Clean Coal Technology

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Week-10

Lecture-49

Hi, I am Professor Barun Kumar Nandi, and I welcome you to the NPTEL online certification course on clean coal technology. We are in module 10, discussing coal gasification. In our previous lectures, I have discussed the working principle of fixed bed, moving bed, fluidized bed, and entrained bed gasifiers. So, in this lecture, I will be discussing product gas cleaning, removal of H2S, ammonia, etc.

So, let's start lecture 4 on syngas cleaning. Now, if we see the composition of syngas released from different types of gasifiers. During gasification, syngas is produced, which mostly consists of hydrogen and carbon monoxide gas. So, it mostly consists of these two gases, which are the most useful, required, valuable, and desired gases. However, during the process, depending on the type of reactor used, there can be many other types of gases as well. There can be different types of organic compound vapors as well as some fine particles. So all these organic vapors, fine particles, and other types of gases are present in the syngas, and they must be removed or cleaned so that the produced syngas mostly contains hydrogen and carbon monoxide gas. Major contaminants present in syngas generally include suspended particulate matter. These materials come from the coal particles or biomass particles, whatever is used during gasification, either unburned coal particles or after burning or after gasification. Whatever ash particles are there. So, all these ash particles, as well as the unused or unreacted coal particles, will create suspended particulate matter.

Their size will depend on the reactor design, whether they are using lump-sized, bigger-sized coal or fine-particle coal size or pulverized coal. There can be different types of condensable hydrocarbons also. which is typically part of volatile materials. So, these volatile materials are released during the pyrolysis stage. Now, depending on the reactor design, either these volatile materials may go through further reduction stages at high temperature, followed by oxidation or combustion stages, or they may directly go to the syngas.

It may contain tar, different types of organic oils, etc. It can have different types of sulfur compounds like H2S and others. It can have different types of nitrogen compounds. So, these sulfur and nitrogen compounds mostly come from the feedstock characteristics. If the feedstock contains some amount of sulfur compounds, it will always have some amount of nitrogen compounds. Like if we see, coal consists of C, H, N, S, O. So, from this N and S part, whatever organic compounds are present in this coal, they will be converted to different types of sulfur-rich compounds as well as the nitrogen compounds. It can have different types of alkali metals also, which are typically part of the mineral matter of the coal. If it is coal, then the concentration of alkali metals like sodium, potassium, magnesium, calcium will be on the lower side. But if the feedstock contains some amount of biomass as well as municipal waste, it may contain higher amounts of these alkali metals, depending on the elemental composition of the mineral matter. and they can start from different types, and there can be different types of chloride-rich components also, like chlorine, because chlorine can also be present as part of coal. At present, we do not analyze chlorine compounds as part of ultimate analysis, but some amount of chlorine is always present, maybe in the form of sodium chloride or potassium chloride or as part of organic compounds present in the coal. So, the exact gas composition will depend on the feedstock characteristics.

If the feedstock contains a higher amount of sulfur or nitrogen, the product gas will have different types of sulfur-rich compounds. If the feedstock contains more chlorine, perhaps other halogens or phosphorus as well. Therefore, the product gas will be contaminated with different types of gases. It entirely depends on the feedstock characteristics as well as the gasification reaction—whether the condensable vapor or released hydrocarbons go to the high-temperature reduction zone, the combustion zone, or directly into the syngas. If they go to the reduction zone and the oxidation zone, depending on the temperature of both zones and the other chemicals present, different types of condensable hydrocarbons or other materials may convert into other chemicals, depending on the chemical reactions occurring under those specific conditions, including pressure and temperature. These are the typical impurities that can arise from different types of feedstocks, such as wood, wheat straw, or coal. These are some general examples. The composition will vary depending on the source—for example, different types of wood will have different compositions. Similarly, wheat straw from different sources will also vary in composition. Coal composition also varies by source, but generally, the values fall within a similar range. For instance, sulfur compounds in coal can range from 0.1% to as high as 5% in high-sulfur coal. If coal contains 5% sulfur, the syngas will reflect that accordingly. Similarly, in the case of wheat straw and wood—typical biomass sources—sulfur compounds are less abundant. Nitrogen concentration in coal is not significantly high, whereas wheat straw and wood may have lower concentrations. Chlorine is also present in coal, usually in lower concentrations, but wheat straw has higher levels. Alkali compounds like potassium oxides, silicon oxides, chlorine compounds, P2O5, and others are present in coal in varying forms. Potassium oxide in coal may be relatively high, whereas in biomass, it can be extremely high, as in the crystal. Therefore, depending on the composition of these undesirable materials present in coal, the syngas impurities may vary in type. Thus, contaminant levels vary greatly and are heavily influenced by feedstock impurities.

If we are using coal, their components can be different, and if we are using wood as the feedstock, their components will be different. So, depending on the feedstock characteristics, the contaminants present in the syngas will be different. Like, if we see the ash percentage in both cases, it will be high. And even if it is 7.8%, 9.85%, in all these cases, these potassium oxides are extremely on the higher side, Silicon oxides are also on the higher side. So, it is desirable or expected that the syngas may contain some mineral matter or fly ash particles, which are rich in silica, potassium oxides, etc. So, that all depends on the feedstock. What feedstock we are taking and what are the characteristics of that feedstock. So, depending on this, the contaminants present in the syngas will vary.

And these are typically the permissible limits of syngas components as per the applications. Like, if we are utilizing this syngas in any IC engine, their permissible limits are like particulate matter or suspended particulate matter, which contains soot, dust, tar, ash. So, they all can be in the range of 50 mg per meter cube. Whereas the tar concentration should be less than 100 mg per meter cube. But if we use the same gas in the gas turbine, their permissible limits are much less. Here we take PM5, which refers to particles less than 5 microns, but here a particle up to 10 microns may be present. In the case of methanol synthesis, which is a chemical process, the permissible limits are far lower. In methanol synthesis, there should not be any particulate matter that could disrupt the reaction. For Fischer-Tropsch synthesis (FT synthesis), meaning the Fischer-Tropsch chemical reaction, no suspended particulate matter should be present. Similarly, if we examine tar concentration, it should be extremely low in methanol synthesis. Sulfur compounds like H2S and carbonyl sulfide should be less than 20 mg per liter. However, in chemical processes, if used in a chemical plant, for methanol synthesis or FT synthesis, there must be very little H2S, ammonia, HCN, or alkyl metal halides. Typically, if we review all these compounds, if used as fuel gas—meaning syngas in engines like IC engines or gas turbines—the permissible limits remain higher. But if used as feedstock for chemical production, such as methanol synthesis or Fischer-Tropsch reactions, the permissible limits are extremely low. Thus, we must clean this syngas according to the requirements of the user industries, such as methanol synthesis, Fischer-Tropsch synthesis, or other processes. We must clean all these materials in the syngas to the lowest possible levels, as these values are far lower than those in actual syngas. The required level of cleaning may also vary significantly depending on the end-user technology and emission standards. CO2 is also considered an impurity if not desired by the user industries. Typically, syngas or gasification gases released from the plant always contain some carbon monoxide. Carbon monoxide is not considered an impurity when used in IC engines or gas turbines, as it poses no issues there.

Although if CO2 is present, then the calorific value of the gas will be lower. But if CO2 is present, it will not create any harmful effects on the IC engine or the gas turbine. It will only be present as an inert gas or unnecessary waste gases from the heat or other sources. But it will not cause any damage to the reactor. But if we consider methanol synthesis and Fischer-Tropsch synthesis, there should not be any amount of CO2 or similar gases present. It should have purely carbon monoxide and hydrogen. These two gases are typically required. So, in such cases, CO2 also has to be removed from the syngas. So, depending on the user requirements, CO2 and other gases may be permissible. That means they may be allowed or they may not be allowed. So, it entirely depends on the user industry—whether they will accept CO2 in the syngas or not. Now, if we see what different types of materials are present in the syngas. If we consider the suspended particulate matter or particulate matter, this particulate matter released from the gasifier typically ranges from 1 mm to 100 mm. This 1 mm to 100 mm range entirely depends on the reactor type and feedstock used. This 1 mm size is possible if we are using larger coal particles, as in the case of the Lurgi gasifier, where we use half-inch or one-fourth-inch coal. In such cases, released coal can have 1 mm or larger particles. Whether this suspended particulate matter is unburned coal, unreacted coal, or unreacted other materials, it is a char particle, depending on that. So, this particulate matter is typically on the higher side, but it may be lower if you are using pulverized coal or fine powdered coal. So, it will vary widely depending on the feedstock characteristics and the process used.

If we are using a very high temperature, so in such case the suspended particular material will not have any amount of unburned carbon material or like this. But if we are using at low temperature, there will be possibility that some of the unburned or unused coal particle, coke particle may be present as part of suspended particular matter along with the regular ash or fly ash present. Inorganic compounds and residual solid compounds from the gasification of coal biomass constitutes bulk of the suspended particulate matter. Mostly this material contains the inorganic compounds like sodium, potassium, silica, alumina and their oxides. And it can also present some of the bed material or catalyst. Like in the bed material we use some of the inert material. To maintain the temperature of the fluidized bed or other. So, this bed material also can be part of the suspended particular matter. It can be also part of that catalyst can also be present in the flue gas if they are in the fine size. So, some of the catalyst may be converted to the fine size and they may come out along with the syn gas also. This organic constituent includes different type of alkali metals like sodium, potassium, magnesium. It can have different type of alkaline earth metal also like calcium as well as the silica and it can also other type of material like iron, magnesium etc. And minor constituent present in trace amount of Primarily derived from solid fuel, fossil fuel, carbon, feedstock, input, arsenic, selenium, antimony, zinc, lead, etc. So, these materials, arsenic, selenium, zinc, antimony, lead, they are also present as part of mineral matter.

But in very trace quantities, maybe 1 ppm or 2 ppm or in a similar range. So, these materials may also be gasified and may come out along with the syngas. So, these compounds may also be present in the syngas, and accordingly, we have to clean or treat the syngas so that these materials are removed. And many syngas applications require more than 99% purity, as we discussed in our previous slide. It depends on the user industries whether they will accept the syngas as it is or need higher purity syngas for their chemical plant. Typically, even if we do not clean the syngas, the pipelines and equipment used for its transportation may face corrosion from organic compounds as well as erosion from solid particulate matter. They will also damage the pipelines. If any alkali material, as well as H2S, ammonia, or similar compounds are present, they may react with the pipe material and other components. They can foul and erode the material, which can cause efficiency and safety concerns for the pipeline. Now, if we see the tar material, tars are typically composed of different types of organic compounds. They vary from primary-originated products to heavier deoxygenated hydrocarbons and polycyclic hydrocarbons.

So, typically, these tar materials originate from the volatile matter of the coal or feedstock. So, if we use coal as the feedstock, there can be heavier molecular compounds present. If we use biomass as the feedstock, the tar compounds or volatile material released from the biomass will have different characteristics. They can have chlorine-rich compounds, bromine-rich compounds, oxygen-rich hydrocarbons, etc. So, it entirely depends on the feedstock used, as well as the process, and during thermochemical conversion, it creates hundreds or thousands of different species at different operating parameters. So, as it is a reducing environment—not a totally oxidizing environment—in the presence of heat, these reactions occur.

So, all these biomass and coal, from their original hydrocarbon, can decompose into different types of hydrocarbons. So, these hydrocarbons may number 100 or 1000, depending on the operating temperature, pressure, and other mineral matter which may act as a catalyst or otherwise. This is quite different from the combustion process. In the case of the combustion process, if we achieve adequate or high temperatures around 1000 degrees centigrade. So, all these hydrocarbons, whether there are 100 or 1000 types, will undergo combustion reactions—oxidation reactions—in the presence of oxygen.

As a result, the flue gas released from combustion utilities may not contain such a wide variety of hydrocarbons. But in the case of gasification, since there is not an adequate amount of oxygen but temperature is present. So, all the hydrocarbons will be formed, but they will not decompose or convert into carbon dioxide and other gases. As a result, whatever lower molecular weight hydrocarbons are formed by the gasification reaction in the reducing environment, they will all remain present. Unless they undergo some oxidation condition where they will be converted to carbon dioxide as well as water, or they are converted to methane or other gases. So, if these hydrocarbons do not pass through a very high temperature of 1400-1500 degrees centigrade, they may remain in their gaseous and unreacted form, produced by the thermal cracking or thermochemical conversion reaction from biomass and coal, but they will persist as hydrocarbons. They will create different types of pollution issues, and user industries will not accept such gases. So, it entirely depends on the operating conditions. The complex nature of tar creates difficulties in collecting, analyzing, and even defining what is actually present in the tar.

So, as this material may contain 100 or 1000 types of different chemicals, it is very difficult to even identify the exact composition of this. So, we need very highly sophisticated instruments to analyze the exact component composition of individual tar. And if we see the sulfur compounds, sulfur contaminants occur mostly as H2S, which is originally present from the sulfur compounds in the coal. Also, some amount of carbonyl sulfide (COS) may be present. So, whatever sulfur is present in coal may be part of organic sulfur as well as inorganic sulfur.

So, they will be converted or reduced to H2S gas as well as COS gas. So, H2S may range in concentration from 0.1 ml per liter to 30 ml per liter depending on the feedstock characteristics. If the feedstock has a higher amount of sulfur, it may go to a higher value, and if the feedstock does not have a very high amount of sulfur, it may be a very small quantity and come to the lower side. So, if we see that H2S concentration may go up to 30 ml per liter, which is a significantly higher value. So, it entirely depends on the feedstock characteristics, and typically biomass has less sulfur compared to coal. Also, some biomass may have a higher amount of sulfur, like if we see the black liquor used in the pulp and paper industries, which has a higher amount of sulfur. It can even go up to 1 gram per kg sulfur compounds also corrode metal surfaces. If syngas is burned, in such cases, whatever H2S is there in the syngas will be converted to sulfur dioxide or SOX gases. So, even small amounts of sulfur can act as a catalyst poison. So, if sulfur compounds are present, they may deactivate the catalyst used in any chemical synthesis process, like the Fischer-Tropsch reaction or methanol formation reaction. In all those reactions, some amount of catalyst is used, and if sulfur is present, it may react with the catalyst, deactivating it, and the reaction kinetics will not proceed as per the requirement.

So, even if a small amount of Sulphur is present, it must be removed. So, sulphur tolerance, as well as the tolerance for other gases, is very low if we are using syngas for chemical synthesis. Sulphur must be reduced to the level of PPB (parts per billion), not in the level of PPM, as required. So, sulphur Removal to the highest extent possible is required to avoid any detrimental effects of catalyst deactivation. If we consider nitrogen compounds, most nitrogen contamination in syngas occurs either as ammonia or HCN gas during the pyrolysis stage of gasification. Combustion gases release nitrogen from the coal, and this nitrogen mostly comes from the protein structure as well as the heterocyclic aromatic compounds present in the feedstock. The amount of ammonia and HCN released is heavily dependent on intrinsic properties, such as nitrogen content, its exact chemical form, nitrogen functionality, physical properties, particle size of the coal, as well as the process conditions, including the temperature at which the reaction occurs. Typically, nitrogen does not react at atmospheric conditions or at lower temperatures, but if the reactor temperature is excessively high (above 1000 degrees Celsius), all this nitrogen may react, and its reactivity is significantly high. Depending on the conditions—whether reducing or oxidizing— it may form NH3, hydrogen cyanide, or others. Typically, NH3 is the dominant compound present compared to HCN or other gases. However, both ammonia and HCN are very toxic to the environment as well as to user industries.

It can form directly from biomass in primary reactions. or from HCN in secondary gas-phase reactions as the temperature increases, as well as with increasing HCN and ammonia concentrations, because at higher temperatures, nitrogen reactivity increases. At normal temperatures or below 500 degrees Celsius, nitrogen reactivity is typically low. So, it will not react heavily, but if we go for high temperatures, the reactivity of nitrogen increases, and in such cases, the concentration of ammonia and HCN will increase significantly. It also depends on the availability of hydrogen in the reactor. If hydrogen availability is in excess, and the residence time in the gasifier is long, there is a probability of reaction between nitrogen and hydrogen to form ammonia or similar hydrocarbons. In such cases, HCN may also be converted to ammonia gases. If we consider alkali compounds, many gasification feedstocks naturally contain different types of alkali and alkaline earth metals as part of mineral matter. Different types of biomasses, wood, and coal contain various alkaline materials like sodium, potassium, magnesium, calcium, and others. These will always be present in coal, biomass, or whatever feedstock is used. The concentration of alkali in biomass is higher, whereas in coal, it is lower. Typically, the woody biomass tends to contain more alkaline earth material, whereas the other type of biomass, it contains lower amount of, it contains other, maybe even higher amount of alkali metal. The alkali metals are primarily potassium and are lesser than sodium, are more problematic in greenhouse application than alkaline earth metal. during due to their higher reactivity if sodium potassium materials are there they are highly reactive compared to the iron silica alumina and there. So, this sodium potassium may also react with the chemicals present and they also may act as a catalyst and others. So typically they if these materials are present then the user industry will not be interested to use such gases and even if we see the chlorine compounds chlorine are also predominant in the syn gas usually in the form of HCl is already an acid gases chlorine in the biomass occurs as a part of alkali metal like sodium chloride potassium chloride etc. which during Pyrolysis or during the reduction reaction, they vaporize at higher temperature and in the environment of combustor, pyrolysis as well as gasification and they react with also water to form HCl.

Raw syn gas may contain up to several millimeters of chloride. For every liter of syngas, typically if the biomass is used there or any similar feedstock is used where the presence of sodium chloride, potassium chloride, calcium chloride, such salts are there and there is the reducing environment is at very high temperature. In such case, all this chlorine compound reacts, they decompose and they react with the water from HCl. So, if we see that there can have different type of contaminants present in the syn gas. Now how to clean or how to remove all this syn gas.

So, these different types of variable methods in the gas cleaning and the precise area of application of the given process is difficult to define although there are several factors that may be considered. So even if we see that there is not any fixed method that can be followed for cleaning of these gases. As this gas composition may vary with wide types of impurities. So, it this process will entirely depends on the types and concentration of the contaminants in the gas that means whatever process is suitable for particular type of biomass that may not be suitable for other biomass as well as the gas because the presence of contaminants their type, their concentration will vary depending on source as well as the process. So, there is not any straight cut method that only these two or three methods will be used in the gasification. So, these methods will be based on the components present in the syngas and their percentages. So, that depends on the degree of contaminants to be removed. Selectivity of the acid gas is important. Required as well as the temperature, pressure, volume, and composition of the gas to be processed. We have to consider all these parameters and the desirability of sulfur recovery due to process economics or environmental issues, as well as the CO2, hydrogen, and sulfide ratio in the gas. All must be considered during the design of how to clean this syngas. So, this entire method depends on the impurities present, as well as the individual and combined pollutant removal mechanisms to be adopted. Typically, if any suspended particulate metal is present, we have to use methods like a cyclone separator or settling tank. Typically, bag filters and ESPs are not recommended here.

They are not used here as the particle size is on the larger side. So, typically, different types of cyclone separators can be used, as well as different types of settling tanks or settling tanks with water spray or other chemical sprays, which can also be used for the removal of suspended particulate matter, as the suspended particulate matter is on the higher side. But if we are using very fine coal particles, we may have to use bag filters as well as ESPs in some extreme cases. Otherwise, in normal cases, cyclone separators, as well as settling tanks with water spray methods, are suitable for the removal of suspended particulate matter. Now, for sulfur and nitrogen compounds, we have to use suitable chemicals or reagents like amines and other solutions or any alkaline solution, which will react with the sulfur and nitrogen compounds, and they will get absorbed in the liquid solution.

So, it has to be any suitable chemical-based method absorption or adsorption method has to be used or may we have to use some of the catalytic reaction where the sulfur compounds, nitrogen compounds will be dissociated to their individual nitrogen gas, oxygen gas, sulfur and etc. So, it can have been any type of chemical-based absorption or adsorption method or maybe any of the catalytic method may be there. And for hydrocarbon as well as tar, it is mostly the suitable catalytic oxidation method has to be used so that this unburned hydrocarbon or this tar material get burned there and they converted to carbon monoxide, carbon dioxide or hydrogen gases through some of the catalytic reaction. So typically, this catalytic reactor is there where all this hydrocarbon tar compound will be converted to their safe compounds like carbon monoxide, carbon dioxide and other gases, carbon monoxide to be less but mostly to be the carbon dioxide hydrogen gas and other gases. So, or it can be removed by suitable absorption or adsorption-based technologies. So overall if we see that in the syn gas there can have different type of impurities present based on the types of feedstocks as well as the chemical reactions going inside the reactor So, the cleaning method has to be followed to meet the user industry requirement and this cleaning method will be depend on the individual feedstock as well as the temperature, pressure and other condition in the reactor. So, if we go through the previous reactors like in the case of fluidized bed reactor where the temperature is 900 or 1000 degree centigrade or in case of Lurgi gasifier temperature is around 500 to 600 degrees centigrade in such case flue gas will have higher number of towers and other. So, in such case if we are using it as in fuel gas we can use it directly without any combustion but if we are using this feedstock for chemical synthesis or other purpose we have to go for severe cleaning So that all this material that products syn gas passes through the is removed from the all types of impurities and they can be used as a pure hydrocarbon source or gaseous feedstock.

But if we go for very high temperature reactor like operating at 1400 to 1800 degree centigrade, in such case All these hydrocarbons, tar, sulfur compound, etc. may be converted or may be decomposed to other form and their percentage in the flue gas or syngas will be on the lower side. So, it entirely depends on the process how we are using it. But syngas cleaning is required and it will depend on the exact process flow sheet where we are using it and accordingly we have to design the process.

Thank you.