Clean Coal Technology

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Week-04

Lecture-16

Hi, I am Professor Barun Kumar Nandi, welcoming you to the NPTEL online certification course on clean coal technology. Today, we will start with Module 4, discussing coal combustion fundamentals. In this module, we will discuss different aspects of coal combustion, some preliminary theory on coal combustion, the shrinking core model, the burning profile of coal, heat release rate, burning time, and unburned carbon control, which originates from coal combustion. So, let's start with Lecture 1 on coal combustion. If we examine coal combustion, it is actually a chemical reaction that occurs between the hydrocarbons present in coal and oxygen.

Overall, coal combustion is a type of chemical reaction. Not only coal combustion, but in other applications like coal gasification, coal carbonization, and coal pyrolysis, it involves chemical reactions between the hydrocarbons present in coal and other reactant gases in the presence of higher temperature, heat, or other factors. When we perform coal combustion, we typically use air as a source of oxygen gas because, in combustion methods, we need to supply an oxidant. Oxygen acts as this oxidant, and it is available in the air. So, in most combustion applications, air is used as a source of oxygen, though in some cases, pure oxygen or high-concentration oxygen is also used—not in all cases. If we examine the composition of air, it contains about 20% oxygen by volume and 23% oxygen by weight. These are approximate or rough values; exact values may vary from location to location or depending on the presence of other gases. Broadly, when performing combustion calculations, we assume that, by volume percentage, air has 21% oxygen and the remaining 79% is nitrogen gas. By weight percentage, it is about 23% oxygen gas and the remaining 77% is nitrogen gas. So, in general discussion, we assume that roughly 20% or one-fifth of the air is oxygen, and the remaining 80% is nitrogen.

So, in calculations, we have to use the exact percentage of oxygen present. So, for general discussion, when we discuss coal combustion in air, We mostly say that air has about one-fifth oxygen and 80% nitrogen, but it is not the exact value. It is only for general discussion. The exact value is about 21% and 23%. And if we see some more precise values, air contains other gases like carbon dioxide, carbon monoxide, NOx gases, some moisture, some inert gases, etc. Those are available in general textbooks. So, in combustion calculations, we will use 21% or 23% values. As per the stoichiometric calculation, what will be used? Calculating by volume percentage of oxygen, we will use 21%. If we consider the weight percentage, we will use 23%. And in many discussions, we may talk about that. About 20% is oxygen. This is in general discussions or general talk, not the exact value. Overall, if we consider the combustion process, it is an exothermic chemical reaction. Now, why do we combust coal? Combustion of any fossil fuel because, by doing this combustion of fossil fuel, we get some heat energy out. That heat energy originates from the chemical reaction, as combustion is generally an exothermic chemical reaction. An exothermic chemical reaction means by which we get some amount of energy output. Whereas endothermic chemical reactions mean where we have to supply additional heat to perform the chemical reaction. So, in the case of the combustion process, energy is released by the combustion of coal. Now, from where is this energy released? This energy is released from the internal energy stored between the different hydrocarbon bonds, like carbon-carbon single bonds, carbon-carbon double bonds, carbon-carbon triple bonds, aromatic bonds, as well as carbon-hydrogen bonds, carbon-oxygen bonds, or maybe carbon-sulfur bonds, carbon-nitrogen bonds. Whatever those bonds are there, they are broken by the action of heat. At high temperatures in the presence of oxygen. So, these carbon-carbon bonds break and create some new bonds of carbon-oxygen, like carbon dioxide. So, the differences between the bond energy or internal energy present in the hydrocarbons in the feed material, and if we see the internal energy available in the product gases like carbon dioxide and water, they are the typical products of the combustion process. So, the differences between the internal energy of reactant material, like coal here, as well as the product material, like carbon dioxide and H_2O, so there are differences we get it as exothermic energy or heat release. So, in general, any chemical reaction involves the breaking of bonds. So, in the case of coal combustion, these bonds are broken, and reactants form and in the products, we also get some new types of bonds. So, the difference between this bond energy, we get it as an energy output. So, if we see in the case of coal or other types of fossil fuel, depending on the number of these carbon-carbon bonds, carbon-hydrogen bonds, etc.

That means the amount of internal energy stored in all these bonds. And depending on the product gases we get. If we are getting carbon dioxide (CO_2), methane, or other gases. So, the differences between these two factors or these two compounds, or the differences in the internal energy of these compounds—the remaining amount we will get as heat output, as coal combustion or fossil fuel combustion is an exothermic chemical reaction. So, in the case of coal or any fossil fuel, energy is available in different types of bonds. The energy level of hydrocarbons typically those we consider as volatile material and fixed carbon because, in coal, we broadly classify them as fixed carbon and volatile material. The energy level of hydrocarbons in combined volatile material and fixed carbon is higher than that of products like carbon dioxide, H2O, and other gases. During any chemical reaction, as we all know, some amount of activation energy is required to initiate the chemical reaction. So, what is this activation energy? To start this bond-breaking reaction or bond-breaking phenomenon, some amount of external energy is always required. This external energy, after being supplied, will bring any compounds or reactants to an equilibrium stage, and then it will create some product compounds. This minimum amount of energy is called the activation energy. Like in this plot, if we see this enthalpy—meaning this is the energy content available—when it starts with the reactant, the reactant may have an energy level at this particular point, and the products may have an energy level at this particular point. So, although they have differences in their energy levels, here the feed component or reactant has a higher amount of energy, whereas the product has a lower amount of energy. But still, we cannot directly go through this process. This is not possible. To make these reactions happen, initially, some amount of energy has to be supplied externally. So, this amount of energy we have to supply externally is known as the activation energy.

So, for this case, we have to supply this amount of additional energy or starting energy to activate the reactant or to initiate the chemical reactions. Later, this entire energy will be released, and some more energy will be released from these products. So, the difference in the energy level, whatever we get, we will obtain it as the heat output. So, this type of reaction is called an exothermic reaction, where the energy level of the reactant is higher than the energy level of the products. Whereas, in the opposite case or in other instances, the reactant can have this energy level, and the product can have a higher amount of energy. So, even in this case, we have to supply an additional amount of energy, which is this amount of energy we have to provide externally. So, this will be the activation energy, and after this reaction is complete, the final product may have a higher amount of energy. So, their delta H or enthalpy is positive; here, the delta H value or enthalpy value is negative.

So, this type of reaction is called an endothermic reaction, where effectively we have to supply an additional amount of energy to the reactants so that they create some final product which will have a higher amount of energy. Whereas, in an exothermic reaction, the reactant will have a higher amount of energy, and after reacting with other compounds or materials, the final product will have a lower amount of energy. So, such a reaction is called an exothermic reaction. This reaction is called an endothermic reaction, but in both cases, we have to supply activation energy from external sources. So, this activation energy is supplied to the reactants in different forms, maybe as heat energy, light energy, or other types of energy. So, this activation energy needs to be supplied to the reactant so that they reach the same level. This level is same for a particular set of reactions. They reach to the same level and after reaching this level, they will either release the energy or they will store some amount of energy. So, total energy release per unit mass of fuel, so these differences in this energy level, this delta H value, which in case of fuel, we consider it like a gross calorific value of fuel, which is expressed as kilocalorie per kg or calorie per gram or maybe megajoule per kg as per different units of energy. Now, when we consider or when we discuss about the combustion of coals, some other fundamental parameter, we also has to be known or we also should know all these other parameters like what is space time. Space time for chemical reaction like it in any of the chemical reaction it has some space time that means some amount of time is required to perform or to carry some of the chemical reaction. Some minimum amount of time is required like even if we supply this amount of activation energy to the reactant as well as the product. But this reaction will not happen instantaneously at zero time. This reaction may take some more time or some less time depending on these ionic characteristics or types of hydrocarbons present there. All these chemicals or all these combustion reactions, that will happen. They need some amount of activation energy, but they will carry out this reaction or this reaction will undergo only after some time.

So, some time amount is required, which is known as the space time. So, suppose if we give 1 kg of coal, so 1 kg of coal will get burned. but it will take maybe five seconds or maybe five minutes or maybe five hours. So, depending on the reactor design, structure of coal and other conditions, it needs some minimum time for reaction. It is not like that we give 1 kg of coal and within few milliseconds or within just immediately it converted to energy. It always takes some time because this any chemical reactions mean some sharing of electron pair, bond, some ionic interaction, etc. And there are other many parameters involved in this chemical reaction. So, it needs some minimum time duration for completing the reaction. So that time is called the space time which represents or which is linked to the rate of chemical reaction.

Some of the chemical reactions are very fast. Whereas some of the chemical reactions are very slow. Very fast chemical reactions mean that chemical reaction is occurring at very higher rate. So, in such case their space time or time required to complete this reaction will be less. Whereas some chemical reaction can occur at a very slow rate. So, in such case to complete this chemical reaction, it may take some much more time. So, this is about the space time and rate of chemical reaction. Second parameter is that in any of the fossil fuel, it is not only about coal, but also applicable to any of the liquid fuel like petrol, diesel, kerosene, fuel oil, etc., as well as the gaseous fuel. That individual hydrocarbons present in coal or fossil fuel; they react with oxygen. Like we call it maybe a particular type of fossil fuel. Maybe we call it or name it like this: this is coal, this is biomass, this is petrol, this is diesel, whatever. But when we burn it, the individual hydrocarbons present in this fuel or fossil fuel react with oxygen. So, depending on the types of hydrocarbons present, what hydrocarbon is present there? Like if we say in natural gas or even if we say in LPG gas. So in LPG gas, it contains propane and butane. So, when we burn LPG gas, individually, propane reacts with oxygen. Butane reacts with oxygen. So, the rate of reaction of propane and oxygen is different, whereas the rate of reaction between butane and oxygen is different. Similarly, if it has any other third hydrocarbon, it is applicable to those hydrocarbons also. So individual hydrocarbons present in this fossil fuel react with oxygen. So, the entire combustion characteristics or entire reaction kinetics will depend on the individual hydrocarbons present.

Whether this hydrocarbon reacts easily with oxygen or it does not react easily with oxygen. So, all these phenomena, all these things will impact the rate of combustion when we use it in the burner. So, the rate of reaction is different for different hydrocarbons. As different hydrocarbons have different amounts of activation energy required. Like if we say this plot, this is the activation energy required maybe for methane.

But for other gases, it may value may be lower or this value may be on higher side. So, this value activation energy will be different for different hydrocarbons. So, individual hydrocarbons present in this fuel, they react. So, rate of reaction is different for different hydrocarbons. It will not be same for all types of hydrocarbons. So, although we call it coal from mine A or mine B, but depending on the hydrocarbons present, as the individual hydrocarbons react with oxygen, Rate of reaction is different for different hydrocarbon. So, rate of combustion for coal will be different for different mine coal. For same 1 kg mass of coal, some fuel may take less time if the hydrocarbons are highly reactive. So, in those cases, fuel may take less time to complete combustion, whereas other hydrocarbons, if they are not reactive or they are reacting very slow, they may take some longer time to complete the reaction. So that difference we get it in the space time so space time will be different for different hydrocarbon. So, space time will be different for different types of fuel. Hence two different coal of different origin as their hydrocarbons are different they may burn slow or at a faster rate. So, their burning rate or their heat release rate, as they are burning at slower rate or higher rate, their heat release rate like amount of heat release per unit time, that means kilocalorie per minute or kilocalorie per second, megajoule per second, whatever unit take. That means per unit time, the energy release will be different as they may burn at slower rate or faster rate. During coal characterization, typically we do not consider the chemical compounds present in coal and we only see their behaviour in the presence of heat and we nomenclature them or we consider them whether they are volatile material or they are fixed carbon or we measure the Total amount of energy released, that is we call it like gross calorific value.

So that is a fundamental or a significant difference between the actual fuel characteristics and how we characterize the coal or any such fuel. During in general characterization, when we consider that this coal has this amount of volatile material and fixed carbon, we characterize them by their thermal behaviour that at 925 degrees centigrade, how much volatile material has been released, how much hydrocarbon has been there, how much hydrocarbon is not reacting. We consider all these things at a fixed time of 7 minutes. Similarly, when we consider the calorific value or GCV, we consider the total amount of energy released. So, we do not exactly consider what is the chemical compounds present in this fuel, because when we consider the chemical compounds, maybe some fuel have methane plus propane, Whereas another fuel can have methane plus ethane plus butane. So, these two different fuel have different hydrocarbons composition. So, they may, their entire energy release can be same. So, their calorific value may be same. Even their volatile material, fixed carbon, similar characteristics may be same.

But there is some difference in the chemical compounds. So, rate of chemical reaction for this mixture and rate of chemical reaction for this mixture, it is certainly not the same. although their total amount of energy may be same. So, in case of conventional coal characterization, that does not reflect the exact chemical compound. When we characterize the coal, typically the exact chemical compounds are not considered. So, that characterization does not exactly represent the chemical compound present in coal. As such analysis is so much time consuming and sometimes very difficult to carry out such analysis and it may be very much costly. So, in conventional coal characterization, we do not consider or we do not characterize the exact amounts of hydrocarbon or exact composition hydrocarbon present. We characterize in some different way That's why the proximate and ultimate analysis, volatile material, fixed carbon, they represent some of the general characteristics but not the exact characteristics it is very difficult to do exactly analysis or exactly analyse all these hydrocarbon structure, their percentage etc. They are too much costly. They can take some much more time. So, for very easy and quick analysis we do all this analysis but they may not 100% represent the exact hydrocarbon present in coal but they somehow represent. So, there is some difference that means they are partially representing the coal chemical compounds and they are not totally representing the total chemical compounds.

And as the origin of coal can be different from different plants, even if we consider the coal mines of having similar type of proximate analysis, as their origin of coal, it can originate from different type of plants or living materials. The age of plant matters. If any plant was of 10 years old and if any particular tree was of 100 years old, their hydrocarbon structures, their body parts, even it can have some branches of the tree. It can have the main part of the tree. It can originate from the root of that particular tree from which coal has been originated.

So, depending on the origin of coal, when we consider that origin of coal, That means coal can be originated from different type of trees as different type of trees has different chemical composition. Individual tree can have different maturity level as their age can be different and even different body parts of the same tree has the different chemical composition in terms of hydrocarbons. Their chemical structure varies so much. So hence proximate analysis, ultimate analysis, gross calorific value analysis, they does not reflect 100% what is there inside the coal or inside any of the fossil fuels.

Apart from this, the chemical composition of mineral matter, salts, and inorganic salts also modifies the reaction kinetics. As we have discussed earlier, the chemical composition of ash or mineral matter also varies from source to source. So, they sometimes impact, improve, or decrease the rate of reactions and other chemical reaction kinetics; they can have some impact. Hence, two coals or two fuels of similar characteristics can have different rates of chemical reaction. Due to all such variations, two fuels of similar characteristics, like two coals, may be from the same mines but from different seams, or coal extracted today and coal extracted the next day may have different chemical compositions. As their chemical composition differs, they can have different rates of chemical reaction. So, when we consider this chemical reaction, it is applicable in all types of such applications, like when we burn them, we call it coal combustion or the combustion process. The same thing will happen when we pyrolyze or heat them, when we gasify them, or when we utilize them in any other applications where some chemical reaction occurs. As the hydrocarbons present in this coal vary, they can have different types of chemical reactions and different rates of chemical reaction. So, we must understand coal combustion or its reaction mechanism. When we discuss the combustion of coal, we have to understand how this coal reacts, its reaction mechanism, and how other parameters affect coal combustion. We must know all these aspects so that we can understand exactly or most of the methods or phenomena occurring during coal combustion before we fire them or burn them in a boiler. In general, when we talk about combustion reactions for coal, we represent these combustion reactions as coal, represented as a hydrocarbon like C_xH_γ, where X and Y represent the number of carbon and hydrogen atoms. Like $C_{100}H_{200}$ or maybe $C_{10}H_{22}$ or $C_{10}H_5$, whatever. So C_xH_γ represents the hydrocarbons present in coal, and it reacts with oxygen. The two products we obtain from the combustion of any fossil fuel are carbon converting to carbon dioxide and hydrogen converting to hydrogen oxides or water. This represents complete combustion—if combustion is complete, that means all the hydrocarbons are burning properly, and all the energy available in the fossil fuel is released. In such cases, the products are carbon dioxide and water. In the case of partial combustion, the oxidation reaction from carbon to carbon dioxide is not totally complete; it may be partially completed.

So, in such cases, we primarily get carbon monoxide, hydrogen oxides or water, as well as other hydrocarbons like methane or maybe hydrogen gas, and others may be present. So, such a type of chemical reaction or combustion is known as partial combustion. So, when we discuss coal combustion, it can be complete combustion where all the hydrocarbons or all the fossil fuel, all the coal, will be converted to the final end products, which are carbon dioxide and water. In cases where they are not the final products, much more energy can also be released or extracted even from these products, like carbon monoxide. What may be other hydrocarbon gases? These are called partial combustion, as even if we burn this carbon monoxide, it can again be converted to carbon dioxide. So, carbon monoxide is effectively an intermediate product of this combustion. So, in combustion where we are getting carbon monoxide and other similar hydrocarbons, we call them the partial combustion, meaning it is some 50%, 60%, or partially finished combustion, not that total combustion is completed there. So, for simplicity, as coal is mostly rich in carbon and has a very small quantity of hydrogen, in general, when we write the coal combustion reaction, we write it as C plus O2 equals CO2. But it is only for representative purposes to make it simple. But exact coal combustion means it will have the products of carbon dioxide and water. So, this is the exact chemical reaction that happens. But for representative purposes, for quick understanding or writing, we write it as C plus O2 equals CO2 for coal combustion. Any other chemical elements, present as part of hydrocarbons like sulfur, nitrogen, phosphorus, chlorine, oxygen, which are also part of hydrocarbons. They also take part in this oxidation chemical reaction. So not only carbon and hydrogen, but sulfur, nitrogen, phosphorus, chlorine, oxygen, and any other elements which are part of coal also take part in this oxidation reaction, and corresponding oxides are formed.

Like if sulfur is there, sulfur dioxide, sulfur trioxide will be formed. If nitrogen is there, nitrogen oxide NOX, N2O, N2O3 all these gases will be formed, phosphorus is there, then P2O5 and other gases will form similarly chlorine will form other oxides. If it get the desired reaction condition like temperature, pressure etc. see these all these oxides will form depending on the temperature, pressure and other nearby conditions required. Like if they get their desirable activation energy, like if they get that supply of activation energy at higher temperature, nitrogen may react, phosphorus may react or chlorine may react. So whether these elements will react or not, that depends on the reaction condition like if we do the chemical reaction at higher temperature like we are combining it this coal at very high temperature maybe 2000 degree centigrade so that temperature nitrogen may be reactive but if the we are doing reaction at 500 degree centigrade nitrogen is not getting its desirable reaction condition to do the chemical reaction so in such case nitrogen will not react Similarly, for chlorine, whatever the reaction condition is required, if it gets that reaction condition, then only it will react. If it does not get that condition, it will not react. So, if they react, they will form their individual oxides.

Otherwise, they will be released as unburned hydrocarbon. If they are not getting their desirable condition, they will be released as Unburned hydrocarbon, whatever the hydrocarbon they can make at the available reaction condition, they will form such condition. Like if nitrogen is there, it can form some condition to make it ammonia. It can make ammonia. If the condition is not suitable for forming ammonia, it will not form ammonia. It may form pure nitrogen gas. If sulfur is present and the reaction conditions allow it to form sulfur dioxide, it will make sulfur dioxide. If the condition is not met, it can be released as H2S gas or pure sulfur. So that depends entirely on the reaction conditions and what is available. And if we make the enthalpy balance, the enthalpy of the feed hydrocarbon side (reactant) will be the enthalpy of the product reactant as well as the amount of heat released. So, there will be a total energy balance or enthalpy balance across the reactor as well as the product side. The same amount of energy that will be used during the photosynthesis reaction, the same amount of energy will be released in the presence of sunlight. As we all know, trees or plants originate from, or they start, they get their energy from the photosynthesis reaction. Because in the photosynthesis reaction, carbon dioxide and hydrogen react to form glucose. So whatever energy was applied by the photon, to convert CO2 plus H2O into glucose, the same amount of energy we will get out when we burn the coal. So, in general, the amount of energy stored by the photosynthesis reaction of CO2 and H2O to form glucose is the same amount of energy that will be released. In some cases, after photosynthesis, individual plants or trees modify this glucose into other forms of hydrocarbons, such as from glucose to fructose, sucrose, and maybe lignin, cellulose, hemicellulose, etc. So, all these aspects also need to be considered, and the rate of reaction, is different for different values of x and y, as we have represented, or if we have represented the hydrocarbon as CxHy. So, if the values of x and y vary, that means the types of hydrocarbons present in that fuel vary. So, depending on the values of x and y, the rate of chemical reaction will be different, depending on the hydrocarbon structure like the source of coal maturity will result in different values of X and Y. Other materials, as we have discussed, like the composition of mineral matter and others, will influence the rate of chemical reaction. Some of the composition of mineral matter may have a catalytic effect, like they may increase the rate of reaction, or they may have a poisonous effect or inhibitor effect. So, their rate of reactions may be So, overall if we think about the combustion fundamentals about the fossil fuel, if we summarize, first thing is that individual coal will have different type of hydrocarbon present. So, as they have different type of hydrocarbon present. Their rate of chemical reaction, wherever we do or we utilize this coal, whether it is combustion, it is gasification, it is pyrolysis, all these rate of reactions will be different. There may not be significant difference, but there will have some actual difference. So, they will be somehow different depending on the types of hydrocarbon present.

These types of hydrocarbon varies depending on the maturity of the tree, type of tree, from which part of the tree this particular fossil fuel has been formed, originated, etc., Also the mineral matter present, they will have some impact, maybe some positive impact or they may have some negative impact during combustion of any of the fossil fuel. And mostly we see all these differences broadly in case of coal. We may not see such differences to a higher extent in case of liquid fuel and gaseous fuel. As coal is extremely heterogeneous we broadly see their differences in a higher scale or magnifying scale but we may not be seeing such differences in a liquid fuel or gaseous fuel, are somehow better homogeneous compared to the extremely heterogeneous coal.

Thank you.