Clean Coal Technology

Prof. Barun Kumar Nandi

Department of Fuel, Minerals and Metallurgical Engineering

IIT ISM Dhanbad

Week-08

Lecture-37

Hi, I am Professor Barun Kumar Nandi, welcoming you to the NPTEL online certification course on clean coal technology. We are in module 8, discussing emission control strategies for combustion utilities. So, in this module, we are discussing SOx and NOx control strategies. during combustion and after combustion, oxy-fuel combustion, carbon dioxide capture and storage. So, in this lecture 2, I will be discussing NOx emission control strategies for combustion utilities. If we see how NOx emissions from combustion utilities occur, typically, NOx or nitrogen oxides, either NO, N2O3, or NO2, all these nitrogen oxides are generated during combustion when oxygen reacts with nitrogen.

So, this is the main thing or the main part of how NOx is generated. in a combustion chamber. As in the combustion chamber, we are using air, so in the air, nitrogen is about 80 percent and oxygen is about 20 percent. So, this nitrogen and oxygen typically react at high temperatures, and as a result of this reaction, depending on the temperature and chemical kinetics, it may form different types of nitrogen oxides. So, such NOx formation reactions take place typically at higher temperatures. So, if we see the reaction of N2 plus O2, which may form either NO, N2O3, NO2, N2O5, or whatever. So, all these reactions typically happen only at higher temperatures. Like if the temperature exceeds 1000 degrees centigrade. So, if we see that all these reactions, their rate constants or the rate of all these reactions, this rate of all these reactions is typically very low. In any chemical reaction, whether it will give a significant amount of yield or not, like if you are reacting A plus B, whether it will give C, but it can give C, but only 1% or maybe 0.5% or maybe 100% conversion is there. So, this rate of conversion, how much reactant will be produced.

So, although it can produce compound C, the amount of compound C produced is very small. Or it can be very high, depending on the rate constant—at what rate the chemical reaction is happening, whether it is a reversible reaction, an irreversible reaction, and what the rate of that reaction is. There are several reactions available where it can react to produce some of the product, but the yield—that is, the amount of product converted—is very, very small. So, if that value is very small, then in such cases, we say that the rate constant is very small. Whereas, if the conversion is very rapid, the rate constant is very high.

So, in the case of NOx formation, this reaction takes place at higher temperatures, approximately above 1000 degrees centigrade. So, if we see the rate constant at 1000 degrees centigrade, this value is very small. That means we can say that there is almost zero amount of NOx formed, or only a very minor quantity of NOx is formed. So, typically, the rate of reactions between nitrogen and oxygen is very small. It typically starts around 1000 degrees centigrade, and this rate constant increases with an increase in temperature. Typically, in any chemical reaction, the rate constant or rate of reaction almost doubles if the temperature is increased by 10 degrees centigrade. This is the general theory for any chemical reaction. So, the reaction rate at 1000 degrees centigrade is very small, and if we increase this temperature to a higher level—maybe 1400 degrees centigrade or 1500 degrees centigrade— the rate constant value will become significantly higher. So, in such cases, as the rate constant is significantly higher, the amount of NOx formation will increase significantly. So, what we can conclude is that at about 1000 degrees centigrade or at lower temperatures, the rate of the NOx formation reaction is very small. A very small amount of NOx will form, or we can say almost zero quantity or no NOx will form if the temperature of the reaction is very low. But if the temperature of the reaction is significantly higher, like 1400 or 1500 degrees centigrade, the yield will be significantly higher—that means maybe 20 percent or 30 percent will get converted to NOx. And if we see typically NOx is originated from the combustion if N2 is originated in the combustion chamber either as part of fuel hydrocarbon in the ultimate analysis of the fuel or coal biomass. It always has nitrogen compound as part of organic compound structure. As we have seen the different organic compound, in all these compound nitrogens is sometimes and compulsory part of this structure. In many compounds nitrogen molecules are present, nitrogen atoms are present. So, this nitrogen can be originated from the fuel hydrocarbon.

That means coal itself has some amount of nitrogen. Typically, in ultimate analysis we can see that nitrogen quantity is around 1.5 to 2%. or in higher quantity it is always available from the air when we are burning fuel with the air in the air about 80 percent nitrogen or one or exactly 77 or 79 percent nitrogen is there. So, you can say 80 percent nitrogen is actually coming from the air. So, in the system there will always be having nitrogen is possible. So, we cannot remove nitrogen from the combustor very easily. So, nitrogen will always be part of any of the combustion utilities where we use air.

If we are not using air, if we are using pure oxygen or any other compound, this is a different case. But when we are using air, we cannot avoid the nitrogen will always be present in the combustor. So, what we can do? Only we can the rate of NOx formation that only what we can do is that we can only control the NOx formation or NOx generation rate that only can be controlled by modifying the kinetics.

So, we have to modify the rate constant of this chemical reaction that how we can control how we can modify the rate constant for this NOx formation reaction. So that the overall yield of this NOx formation reaction is very less. So, there are different methods typically to control the NOx emission in the coal-fired utilities or any of the combustion utilities. First method is the use of low temperature that during the combustion process if we can keep the combustion temperature on the lower side like preferably below temperature of 1200 to 1300 degree centigrade. If we can keep this combustion temperature or maximum temperature in the combustor below the 1200 or 1300 degree centigrade that means if we can avoid achieving high temperature like this 1400 degree centigrade if we use 1400-degree centigrade yield will be always on the higher side. So, if we want to reduce the NOx formation we should use the maximum temperature or highest temperature in the combustor in the range of 1200 to 1300 degree centigrade if we can keep this temperature in the combustor, so their rate of reactions of nitrogen and oxygen will be always on the lower side. So, we can make that rate of formation of reaction is very less. So, less quantity of NOx will be formed. So, if we see that very good method is always to having the combustion below 1300 degree centigrade or 1250 degree centigrade in most of the coal fire utilities where normal coal combustion is done. Using the super thermal power plant or ultra super thermal power plant, in most of the cases maximum temperature is kept around 1250 or 1300 degree centigrade and if we see in the other side this 1200 degree centigrade or this 1300 degree centigrade. This is the temperature where NOx formation is low as well as this is the temperature where ash fusion of the coal is also there. In most of the cases coal ash they have the ash fusion temperature. around 1200 or 1300 degree centigrade. So, if we go beyond 1300 degree centigrade there is always the possibility of ash fusion occurring in the combustion chamber as well as there is always the possibility of NOx permission in the combustion chamber. So, from considering both the side most of the coal combustion utilities they keep the maximum temperature or they burn the coal temperature always below 1300 degree centigrade or nearby 1300 degree centigrade. If we increase the temperature above 1300 degree centigrade what will happen?

This NOx formation will start as fusion temperature will be achieved so ash will get fused. And further if we see this N2 plus O2 reaction this N2 plus O2 this reaction is need some heat. So, this is the endothermic reaction. That means whenever this NOx formation occurs, this is the endothermic reaction. It also needs some amount of heat. And from that heat will be collected from the combustion chamber itself. So, whatever is the heat released by the coal by burning that hydrocarbon some part of the heat will be used for NOx formation some amount of heat will be used for melting of ash or latent heat required for the phase change for ash from solid phase to liquid phase. So, if we go beyond 1300 degree centigrade, there will be significant amount of heat loss or thermal efficiency loss as heat will be used for NOx formation as well as melting or fusion of ash. So, to avoid this, in the most of the thermal power plant, most of the combustion utilities, they try to burn coal in the range of 1300 degree centigrade or below that. most of the cases it is like 1240-degree 1245- or 1250-degree centigrade temperature that is the maximum temperature in most of the combustion utilities. So, first method or we can say is the best method is to use the low temperature so that we can avoid any type of NOx formation in the coal combustor second method is the use of excess air. If we use the excess air in the combustor like as we know that there is always some amount of excess air is required. So, this excess air means theoretically 100 percent air is required we can burn it even at 100, 105 percent air, 110 percent or we can burn it like 120 percent. So, if we increase this to 120 percent excess air. So obviously there is an excess amount of oxygen is also available for the reaction, if we use the 100% air, so whatever oxygen is possible, available, it is possible that this entire oxygen is consumed by the carbon. So that less amount of oxygen is available to make it NOx. But if we use the higher amount of excess air like 120%, whatever this 20% excess oxygen is there, that will be used to produce NOx. So, if we can use NOx, less amount of excess air or precisely we supply the primary air as well as the secondary air.

That means if we control the amount of oxygen available inside the reactor. That means whatever oxygen is available inside the reactor. If we ensure that all the oxygen is consumed by the carbon to form carbon dioxide. So, there will not be any amount of oxygen available to form NOx. So effectively, we can avoid any type of NOx formation by such a reaction.

So, this is another method. Precisely control the amount of primary air and secondary air. We should closely monitor the gas concentration inside the combustor. What is happening inside the combustor—whether there is carbon monoxide formation, carbon dioxide formation, or NOx formation. By monitoring all of these, we can accurately control the excess air.

Excess air already causes heat loss due to the sensible heat loss by the excess amount of nitrogen and oxygen. Apart from that, if we supply too much excess air, that air will be used to convert nitrogen to NOx. So, if we want to avoid NOx formation, it is always better to maintain very good or sensitive control over the excess air. The third method is flue gas recirculation. Flue gas recirculation is another way to control the temperature inside the combustor as well as to control other pollutant gas emissions, unburned hydrocarbon release, SOx emission, and the excess oxygen used entirely can be controlled if we do it. Some amount of flue gas is recirculated inside the combustor like if the combustor having the temperature of 1200 degree centigrade whatever the flue gas is going if some part of the flue gas is recirculated back. So, this flue gas recirculation will help to maintain or control this temperature of this reactor very efficiently as this flue gas contain higher amount of or higher temperature So, this flue gas can efficiently maintain or control the accurate temperature inside the reactor. In the second way, if it has any amount of unburned carbon monoxide, unburned hydrogen, unburned hydrocarbon available inside this flue gas. So, if those gases are generated during combustion due to incomplete combustion or inadequate supply of oxygen due to poor mixing of oxygen and coal. So, if these are the gases released from the combustor, if you can recirculate them in the chamber.

All these gases will get adequate residence time to react to burn completely. So overall combustion efficiency will get improved and we can efficiently reduce the amount of carbon monoxide, hydrogen, methane etc. in the combustor as well as we can efficiently maintain the temperature in the reactor. Apart from this what the main advantage we will be getting is that whatever is the excess oxygen was used. if we recirculate this excess oxygen, so whatever the 20 percent excess oxygen we have used that means whatever the unused oxygen was there so that oxygen if it returned back to the main reactor effectively we can reduce the amount of fresh air to be supplied inside the reactor as oxygen is getting recirculated. So, whatever is the air has been entered in the reactor or we have sent to the reactor the entire amount of oxygen will get reacted. So effectively there will be better mixing with the oxygen as well as the other hydrocarbon and coal. So effectively this flue gas recirculation that through some of the percentage of the flow gases return back to the combustion chamber, it will easily able to maintain the desirable temperature and it can easily able to maintain the peak flame whatever that temperature if in some of the cases goes beyond 1300 degree centigrade due to some of the sudden high rate combustion or if some of the coal has very higher combustion rate, all such cases we can easily monitor or maintain the temperature in the flue gas or in the combustion chamber if we recirculate the excess oxygen or oxygen inside the reactor. So, it also recycles the excess air.

So, we can use less amount of excess air and which can be very much useful and for beneficial to maintain the combustion kinetics very well to maintain the unburned hydrocarbon coal combustion rate very well as well as maintaining the temperature as well as reducing the NOx formation. Other way is to avoid any amount of nitrogen inside the reactor. Like if we can burn the coal or burn the fuel in the presence of pure oxygen. Like if we eliminate entirely the nitrogen availability inside the reactor. Whatever the nitrogen available from the fuel, it is okay.

But if we can reduce that, there will be no such nitrogen entering along with the oxygen. That means if we can send pure oxygen. That means if it is like 100% oxygen or it can be 99, 95% oxygen or remaining 5% maybe carbon dioxide or other inert gases, but not the nitrogen. So, if we use pure oxygen, that means if we can eliminate nitrogen from the flue gas, that means from the air, whatever you are using for the combustion. We can use pure oxygen; we can use oxygen as well as the carbon dioxide mixture that is the part of air flow gas recirculation to eliminate entire amount of nitrogen.

So, if there is no amount of nitrogen is there in the reactor that will avoid any type of NOx formation and in such case we can even burn the coal even at higher temperature 1500 degree centigrade. As there is no nitrogen, no NOx formation will be there. If we burn coal at very much higher temperature, coal combustion rate will be high. High temperature air in the combustor that will be used in many other applications where we need high temperature like in the case of blast furnace and other cases. So that is the process typically known as the oxy fuel combustion.

This oxy-fuel combustion will be discussed in our next module or next class. However, this oxy-fuel method is very costly as obtaining pure oxygen and removing nitrogen from the system is a bit expensive. There are many other modifications and ongoing research on how we can use this oxy-fuel. A very good example of oxy-fuel combustion is our day-to-day life where we use it in gas welding and gas cutting. We have seen gas cutters or gas welding where we use either oxy-acetylene flame or nowadays oxy-LPG flame, where LPG gas is burned along with oxygen, typically supplied from a gas cylinder. This produces a very high temperature of around 2000 degrees Celsius, which is used to cut the metal melting of metal, welding of metal, and all these processes. A typical example of oxy-fuel combustion is our gas cutter or gas welding, which we see in our day-to-day life and the last and final option is to remove any amount of NOx from the flue gas. For example, if we know that we cannot avoid NOx formation entirely, as some amount of NOx will always be produced.

For instance, if we cannot avoid burning coal at lower temperatures because it may not be effective for the specific application where we are burning the coal. In such cases, we may have to burn the coal at higher temperatures. In such cases, the only thing we can do is remove NOx from the flue gas using methods similar to those used for SOx emissions. For example, if SOx are formed, we can trap or capture it using different types of dry or wet methods, such as solvents or other liquids. Alternatively, we can use chemical catalytic reactions where NOx is converted back into safe nitrogen gas using ammonia or another reactor that converts it back to nitrogen. This is the typical reaction that occurs in a NOx reduction process. This means if we want to reduce NOx formation, we can install a catalytic converter unit that will convert any NOx formed during combustion back into nitrogen. In most such cases, ammonia is primarily used as it is a very effective reducing agent in the presence of a catalyst.

So that's why it is called the catalytic converter or catalytic reaction, where this ammonia, in the presence of a catalyst and oxygen, converts NO back to nitrogen. So, whatever the NOx form is—whether NO, NO2, or any other gas—they can be converted. They can be converted back to nitrogen using the catalytic converter reaction with ammonia or urea. They can be injected and mixed with the gases, and this can be done in the presence of a catalyst. This chemical reaction converts the nitrogen and NOx forms back to nitrogen.

The nitrogen can then be released. This ideal reaction has an optimal temperature range of 357 to 447 degrees Celsius and can operate even at lower temperatures with longer residence time. This catalytic reaction can also be used as a last option to reduce any amount of NOx formation. Whatever the NOx form is, it can be converted back to nitrogen using this reduction process, which relies on the reducing agent ammonia. Ammonia converts them to nitrogen, but the reaction rate is low at lower temperatures. Typically, it occurs at higher temperatures, around 357 to 447 degrees Celsius. Typically, if we consider the catalytic converter unit, there is some cost involved, as we need a regular supply of ammonia and catalyst. Overall, the catalytic converter unit should be the last and final option to control NOx emissions from combustion utilities, as it is a costly method. Compared to that, the best method is to use these three approaches: avoid achieving higher temperatures inside the reactor, control excess air and flue gas recirculation, and recycle excess air. Control the primary and secondary air. We can also design our reactor or combustor so that nitrogen is present in the main combustion unit, where temperatures are lower, while higher temperatures are achieved in other sections. In those sections, we can avoid using excess air and perform the reaction with little or no oxygen available. So we can even design the burner or design the combustor, which is also known as the low NOx burner. So those types of designs are also available in some of the cases where by modifying the supply of primary air and secondary air, we can avoid the NOx formation reaction. So overall, if we see NOx formation in that combustor, we cannot avoid it in any way; we can only control the NOx formation by playing with the chemical reaction kinetics of this NOx formation so that the chances of NOx formation are less, either by controlling the temperature or by controlling the oxygen available or nitrogen available, or if it is formed, then either by this catalytic reaction. Overall, these are all very costly methods. So, in most cases, combustion is done if it is at low temperature or if it is air combustion. Mostly, the temperature is controlled below 1300 degrees centigrade, and in cases where we have to go beyond 1300 or 1400 degrees centigrade, mostly oxy-fuel combustion is preferred to avoid any type of NOx emission in the air. In the same way, nowadays, a new technology or new method is emerging as part of oxy-fuel combustion for the removal of NOx or to avoid any type of NOx formation, which is chemical looping combustion. In this method, from the air, any reactant is present where nitrogen and oxygen can be found, and from that, some metallic compounds are used which typically adsorb oxygen. So, these metallic compounds or metallic catalysts adsorb oxygen to convert it into metal oxides, where oxygen will get adsorbed, and that oxygen is sent to the reactor where in the reactor, oxygen will be released. That will burn the coal or that will burn the fuel. And after it is burned, whatever the spent catalyst is, it is returned back to the reactor where it will again capture the oxygen.

So typically, here the metal oxides or catalysts are used as oxygen-transporting agents. So, in the case of chemical looping combustion, typically, these metallic compounds or particular types of catalysts or adsorbents are used, which efficiently transport oxygen from the normal air reactor. So, from the air, it selectively adsorbs oxygen, which is sent to the main combustor where the combustion happens in the presence of pure oxygen, and after that, the catalyst or metal is returned back, which will again capture the oxygen. So, in this way, this metal supplies the oxygen to this reactor, whereas from the air, we can get any amount of excess oxygen and nitrogen, which will avoid any type of nitrogen in this reactor and produce pure carbon dioxide or pure hydrocarbons. This will also improve the combustion efficiency inside the reactor. So, although it is in the research stage and not many plants are using this technology. In the future, chemical looping combustion will be used in many coal combustion utilities or any other liquid or gaseous fuel combustion utilities. Typically, metal oxides act as oxygen carriers to transport oxygen from air to the fuel, avoiding direct contact between coal and air. Thus, there will be no direct contact between coal and air. If the fuel is in the gaseous reactor—typically gaseous or solid fuel—any type of fuel can be burned. The oxygen carrier will convert it into carbon dioxide and water as per the stoichiometry of coal combustion, allowing pure carbon dioxide to be recovered and used for other utilities as pure carbon dioxide gas. The reduced form of oxygen carriers from the main reactor is transported back to the air reactor, where it will react with oxygen again and absorb some of the oxygen available in the reactor. Thus, it will be recycled again. The exit gas stream from the air reactor contains mostly nitrogen and some amount of unreacted oxygen.

This process is a new technology, particularly focused on improving combustion efficiency and reducing NOx emissions in various utilities. Currently, it is mostly in the development stage. In the next 10, 15, or 20 years, this technology may be used in many combustion-based plants, at least in small-scale utilities. For larger applications, it must be designed for the availability of large quantities of metal oxide carriers and other components. Economic analysis and other assessments must be completed before it can be utilized or implemented in a plant. Overall, if we consider NOx emission control, it is only possible for by controlling the temperature and pressure or excess oxygen supply. So, by only controlling the chemical reaction kinetics, how to avoid NOx formation is the best method to prevent any amount of NOx formation, as the utilization of pure oxygen is a little costly and there are many other technical challenges. So, until now, the best method is to avoid direct contact with air or direct contact with oxygen and nitrogen at high temperatures. That is the best method at present till date, whatever is mostly used in the plants. Chemical looping combustion will be the future or maybe the near future. Similarly, many more methods will be developed by scientists.

Thank you.