

Clean Coal Technology
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Week-09
Lecture-43

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 our previous classes, we have discussed some of the chemical reactions involved in coal gasification. We will continue with our previous discussions on those topics. So, let's start lecture 3 on the fundamentals of coal gasification.

So, in our previous class, we have seen that both air and steam can be used for gasification purposes. Now, if we only use air, if only air is used, in such cases, we can find that the concentration of H₂ in the product gas is very low. If we are using only air, it will have partial combustion, and the product gas will be rich in carbon dioxide and carbon monoxide gases. But if the H₂ concentration is on the higher side, then the applicability or usability of the product gas is significantly improved because hydrogen in the syngas improves the calorific value of the syngas, as well as the utilization potential of that syngas, because if hydrogen gas is present, we can use it in different applications like producing some chemicals, as well as it can be used for coal-to-methanol or syngas-to-methanol and similar applications. So, it is required that the hydrocarbon part in the syngas should be on the higher side, and carbon dioxide in the syngas should be on the lower side. So, if we use only air, in such cases, the hydrogen concentration in the syngas will be very low. So that is the demerit of typically the air-blown gas producer. If we are using only air, then the hydrogen concentration will be low, as well as the temperature of the reactor will be significantly high. If the temperature of the reactor is significantly high, then ash fusion and other problematic consequences may also appear. So that is the reason why this steam or moisture is used, that is, steam or water is used. That is the demerit of the air-blown gas producer. We can remove or reduce those demerits by using steam along with the air. If we are using steam, in such cases, we enhance the hydrogen percentage in the producer gas. Furthermore, if steam is present, then it can also react with carbon or coal to produce carbon monoxide and hydrogen gas. So, in both cases, that is reaction 4 and reaction 5 in our previous discussions, in both reactions, we can find that steam itself can do the gasification reaction along with oxygen. So, if oxygen is present, it will do the

gasification reaction. If steam is present, it can also do the gasification reaction by itself. So, in such cases, both reagents can be used for gasification. In such cases, we can get significantly improved carbon monoxide and hydrogen concentrations in the product gas. So, if we want a higher concentration of hydrogen in the product gas or a higher calorific value of the syngas, we should use steam along with air.

We can see that both reactions are endothermic in nature, meaning external heat is required to carry out these reactions. If we are using only air, in such cases, the reaction is exothermic, as heat is released by the partial combustion of coal. or gasification of coal using air, so that heat can be utilized for this endothermic reaction where steam will be used. So overall, if we can balance the steam as well as oxygen in the feed gas, overall, this reaction can be energy-neutral—it will neither be endothermic nor exothermic overall, because the heat released by the exothermic reaction will be absorbed by the endothermic reaction here. So, there will not be any energy loss or energy wastage at the source or at the gasification site. Further, reaction 4 is called the water-gas reaction and is active above 1000 degrees centigrade, whereas reaction 5 typically happens at lower temperatures. The difference between reaction 4 and reaction 5 is that if we are operating the reactor at higher temperatures, like above 1000 degrees centigrade, then reaction 4 will predominate. In such cases, the carbon monoxide concentration in the product gas will be significantly higher. But if we perform this reaction at much lower temperatures, around 500, 600, or 700 degrees centigrade, in such cases, the production of CO₂ will be significantly higher. So, this also gives us the information that we should perform the gasification reaction around 1000 degrees centigrade, not at lower temperatures like 500 or 600 degrees centigrade. If you are doing these reactions at lower temperatures, then reaction 5 will predominate, and in such cases, CO₂ concentration will be significantly high. Although we are getting a higher amount of hydrogen, the CO₂ concentration will be significantly higher. So that will not give any higher calorific value because any improvement by H₂ will be offset by the negative aspects of CO₂. Negative aspects of CO₂.

However, if we do this reaction at high temperature, in such case we can get both hydrogen as well as carbon monoxide and as well as the energy absorbed by this reaction will be significantly higher. So, it is required that gasification reaction should be conducted only at higher temperature around 1000 degree centigrade if we are using steam. And both the reaction is endothermic and they utilize the heat liberated by carbon in the bed that to be potential heat of combustible gases formed by the CO and H₂. As the CO₂ is undesirable component in the product gas, reaction 5 should be suppressed by maintaining high temperature and choosing

proper amount of steam. So, it is essential that we should conduct this gasification reaction or we should carry the gasification at higher temperature to suppress the production of carbon dioxide and to increase the production of carbon monoxide as well as the hydrogen.

So, these are the typical images. which represents the different type of gasification reactions in presence of oxygen as well as steam as well as the product gas composition. We can see that if only coal is there, so gasification of coal with this oxygen, it makes carbon monoxide. as well as if we do the combustion, it will produce carbon dioxide. So, difference between combustion and gasification is here.

If we are doing this gasification, our product should be carbon monoxide, that is our desirable product. If we want to do the combustion, our desirable product is carbon dioxide. So, if we do the Gasification with carbon dioxide also that can do this $C + CO_2 \rightleftharpoons 2CO$ that we have discussed in our previous class and gasification with steam it results production of carbon monoxide and hydrogen. So, if we are doing this gasification with the help of carbon dioxide we can get carbon monoxide.

And if we are doing this gasification with steam, we can get carbon monoxide as well as hydrogen. So, if we are adding steam to the medium, in such a case, the hydrogen addition is there, and that actually improves the hydrogen concentration in the product gas. Similarly, if we are doing the gasification reaction with hydrogen, that means if hydrogen is present, it can also conduct this reaction, where it will be a methane formation reaction. So, all these reactions we have already discussed in our previous class. Overall, what we can get from this image or this picture is that the gasification reaction can happen in any direction depending on the temperature and other conditions. If a less amount of oxygen is there, it will produce carbon monoxide. If a higher amount of oxygen is there, it will produce carbon dioxide. So, if the carbon dioxide concentration is significantly higher, as well as the reaction conditions allow, then it can do this further gasification using carbon dioxide, that is, carbon dioxide will again be reduced by the carbon to make it carbon monoxide. Similarly, if steam is added, it will produce carbon monoxide and hydrogen, and the produced hydrogen may react again with the coal to produce methane. That is the methanation reaction. And if we are adding steam, these are the two reactions possible where CO will react with H_2O to produce hydrogen and carbon dioxide and CO can also react with H_2 to produce methane plus H_2O . See, all these reactions are possible in the gasifier depending on the exact temperature, pressure, hydrocarbon composition, or other reaction conditions. So overall, if we see the gasification product, it can

have a hydrogen concentration around 25 to 30 percent, a carbon monoxide concentration of 30 to 60 percent, and along with that, there will be some amount of carbon dioxide and steam because steam or water will be produced by this reaction, as well as it can have some amount of unreacted steam there, as well as some amount of methane can be present. Apart from all this material, there is some number of impurities always present in coal.

That is, if we see the ultimate analysis results of this coal, it has CHNSO. So, apart from carbon and hydrogen, oxygen, there is also some amount of sulfur and some amount of nitrogen is always there. So, depending on the atmosphere in the reactor, whether it is an oxidative atmosphere or reductive atmosphere, depending on the temperature, other catalysts, and other mineral matter composition. There is always some possibility that sulfur compounds present in that coal may convert to H₂S gas. As this condition is mostly the reduction condition, as excess oxygen is not there. So, whatever sulfur is there, it will reduce to hydrogen sulfide. So, whatever sulfur is present as organic sulfur or inorganic sulfur, pyritic sulfur, whatever, even they may be converted to sulfur dioxide, but in the reducing atmosphere, in the presence of hydrogen and others, they will be reduced to H₂S. So, in the product gas, there will always be some amount of hydrogen sulfide gas. Similarly, some amount of COS will also be there. Whatever sulfur is there can react with carbon monoxide and carbon dioxide gases to produce COS. In trace amounts of 0 to 0.1 percent, there will be some amount of nitrogen, which is unreacted and can come from the coal itself, as well as if air is used, and that air contains about 80 percent nitrogen. So, if you are using steam as well as air, then the nitrogen concentration may be less, so it can also have some amount of nitrogen gas, possibly some number of inert gases like argon and helium, which can also be present in this medium, will come from the air. Apart from all of this, nitrogen can also be reduced in the form of ammonia or hydrogen cyanide. So, these are the different types of impurities that will always be present and will be generated during the chemical reaction of this gasification. So, what we can get from this discussion is that in the gasifier, product hydrogen concentration will be there, and it will be significantly higher, as well as the carbon monoxide concentration will be there. So, these two gases will make up around 80 to 90 percent of the product gas composition. If we are not considering the nitrogen gas, if we are taking nitrogen gas, then obviously the volume percentage concentration will be less. If we are not considering nitrogen gas in the product, then about 50 to 60 or maybe 80 percent will be hydrogen and carbon monoxide gas, and there will be trace amounts of methane gas also. So, the amount of hydrogen or amount of carbon monoxide that will depend on the steam or oxygen whatever we are utilizing for the reaction

if oxygen is used then carbon monoxide concentration will be high H₂ concentration will be less if we are using steam then hydrogen concentration will be on the higher side also some amount of other impurities gases Organic gases like H₂S, COS, NH₃, HCN and others also can be present in the product gas. Apart from this, some amount of ash or slag or fine coal particles, fine ash particles originate from the coal that will also be part of the flue gas composition. So, they can either from a solid ash or maybe in a molten ash or slag or they can also create some amount of particulate matter. So, if we see that total gas, total combustible gas components like CO, H₂ and methane increase in the flue gas if we are using steam and inert gas like nitrogen and CO₂ will get decreased.

So, if we are using steam, advantage we will get is that these valuable gases will increase as well as the nitrogen and carbon dioxide gas will be decreased. So, in such case calorific value of this product gas will increase as part of the sensible heat. Liberated by combustion of carbon is used for the conversion of hydrogen producing reaction. So some amount of heat is released by this combustion reactions or carbon monoxide formation reaction that will be used for the hydrogen production in case only air is used in such case bed temperature will be extremely high if you are using only pure air or if you are using oxygen in such case it is it will be extremely oxidative condition and bed temperature may increase to 1200 1300 and 1400 degrees centigrade in such case the whatever ash is there that will get melt or that will that will get fused So ash melting or ash fusion probability will be higher and if we are using steam in such case temperature is also reduced as the heat released by this oxidation reaction will be absorbed by the reduction reaction read out by this steam. So, if we see the shift gas reactions also, here this steam also reacts with this carbon monoxide to produce hydrogen also. In addition to the above reaction, methanation reaction is also there which is taken by this steam as well as the carbons and others. So, overall if we see that the addition of steam greatly improves the product gases which will make it enrich the hydrogen gas as well as some amount of methane gas and these are the structure which shows that how this coal gasification reactions occurred at each and every stage in an actual reactor in an actual reactor it can be co-current or counter current operating Like in this reactor, we can see it is the picture showing the biomass or it can be coal and other. So here we can charge the coal from the top side and we can send the reacting medium for air in the bottom side. So, depending on the feeding point, in the second case, we can see we are feeding the coal and biomass here as well as we are sending here. So here both products go in the same direction or they are going in the co-current direction.

In the case A, they are going in the counter-current direction. So, depending on this co-current or counter current the freshly available coal or feedstock material they are exposed to different condition like initially they will go for the drying zone. So, in the drying zone they will always having some release of tar and volatile material is there. There is a pyrolysis zone they are also will have this type of material will also get released and third will go to the reduction zone and fourth will go to the oxidation zone in such case if we see that firstly air is exposed to high temperature. So at this high temperature it will do the combustion or oxidation reaction after this oxygen concentration is less it will go to the reduction zone and accordingly the gas mixer whatever will come out from this reactor it will be reaching all these volatile material and other components because these volatile material and other components are releasing at this coal at this point and they will go along with the flue gas that is the product gases whether in the case second case this all this volatile material whatever is released here they will go to the oxidation zone first because fresh oxygen is available initially and they will go to the reduction zone. So, this presence of oxidation zone and reduction zone it will be different into different case depending on the type of reactor and accordingly the different reactions happen at each and individual zone it will be different because in first case we can see that initially that phase of air is available at on at higher temperature. So, all the oxidation reaction will happen here and further they will go for the reduction process. So, in this reduction process and finally at this end point their concentration of oxygen will be very less. So, whatever the hydrocarbons or volatile materials are released from the coal at the devitalization stages, so they will not be getting adequate temperature for reduction, so all these volatile materials and other components will be part of product gas. and the sequences of this reaction will also be different as the availability of oxygen availability of steam as well as the temperature zone is different whether as in the case of B we can see is that whatever the volatile materials are released during this pyrolysis zone they are also exposed to the high temperature oxidation zone. So here also volatile material will get the chance to get it further oxidized and to increase the yield of carbon monoxide hydrogen and other gases in the product. So as a result, the gas composition in both the cases will be different depending on it is a co-current or counter current reactor as well as the sequences of this chemical reaction what is the exact type of chemical reaction it will happen in the gasifier reaction it will also depends on the reactor design. So, whatever the reaction we have studied earlier reaction 1 to reaction 7. So, all these reactions will happen depending on the reaction condition whether it is the oxygen is excess or hydrogen is excess coal is excess or carbon monoxide is excess depending on that either methanation reaction shift reaction reversible shift reaction and other reaction will happens depending on the reactor

condition and further another important parameter is there. Here we can see that the flue gas is releasing at lower temperature. So here the exit flue gas will have the lower temperature. So, it will from this flue gas it may or may not require any type of heat recovery from the flue gas because flue gas is coming out at almost ambient or nearby 100 degrees centigrade. Whereas the ash is coming out at very high temperature above 1400 or 1200 degree centigrade.

In such case ash will have very high temperature. So, heat recovery from ash is required. Whereas in this second case. the ash is also coming at lower temperature and flue gas is temperature coming at also at higher temperature because this flue gas temperature is significantly higher from this earlier case the flue gas temperature will be different in both the case ash coming out temperature will be different in the both the cases. So overall what reactions will actually happen that will depend on the type of reactor what is used it is the co-current reactor counter current reactor in or any other type of reactor as per the design. So all these chemical reactions can happens depending on the inside condition whether they are exposed to the oxidation zone here the reduction zone or they are in the pyrolysis zone and if we see that in this simply plot where this concentration of different gases is there, if we can see that the highest amount of gas concentration we can get it like at this point where steam supply rate is about 0.4 per minute. 24 kg per kg of carbon gasified. If we can see is that if we are initially increasing the steam concentration, so in such case product gas will have higher amount of carbon monoxide and calorific value is also increased, thermal efficiency is also increased, hydrogen concentration is increased and CO₂ concentration is slightly increased whereas the carbon monoxide concentration is decreased because carbon monoxide concentration decrease is offset by the increase in the hydrogen concentration. But if we increase this concentration beyond 0.4 or beyond 0.5 what happens is that due to the very low temperature because if you are using this steam the endothermic reactions will happen they will take predominant as well as the exothermic reactions will be getting on the lower side. Because as heat released by this carbon initial reaction of producing carbon monoxide that will be taken by this endothermic reaction.

So, if we increase the H₂O concentration or steam concentration excessively, in such cases, the bed temperature will get reduced. As this bed temperature gets reduced, the hydrogen concentration will also get reduced to a lower extent; however, the carbon dioxide concentration will significantly increase, as we have seen in our previous discussions here. That is, if we are going for this very high temperature, carbon monoxide—that reaction 4—the carbon monoxide concentration will be increased. However, if we are operating the reactions

at much lower temperatures, in such cases, reaction 5 or this CO₂-forming reaction is predominant. So, overall, this plot says that if we are some amounts of steam addition is beneficial, as if you are adding some amount of steam, the temperature of the reactor will be under control, and we will get reduced CO concentration. But the hydrogen concentration will significantly improve here, as we have seen there. But if we are increasing this concentration very excessively, like above 0.4 or above 0.5, in such cases, the CO₂ concentration in the product gas will be significantly higher, as well as the thermal efficiency of that unit will fall. So, as a result, we can see that around 0.4 kg per kg of carbon is the optimum or the desirable condition. If we increase or if we use a very high amount of steam, in such cases the gasifier will have much more quantity of carbon dioxide, less amount of carbon monoxide, as well as the calorific value of the units will be less. So these plots or this data infer that if coal has a higher amount of moisture or if the coal is of low-rank coal like lignite or any biomass where the concentration of moisture is significantly higher, in such cases, steam addition is— To be under control, not a very high amount of steam has to be used, whereas for highly matured coal like anthracite, bituminous, or coke, where the amount of moisture is very less in that source coal. So, in such cases, steam must be added to improve the thermal efficiency as well as the carbon monoxide and hydrogen concentration in the product gas, and this is the reaction— The concentration of different types of gases as the fuel bed goes on—if we see that in such cases, initially, the oxygen concentration is on the higher side, but as the reaction goes with the height, this oxygen concentration will be reduced, as all the oxygen will be consumed at a very initial stage, whereas the carbon monoxide concentration will increase as the reaction propagates and at a later stage it may decrease, whereas the hydrogen concentration will increase in this way. Depending on the depth of the bed or sampling position at what height we are doing this. Similarly, the carbon dioxide concentration will significantly decrease in this way, and the amount of water vapor concentration will decrease this way.

So, that corresponds to the different zones in the reactor: the ash zone, oxidation zone, primary reduction zone, and secondary reduction zone, as we have seen in this type of reaction. So, that plot is linked to this data, which shows different points or locations in the reactor. The concentration of carbon monoxide, hydrogen, carbon dioxide, and others varies. So, it varies with the locations, such as the final oxidation zone and the reduction zone. So, depending on the reduction zone and reaction zone. The temperature of the reactor is different, as well as the concentration of feed, oxygen, and steam. So, depending on the length, gas concentration changes for different types of reactors. So, overall, if we observe that in a low-oxygen or

reducing environment in the gasifier, most of the feedstock sulfur converts to hydrogen sulfide and other compounds, with a small amount forming carbon sulfide if the reactor conditions have low oxygen concentration or are mostly reducing. Whatever sulfur is present in the reactor will be reduced to hydrogen sulfide, carbonyl sulfide, or similar compounds. Nitrogen typically does not react, but it may form some ammonia as well as other gases like hydrogen cyanide, depending on the reaction conditions.

If reaction conditions favor it, nitrogen may reduce to ammonia or other gases. Otherwise, nitrogen gas will remain as it is. Chlorine will also be present in the coal. It is expected that it will be converted to hydrogen chloride or HCl gas. In general, the quantities of sulfur, nitrogen, and chlorine in the fuel are reduced sufficiently small that they have negligible effect on the main syngas components like hydrogen and carbon monoxide. As the concentration of all these materials like sulfur, nitrogen, chlorine, or any other gases like bromine or maybe phosphorus and other gases is present, they will also undergo either reduction or oxidation reactions during gasification, depending on the reaction environment or type of reactor, whether it is co-current or counter-current. They will also be part of the syngas produced from the reactor. Similarly, the trace elements associated with both organic and inorganic components in the fuel, such as mercury, arsenic, and other heavy metals, will also be part of various products of coal gasification, either in the flue gas, product gases, fly ash, or bottom ash. During these chemical reactions or gasification, they may form new products or remain unchanged. Thus, it is expected that all these products will also be part of gasification products. They may also create gaseous emissions if these product materials are in the gas phase. Therefore, all these materials must be removed from the syngas. This information indicates that whatever syngas is produced from the gasification reactor, it will contain trace amounts of impurities like hydrogen sulfide, carbonyl sulfide, ammonia, HCN, HCl, and other gases.

Thus, syngas must be purified first. Later, to make it suitable for utilization on domestic as well as industrial scales, because all these materials are highly toxic and cannot be directly released into the environment. They can also cause problems in utilization if HCl or ammonia is present along with the fuel gas, which can corrode the combustor or other equipment where the gasification product is utilized. Therefore, purification or cleaning of coal gasification products is required, depending on the feedstock used. If biomass or similar feedstock is used, or if municipal solid waste is used, it may contain higher amounts of sulfur, chlorine, and other gases. In such cases, cleaning the gasified gases is compulsory. However, if only coal or anthracite-type coal is used, the extent of cleaning required may be less.

Thank you.