Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 03
Methods of Hydrogen Production

In this class we will look at the various Methods for Hydrogen Production. Some of the methods which are used on industrial scale will be discussed in more detail.

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However, some of the methods which are still at laboratory scale we will be just touching upon. Now, in earlier class we have seen that most of the hydrogen which is being produced, more than 80 percent of it was being produced from fossil fuels and there are certain factors why fossil fuels is a preferred choice for hydrogen production.

One thing is that fossil fuels are easily available, we already have infrastructure and as such whatever the local feedstock which is available can be used for hydrogen production; whether it is coal, whether it is oil, whether it is natural gas. Besides that hydrocarbons as compared to water are in their higher energy state. So, the process becomes more economical. There are large number of factors which helps in deciding from which feedstock hydrogen is going to be produced, like what is the capacity of end use application. Depending on that the feedstock and the technology could be used for hydrogen production.

For example, having a steam methane reforming plant is cost intensive as well as it requires a larger footprint area. If the end use application demands a very small capacity requirement of hydrogen in that case steam methane reforming may not be the preferred choice rather we can go for electrolysis. However, if the demand is on an industrial scale, i.e., millions of tons of hydrogen in that case economies of steam methane reforming works very well with steam reforming process.

So, as such which feedstock will be used for producing hydrogen also depends upon what is the requirement of end use application. It also depends on what is the local feedstock available. If coal is abundantly available it would be although very polluting and releases lot of carbon dioxide emissions, but still it may be preferred feedstock for a particular region, because the cost of the feedstock would be lower because of its availability. It also depends upon what is the purity requirement of hydrogen for that particular application.

For example, if it is to be used for fuel cell application, we know that the purity of hydrogen should be very high. However, if it is to be used for other application whether it is combustion for gas turbine even lower level of purity will work. It also depends upon what is the pressure requirement for that particular application because we know that the compression of hydrogen again requires certain energy, it requires compressor. So, as such if the production unit supplies hydrogen at a higher pressure that would be a preferred choice.

So, whatever production, supplies at a higher pressure could be used for that particular application. It also depends upon if there is any other byproduct which also has a commercial value then that process could be selected for hydrogen production.

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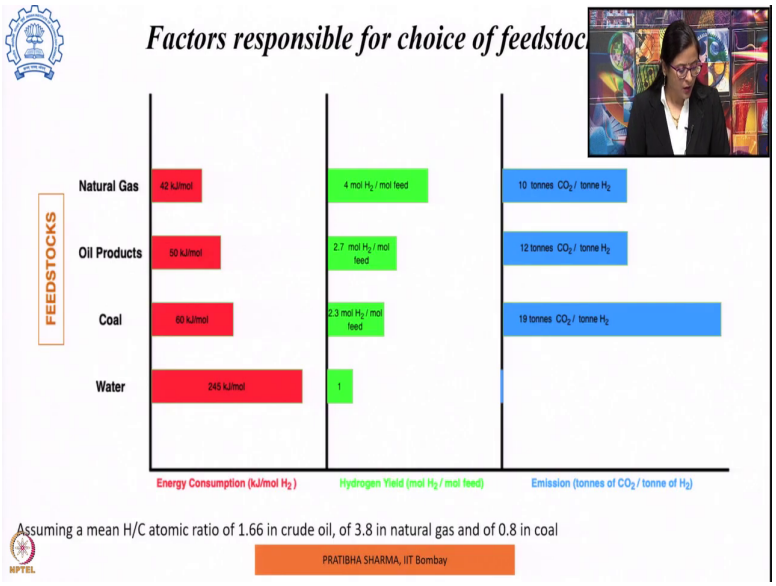

Also it depends on whether some cogeneration of steam and power is also desired.

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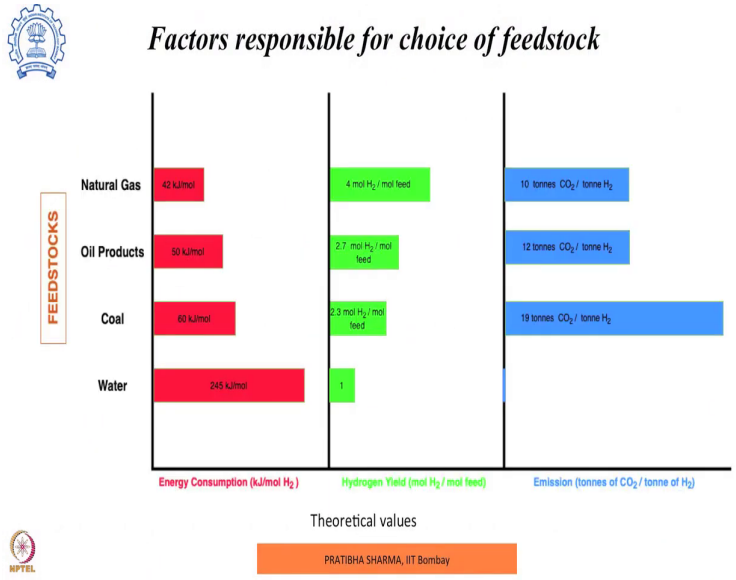

Now, if we look at these numbers, the theoretical amount of energy which is required to produce hydrogen from various fossil fuels as against from water by means of say electrolysis. The amount of energy which is required, theoretical amount of energy required per mole of hydrogen being produced is lowest if it is to be produced from natural gas. And the yield of hydrogen is high when it is being produced from natural gas as against compared to the other feedstock.

If we compare in terms of emission although we know that green hydrogen being produced from water electrolysis that is non polluting, but if it if we compare with respect to fossil fuels then the amount of emissions released when it comes to producing hydrogen from natural gas is the lowest one. That is why the preferred feedstock for hydrogen production as we have seen about 60 percent of it is being produced from natural gas.

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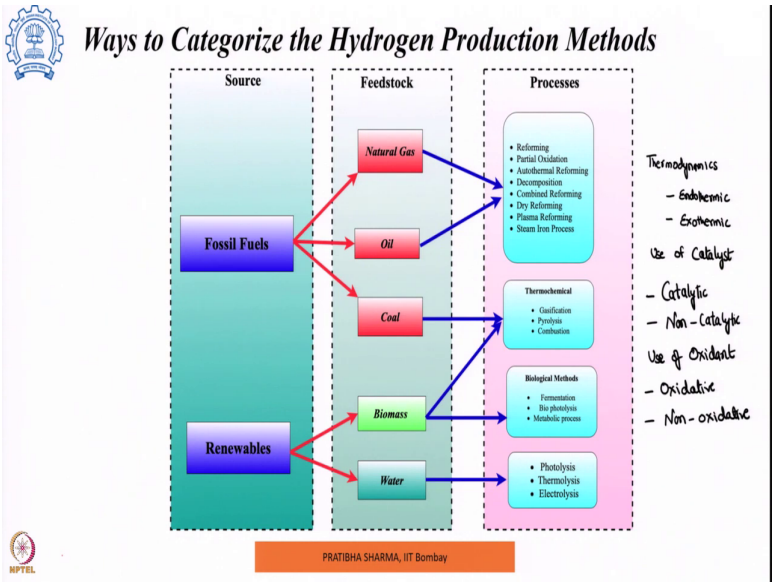

There are large number of ways for hydrogen production and there are different ways in which we can categorize these hydrogen production methods. For example, we can categorize them on the basis of the thermodynamics of the process; like, whether the processes which are used can be either endothermic or the process could be exothermic. We can categorize the processes of hydrogen production on the basis of use of catalyst, the process can be catalytic or it can be non catalytic process.

We can also classify them on the basis of use of oxidant. So, the process can be either an oxidative process or a non-oxidative process depending upon the use of oxidant. Other than this one more method of characterization could be wherein we can classify on the basis of feedstock used.

So, whether the source which is used for hydrogen production is fossil fuel based or it is a renewables based, if it is fossil fuel based then which feedstock is used for hydrogen production like whether it is natural gas oil or coal, if it is produced from renewables then based on the source whether it is from biomass or from water.

Depending upon these feedstock, there are different processes which can be used for hydrogen production there are large number of processes just we have tried to put them together. So, if it is to be produced from natural gas and oil it could be either steam reforming process or partial oxidation auto thermal reforming decomposition of the hydrocarbons, combined reforming, dry reforming plasma reforming or steam iron process.

If it has to be produced from coal or biomass then there are various thermochemical processes from which hydrogen can be produced including gasification pyrolysis and combustion reaction. From biomass, there are biological routes as well by which we can produce like fermentation dark or photo fermentation, bio photolysis or various metabolic processes.

If it has to be produced from water then there are processes like photolysis with the help of light, thermos using thermal energy, breaking down water or electrolysis using electricity. So, these are broadly the different methods for hydrogen production and we will be looking at these in detail. Other than these there are several other processes which are still at research scale or demonstration scale, we will also briefly look into those processes which can be more futuristic.

Now, let us start with the first and foremost process of hydrogen production; that is the reforming and we have seen that 60 percent of it is being produced from steam methane reforming. Now, the term reforming suggest it is forming again.

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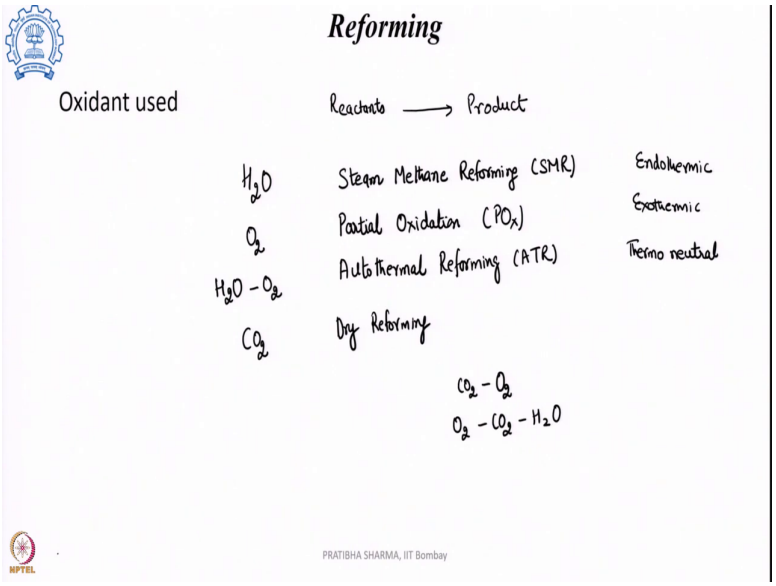

So, we can define it as the reactants which in this case are hydrocarbons and oxidant. So, your reactants are reforming to produce the desired product or the hydrocarbons and oxidant are reacting together under certain operating conditions to form the desired product. So, that is what is reforming.

Now, reforming again can be of various types depending upon which oxidant has been used. So, there are various possibilities of oxidant that can be used like steam can be used as an oxidant. So, if steam is being used as an oxidant the process is known as steam methane reforming. In short it is represented by SMR.

Oxygen can be used as an oxidant, if oxygen is used as an oxidant the process is known as partial oxidation or both steam as well as oxygen in combination can be used as an oxidant for the reforming to take place, then the process is known as Auto Thermal Reforming.

In short it is represented as ATR process. Other than these there are many other ways of combining. So, if oxidant is carbon dioxide the process is called dry reforming or stoichiometric reforming. The thermodynamics of the process can be depending upon which oxidant is being used say for example, if steam is being used then the process will be endothermic.

If oxygen being used as an oxidant in that case it is exothermic. If a combination of steam and oxygen is used as an oxidant like in auto thermal reforming then the process could be thermo neutral. Again there can be other combinations as well like it could be carbon dioxide and oxygen it could be all the three oxygen, carbon dioxide and steam. So, these combinations can also be used for the reforming process.

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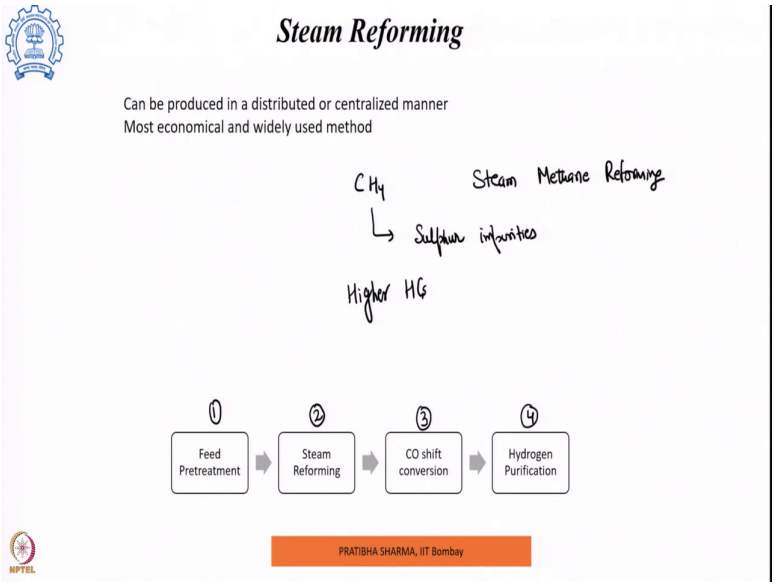

Now, let us start with the steam reforming process for hydrogen production. Now, this steam reforming as the name suggests steam is used as oxidant. This process can be either used in a distributed manner or a centralized manner. Distributed manner; where the requirement of hydrogen is small. At the same time if it is locally produced on site such that it can fuel the requirements of smaller end use applications or refueling station.

So, that we can save in terms of the energy which is required for transportation as well as distribution. At the same time economies of scale works well. So, it can be produced in centralized plants where in the cost can go down, but then there will be a trade off. If we are saving in terms of the cost by centralized production the trade off should be like the cost which we are spending for transportation should be lower as compared to what we are saving in terms of production in a centralized scale.

However, this steam reforming method is the most widely used amateur technology but it is the most economical method for hydrogen production. Now, there are various steps which are involved in steam reformation process. Now, if we look at the steam reforming method depending on which feedstock is being used if it is methane the process is called steam methane reforming or reformation. However, other than methane also any of the hydrocarbons alcohols can be used, liquid fuels can be used or higher hydrocarbons can be used for reforming reaction.

Now, if we look at the process flow then in that case we can see that there is a initial feed pretreatment process wherein we are preparing the feedstock for the reformation reaction. The 1st step is feed pretreatment and the 2nd step is the steam reformation process. There is a 3rd step carbon monoxide shift reaction and finally, the purification process. So, all these steps we are going to look at in detail.

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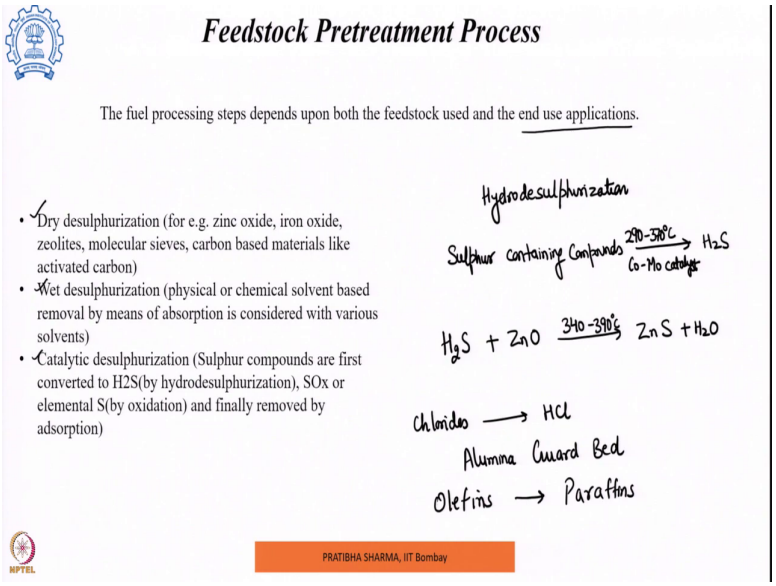

So, let us look at the first step which is the Feedstock Pretreatment Process herein it depends which feedstock is being used for hydrogen production. Say for example, if methane is being used for hydrogen production in that case the major impurities which we can see could be sulfur containing impurities which needs to be removed.

So, that it does not deactivate the catalyst which is being used for the rest of the downstream processes. However, if higher hydrocarbons are being used then they may have other impurities as well as the decomposition of these hydrocarbons can also deactivate the other catalyst.

So, there are other compounds which needs to be removed like chlorides, there are heavy metals or there are olefins that needs to be first taken care of in the feedstock pretreatment process before the feedstock enters into the reforming unit. So, this is a fuel processing step prior to the reforming process which takes care of the unwanted undesired impurities in the feedstock which can be which can deactivate the catalyst in the different downstream processes.

Now, which processing step will be used that depends upon what is the feedstock as I mentioned that in methane the majority of impurities will be either thiols or mercaptans; however, if it is higher hydrocarbons then there could be several other impurities there could be the olefins that needs to be converted into paraffins, there could be chloride containing impurities which could poison the water gas shift reactor. So, those need to be taken care of in the feedstock pretreatment process.

At the same time it depends upon which end use applications we are using that hydrogen being produced. So, what is the desired prior purity level for which hydrogen is being produced. For fuel cell application these have to be very pure in the PPM levels or in PPB levels. So, the impurities needs to be reduced. Now, let us consider for methane the first step which is the feedstock pretreatment process is the hydro desulfurization process. Natural gas based on its source the composition may vary.

However the major constituent of natural gas is methane which is more than 89 mole percent; however, other constituents could be ethane, propane, butane, some amount of carbon dioxide, hydrogen and various other non-organic compounds as well. Now this desulfurization which we are looking is hydro desulfurization process. It can be either a dry desulfurization wherein the sulfur containing impurities are adsorbed onto solid sorbents.

Now, these sorbents could be either zinc oxide, iron oxide, zeolites molecular sieves or carbon containing materials like activated carbon. These can also be removed by means of wet desulfurization like either physically or chemically they can be removed using the solvents and the impurities gets absorbed into the solvent. It can also be done using the catalytic desulfurization method and this is the primary method for sulfur removal in case of methane.

First of all the sulfur compounds they are converted into H2S and thereby it is finally, removed by means of adsorption. So, here in hydro desulfurization is done such that all the sulfur containing compounds are converted into H2S. So, this is done at a temperature of 290 to 370 degree centigrade in the presence of cobalt molybdenum catalyst. This is a sulfur tolerant catalyst which is being used.

Now, this H2S which is being formed here has to be removed. This H2S in a zinc oxide bed is converted into zinc sulfide at a temperature of 340 to 390 degree centigrade removing the sulfur containing compounds. So, this is in case of sulfur containing compounds, these are

converted to H2S and finally, removed on a zinc oxide using a zinc oxide bed. If there are chlorine containing compounds chlorides presents then these are converted into HCl finally, removed on an alumina guard bed.

Usually, olefins these are not there in the natural gas; however, if heavier hydrocarbons are being used in that case olefins if they are present then they are converted into paraffins in the process of feedstock pretreatment. If methane is the primary feedstock in that case this particular step is optional and is not required pre reforming step. However, the higher hydrocarbons are being used.

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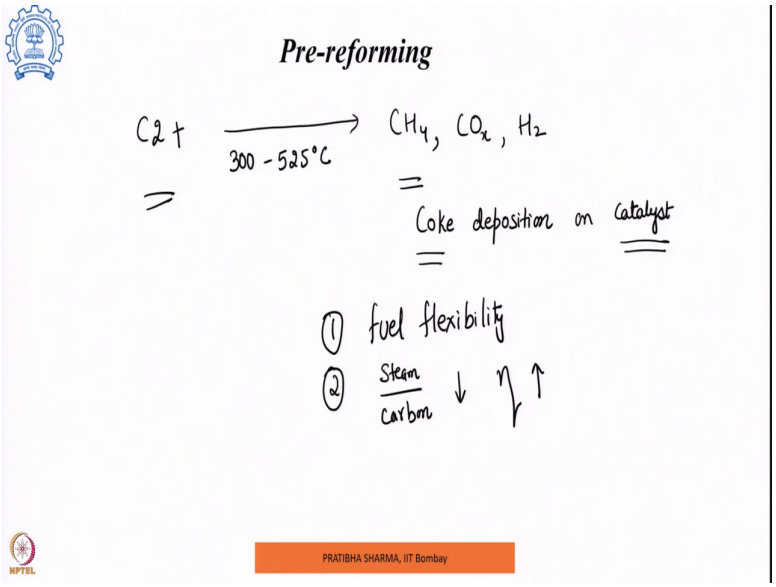

So, any of the C two plus hydrocarbons are being used in the reforming process then they have to undergo an additional step which is known as pre reforming step wherein these hydrocarbons are converted into lower hydrocarbons specifically methane carbon monoxide or carbon dioxide and hydrogen. So, this additional step is only in case of where the higher hydrocarbons are being used. Else in case of methane reforming this is not required.

Now, the temperatures required for this conversion are somewhere between 300 to 525 degree centigrade. Now, this is being done when these higher hydrocarbons needs to be converted into lower hydrocarbons like methane before the reforming step. So, as to avoid coke deposition on to the catalyst which are being used in the various downstream processes.

These higher hydrocarbons are reactive as compared to the methane and during the process they can decompose to form carbon and that carbon on deposition onto the catalyst surface can cause deactivation of the catalyst. Thereby there are several challenges that could be faced, that we will see little later. Now, this addition of this pre reforming step is beneficial, it can provide fuel flexibility.

So, any type of fuel can be used which can then be converted into lower hydrocarbon and thereafter the steam methane steam reforming can be done. Besides for reduction in the coke formation we will see that a higher steam to carbon ratio is required. Now with the additional step of this pre reforming the required steam to carbon ratio could be lower down thereby increasing the efficiency even if we are working with higher hydrocarbons.

Once the feed pretreatment process is done in case of either higher hydrocarbons or in case of methane followed by a pre reforming step only when higher hydrocarbons are present thereafter comes the primary step which is known as steam methane reforming or steam reforming. So, next we will see the steam reformation process.

Thank you.