourth of the calorific value, while the remaining three-fourths of the calorific value.

It will be utilized by the consumer or the end product user who will use the gasified product. So, the expectation is that during gasification, we will release one-fourth of the energy, and during utilization, the consumer will utilize the remaining amount of energy available. So even if we see that this amount of energy is released, that is the wastage from the coal. So, if we can conduct this reaction, which is an endothermic reaction—the first reaction is exothermic, where heat is released from the coal surface—that heat can be utilized to carry out the Boudouard reaction, which is endothermic. By balancing the materials and other factors, if we can utilize the entire amount of heat released by these chemical reactions (1) to carry out chemical reaction (2), in such a case, there will not be any major energy lost or heat loss at the source or during gasification itself. So, this Boudouard reaction actually helps reduce the concentration of carbon dioxide in the product gas. Even in this first case, if we can see that some amount of carbon dioxide is produced. If we can use this carbon dioxide to further reduce or gasify this coal. As in this case also, this solid coal is further gasified.

It is converted to a gaseous medium to facilitate this carbon monoxide production reaction. So, overall, by these reactions, it is also endothermic. Whatever heat is released by this first reaction will be used in the second reaction to carry the Boudouard reaction, and further, some more amount of coal or carbon or char will be classified. So, overall, this Boudouard reaction also helps in further gasifying the coal, as well as absorbing some of the heat released by the first reaction to utilize in the second reaction.

So, there will be a very good energy balance if we carry both reactions in the same reactor itself. Further, if we utilize steam or if some amount of moisture is present in the coal—as coal will always have some amount of moisture, particularly with low-rank coal like lignite, semi-bituminous, or sub-bituminous coal—there will always be some amount of moisture. Also, we can add some amount of the feed gases itself. In such a case, the steam will react with the coal to form carbon monoxide and hydrogen. If we see this reaction, it can happen either with  $1\text{H}_2\text{O}$  to make carbon monoxide or with  $2\text{H}_2\text{O}$  to make carbon dioxide and, as well, it can increase hydrogen production. Both reactions are endothermic in nature, which requires external energy supply or external heat energy from outside.

So, overall, if we see this water-gas reaction, there are several advantages compared to only coal-based or oxygen-based reactions. If we carry only this first-phase reaction, the product gases will have either carbon dioxide or carbon monoxide. Overall, depending on the oxygen supply, we expect that most of the gases will be carbon monoxide. However, if we add some amount of steam or if some amount of water is there, that adds a significant amount of hydrogen to the product gas. Now, if we see the calorific value or energy available from carbon monoxide and the calorific value of hydrogen. Hydrogen always has a higher calorific value or energy available compared to carbon monoxide. So, if some steam is there or some amount of  $\text{H}_2\text{O}$  is present in the coal, it actually improves the calorific value of the coal, as it will be rich in hydrogen and will also absorb the energy released during this fast reaction.

During the normal combustion reaction, carbon monoxide will be produced. where we will release this amount of energy, whereas for this steam-based reaction, all these reactions are in the They are the endothermic reactions where external energy is required. So, the heat released by this first reaction will be utilized to conduct the second reaction, where external heat is required. So, if we add water or if some amount of steam is there, or some amount of water molecules are present in the coal, that will effectively improve or increase the concentration of hydrogen in the product gas. If hydrogen in the product gas is increased, its calorific value will

be increased as well. This hydrogen can further be recovered by a suitable gas separation method to produce hydrogen as a source of energy or fuel, etc. So, overall, this water-gas shift reaction is always favorable in the gasifier reactor, which will effectively reduce the temperature of the reactor. If we carry out only these first reactions, in such a case, the temperature of the reactor will be excessively high because here we are only increasing the temperature and partially burning this coal. So, the temperature in such cases for all these reactions will be significantly high. But if we carry out this water-gas reaction, the temperature of the reactor will be controlled and reduced because the heat released by this first reaction will be used to carry out the second reaction here. Further, there is also some amount of water-gas shift reaction, where carbon monoxide can again react with  $H_2O$ . In the first case, carbon was reacting with  $H_2O$ , which was called the water-gas reaction. However, in this water-gas shift reaction, carbon monoxide reacts with water molecules. So, as these reactions are in the gaseous phase, they will also produce some amount of hydrogen and constant carbon monoxide, carbon dioxide is there, and that is also an exothermic reaction where some amount of energy is released. So, overall, if we see that if we can conduct this water-gas shift reaction, in such a case, carbon monoxide concentration in the product gas is less because carbon monoxide is produced or converted to carbon dioxide, whereas the hydrogen concentration in the product gas will be high.

So, if our target is to produce more hydrogen and less carbon monoxide in the product gas, then we should try to conduct this water-gas shift reaction as well as in higher cases. Similarly, at the same time, in the same reactor, some methanation reaction is also possible. In this methanation reaction, carbon reacts with hydrogen because in the feedstock, there is always some solid carbon present, and by this reaction, some amount of hydrogen gas is possible. So, by this methanation reaction it will effectively consume the hydrogen gas and produce some amount of methane. This reaction is also an exothermic reaction. So, by this methanation reaction, we can see that some methane gas can be produced depending on the conditions, if the conditions favor the methanation reaction. So, we will get some amount of methane gas also by this reaction. Where hydrogen produced by the steam, that water-gas reaction, will be used to convert some amount of coal to methane gas. So, this is an exothermic reaction and therefore largely suppressed by the high-temperature conditions of the bed and even in the high temperature condition some methanation reaction like carbon monoxide reacts with hydrogen to form methane and steam is also possible. So, if high temperature is there it can also that carbon monoxide in the reactor and hydrogen in the reactor they can also go for reaction to

produce methane as well as steam. So overall if we see all this reaction is there. In the product gases, we can have carbon monoxide if this reaction happens here. It can have some amount of carbon dioxide gases also.

It can have hydrogen gases depending on the water gas shift reaction to what extent these reactions happen. Also, it can have methane gases also possible if these methanation reactions happen and if high pressure is there. There can have both methane gas and steam is also possible. So, all these reactions can happen and by all these reactions we can see that this first reaction is a coal gasification reaction where coal is gasified.

In this Boudouard reaction also coal is converted to gaseous product Water gas reaction in both the reactions coal is converted to gaseous product. In this methanation reaction also coal is converted to gaseous product methane. So, by all these chemical reactions we can see that coal will be converted or it will be gasified to a gaseous product. However, the gaseous product can have different concentration of carbon dioxide as well as carbon monoxide, hydrogen, methane etc. and any other gases because the similar reactions or the similar reactions can also produce ethane and other gases also. So, these types of gases are also possible that this some of the chemical reaction will also release like methane. Ethane, Ethylene, Propylene and similar reactions are also possible depending on the exact temperature and pressure. So overall this product gas will consist Carbon Monoxide, Carbon Dioxide, Hydrogen, Methane as well as trace quantity of other similar hydrocarbon rich gases like Ethane, Ethylene, Acetylene etc. So, these will be the product gases.

We can get it from the coal gasification and if we see that the first in some of the cases this first reaction some amount of heat will be released. So, if we are doing only for the oxygen-based reaction it will be completely exothermic reaction where release heat quantity will be significantly higher and bed temperature will be significantly higher but if we can allow this reaction this second and third reaction that is Boudouard reaction, water gas reaction and water gas shift reaction is there. We can control the temperature of the reactor as well as we can increase the amount of hydrogen gas in the product gases in all such cases. the calorific value of the product gases will be significantly higher compared to the only pure oxygen or pure air based medium now difference is that if we use a pure oxygen and pure air if you are using pure oxygen or product gas will have carbon monoxide or carbon dioxide but if we are using here in such case it will have also some amount of nitrogen gas is there and nitrogen gas will also be available in the product side. So, as there is about 80 percent nitrogen is there here also 80

percent nitrogen will be there. So syn gas produced by this reaction will have very less amount of carbon monoxide, hydrogen and other gases because they will constitute about 20 percent and remaining 80 percent or approximately 80% will constitute the nitrogen and similar gases. So, all these reactions can be possible. that depends on the exact temperature pressure and hydrocarbon structure maturity of hydrocarbon and other conditions. So, all these reactions are possible in a coal gasifier and these reactions can happen depending on the temperature and pressure. So, depending on the design of the reactor some of the reactor can have higher amount of carbon monoxide whereas some of the reactor can be used to produce high hydrogen gas in the product So, overall if we see as long as oxygen is in excess in the first slide you can see in such case carbon monoxide will be converted to the carbon dioxide by chemical reaction A. That is  $C + O_2 = CO_2$ . This reaction will happen if we provide excess oxygen in the feedstock or in the feed gases. So, if we reduce the amount of oxygen, so this reaction one will stop air production of carbon monoxide. But if we provide adequate amount of oxygen or higher amount of oxygen, it will produce much more quantity of carbon dioxide. So, whatever initially carbon monoxide was there, that will be further converted to  $CO_2$  by this reaction. So, that is the reason where this oxygen concentration in the feedstock has to be controlled very precisely so that the product gas will have much more quantity of carbon monoxide and lower quantity of carbon dioxide if we provide excess oxygen it will result in higher amount of carbon monoxide and among this carbon dioxide and carbon monoxide. Carbon monoxide has some amount of calorific value because it can do this first reaction if carbon monoxide is there in the product gas then we can carry this reaction in the plant itself so consumer will have availability of some amount of energy from the carbon monoxide but if carbon dioxide is produced it is the end product or final product it will not be releasing any further amount of calorific value so always carbon monoxide concentration in the product gas should be on higher side and carbon monoxide carbon dioxide concentration should be less or zero So, if carbon monoxide is there, then it undergoes the reaction into CO by reaction 2 which is known as the Boudouard reaction and this is the most important or stage controlling reaction because it is the endothermic reaction. So, heat released by the reaction 1 or the first reaction it will be used to do this Boudouard reaction that is the reaction 2. So, this reaction Boudouard reaction will control the temperature of the bed if these reactions happen then the temperature of the reactor will not increase significantly as well as the concentration of carbon monoxide in the product gas will be on the higher side because by these reactions also we are gasifying some amount of coal and it is also absorbing some amount of heat energy this is an endothermic reaction. So, it is equilibrium constant increases with rising temperature the content of co in the equilibrium

mixture of CO and CO<sub>2</sub> at one atmosphere increases as sharply if we increase the temperature above 500 degrees centigrade so if we see the conversion of this first reaction that is CO production reaction as well as the CO<sub>2</sub> production reaction The concentration of CO and CO<sub>2</sub> it will primarily depends on the temperature of the reactor bed. Typically, at one atmosphere if we increase the temperature of the reactor from 400 degree to 1000 degree centigrade we can see that carbon monoxide conversion reaction it will increase from 0.9% only at 400 degrees centigrade. that means at 400 degree centigrade most of the cases it will be converted to carbon dioxide and very less amount of carbon monoxide will be produced and also the reaction rate will be very slow as at 400 degree centigrade coal will not burn properly so if we increase the temperature of the reactor in such case combustion reactions or partial combustion reaction rate will get increased typically it is the theory of chemical reaction kinetics is that for each 10 degree increase in the temperature rate of reaction is typically double this is the in general. So, in such case also if we increase the temperature in the first case only very small amount of carbon monoxide will be produced and very less amount of carbon dioxide will also be produced as this temperature is not adequate for complete combustion also so concentration of carbon dioxide will also be very less. So, if we increase this temperature 2000 degree centigrade and if we can maintain this limited oxygen supply concentration of carbon monoxide will be significantly higher and whatever the carbon feedstock is there that will be completely converted to carbon monoxide. So, to increase the carbon monoxide yield in the gas typically temperature of the reactor is kept above 900 or above 1000 degree centigrade If we do these reactions at lower temperature, carbon monoxide concentration will be less as its conversion to carbon monoxide will be very less and reaction rate will be very slow. But if we increase this temperature to 900 degree or 1000 degree centigrade, so most of the cases complete conversion of coal will happen and it will be converted to the carbon monoxide. That is why in gasification reaction always Temperature of the reactor are kept nearby 1000 degree centigrade so that the carbon monoxide concentration is significantly high as well as the rate of reaction is on the significantly high.

If we do this gasification at lower temperature. this conversion reaction rate will be very slow and carbon monoxide as well as carbon dioxide concentration will be very less rather it will be full of different type of volatile materials because these volatile materials or carbon materials will not be converted to neither carbon dioxide or carbon monoxide they will remain as volatile material of different complex hydrocarbon structure and that will contaminate the product gases And after these gases leave the fuel bed, typically this carbon monoxide partially dissociate

into carbon and carbon dioxide. So, depending on the temperature, pressure and other condition, this reaction is also possible where carbon monoxide can dissociate further to make it carbon dioxide and carbon. So, this is the reversible reaction of the Boudouard reaction.

In the Boudouard reaction, carbon react with carbon dioxide to produce carbon monoxide. So, if this reaction condition is not favored, that means it is an equilibrium reaction. Connected reaction if reaction concentration in the product concentration is  $\text{CO}_2$  is extremely carbon monoxide concentration is extremely high then it can go for the reverse reaction or Boudouard reaction where carbon monoxide will further dissociate to carbon dioxide and carbon. So, reversible or reversal of Boudouard reaction is also possible, which is known as the Neumann reversal reaction. This can also happen if we are unable to control the rate of reaction as well as the  $\text{CO}_2$  concentration in the product. So, in such a case, the product will have carbon monoxide, carbon dioxide, hydrogen, methane, nitrogen, oxygen, and other gases are also possible. Now, this exact gas composition will depend on the reaction conditions such as pressure, temperature, availability of oxygen, coal composition, coal maturity, volatile material composition, etc. So, the exact gas composition will vary depending on the origin of coal as well as the reactor conditions, reactor design, etc. Now, here we have to remember that the purpose of gasification is to convert the coal to a gaseous product, like converting it to a syngas, but the purpose is not to release the heat. Like in this reaction, we can see that some amount of heat is released in other cases, such as  $\text{C} + \text{O}_2$ .

The  $\text{CO}$  reaction is also a production where  $\text{CO}$  is produced, but some amount of heat is released. So, our purpose of this gasification is not to release the heat at the source itself, but rather to convert the coal to a gasified product. Along with keeping the calorific value or energy content of the coal—whatever was there—that same amount of energy should be available in the syngas so that the consumer or the utilization of syngas can be effectively improved because they will also get the same amount of energy, and the main purpose of this gasification will be fulfilled: converting this coal, a solid fuel, to a gaseous fuel. And accordingly, these reactions are conducted or controlled. All these reactions are conducted or controlled so that we can increase the yield of gases like carbon monoxide and hydrogen because these two are the main product gases which provide the calorific value in the syngas. So, all the reactions and all the reactor designs are typically operated and designed so that the yield of carbon monoxide and hydrogen is on the higher side in the reactor, not the concentration of  $\text{CO}_2$  and other gases. So, all the reactions are controlled or modified to increase the yield of carbon monoxide and hydrogen in the product gases. Overall, if we see what happens during coal gasification, it is a

simple chemical reaction involving coal and gas. Overall, if we see the coal gasification reaction, it is a chemical reaction involving coal, and inside the coal, there are different types of hydrocarbons available. So, it is a chemical reaction involving different types of hydrocarbons represented by the coal, biomass, and others, as well as the gaseous stream, which can have air, oxygen, or H<sub>2</sub>O. Thus, all the reaction parameters related to coal combustion will be the same. In the previous chapters, we have seen that during coal combustion, the composition of mineral matter, rank of coal, percentage of volatile material, percentage of fixed carbon, porosity of coal, ash composition, ash fusion temperature, etc., all have an impact during coal combustion. So, all these parameters will have a similar impact during coal gasification. Because both coal combustion and coal gasification are chemical reactions involving hydrocarbons as well as gas as a medium.

So, whatever the impact of the parameters is, that is the concept of the ash layer. If there is some high-ash coal, an ash layer is formed. This ash layer creates difficulty in the diffusion of oxygen, carbon dioxide, and carbon monoxide. So, the same ash layer will have a similar impact when we do gasification. If the temperature—whatever the role of the ash layer is—the ash layer creates difficulty in the diffusion of oxygen, carbon monoxide, and other gases.

So, this same ash layer will have the same impact when we do gasification. Similarly, if VM is released, that improves the rate of ignition and other factors. So, all those VMs will again be released here and will react with steam and oxygen. So, their impact will be the same or similar. Porosity—if porosity is present, coal will be highly reactive or non-reactive. Ash composition can have a positive or negative impact. Ash fusion temperature may occur if we exceed the temperature above 100 degrees centigrade; coal ash may fuse. So, all these parameters will have a similar impact during coal gasification. Similarly, as the reactant source of coal and products are different, reaction kinetics may vary.

Like in the case of coal combustion, we have seen that if we change the source of coal, such as coal from mine A and coal from mine B, their hydrocarbon structures are different because their coal composition varies. In such cases, the chemical reaction or combustion kinetics changes. The same thing will happen with coal gasification as well. So, in such cases, product gases or gasification kinetics may change depending on the temperature, pressure, and the source of coal. And that is very challenging, particularly with coal gasification.

The overall coal conversion may not be the same every time, as these chemical reactions involve coal hydrocarbons as well as gases. Depending on the hydrocarbon structure, chemical

composition, porosity of the coal, and composition of the ash layer, all play a major role during this chemical reaction. So, gasification may not yield the same number of gases in the product. Particularly if we perform this gasification, the product gas will not always have a fixed amount of carbon monoxide or hydrogen. Suppose we are converting coal to carbon monoxide and hydrogen. So, if our expected carbon monoxide is 25% and hydrogen is 30%. Suppose this is our expectation and design.

Our product gas should have this concentration of carbon monoxide and hydrogen. Now, if we change the source of coal, the carbon monoxide yield may drop to 20% or rise to 25%. In such cases, the product gas composition will vary and may not have the same calorific value or gas composition required by the consumer. For gasification, we must ensure that we provide coal of the same or similar quality and composition so that the product gas quality does not vary significantly. And that is the main challenge and the primary drawback of gasification. That's why people always try to obtain a fixed concentration of carbon monoxide, hydrogen, and other gases, which is very difficult.

If you change the coal source from day-to-day life, that means if we get coal from different locations or if we utilize biomass from different origins or sources, it is highly expected that the product gas composition will have varying amounts of carbon monoxide, hydrogen, and other gases. So that may not be desirable for the end user who uses this syngas for their chemical plants as well as for fuel. These chemical reactions are very important. The chemical reactions that occur during gasification depend on the coal composition, reaction kinetics, reaction temperature, pressure, as well as the design of the reactor.

Thank you.