Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 12
Reforming Using Alternate Energy Sources

In the last few classes, we have seen the detailed process of steam methane reforming and the various steps involved. And we have seen that steam methane reforming is a highly endothermic reaction wherein the heat which is required for the reaction is supplied by means of burning the combustion of the methane, natural gas which is also acting as a fuel in the various burners. And combustion of that natural gas results into the high temperature which is required for the steam methane reforming reaction.

Now, this burning up of natural gas results into emissions and that emissions are released into the environment. Now, if that particular part of the emissions can be taken care of by providing the required heat of the reaction by means of a renewable source, then we can reduce the associated emissions in the process. So, if the energy which is required for the reforming that can be provide by means of any alternate source like nuclear energy, or solar energy, or by means of electrical energy.

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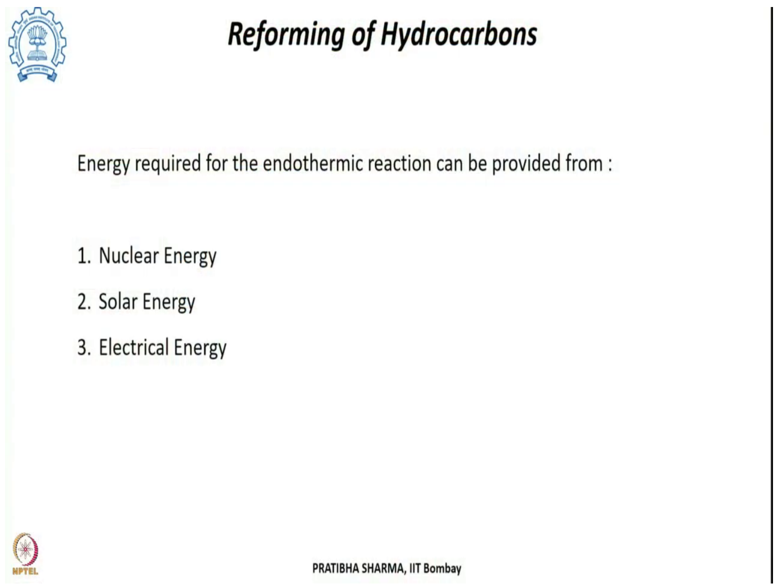

In that case the emissions at the point of supplying the energy could be reduced in the process. Now, let us begin with looking at the nuclear assisted methane reforming, where the endothermic energy for the reforming is coming from nuclear energy. Now, if we compare these with the conventional SMR then there are problems associated with the integration.

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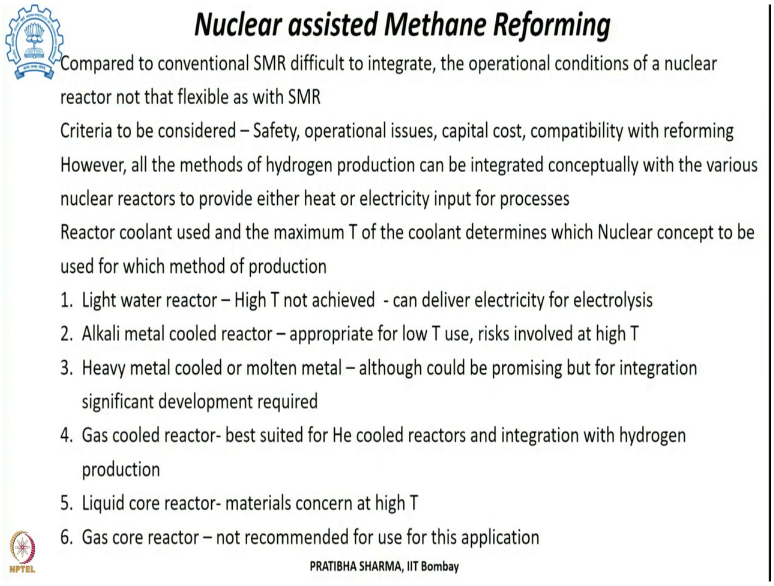

The reason being the operational conditions of a nuclear reactor are not that flexible to integrate with the steam methane reforming. And there are many conditions that we need to consider, there are many criteria's for selecting which particular nuclear reactor is going to provide the required energy. That depends upon the safety considerations, what are the operational issues in integration, capital cost involved, the compatibility with the reformer; so, these are the parameters that needs to be considered.

However, conceptually it is identified that all the hydrogen production methods whether it is reforming, or partial oxidation, or ATR Auto Thermal Reforming, or dry reforming or the other methane decomposition process. They can be integrated with the various nuclear reactors to provide the required heat for the process. It can also be coupled with electrolysers providing the electrical energy input.

Now, what it depends upon is, in the reforming specifically what is the temperature of the reactor coolant? In the maximum temperature of the coolant that determines which nuclear concept we can use for the production of hydrogen. Like if it is a light water reactor, high temperature cannot be achieved; in that case, the required energy could be provided either electricity and that could be used for the energy input in the electrolysis producing hydrogen.

When it is an alkali metal cooled reactor this is in fact appropriate for low temperature usage. As such there are risk associated when we are using high temperature chemical reactions. For heavy metal cooled or molten metal cooled it could be promising, but at present significant development is required for integration.

Gas cooled reactors are best suited where helium is coolant and that helium cooled reactors could be easily integrated with the hydrogen production method. It could be liquid core reactor or the gas core reactor, but then there are certain challenges associated and they are not recommended for use for this particular application.

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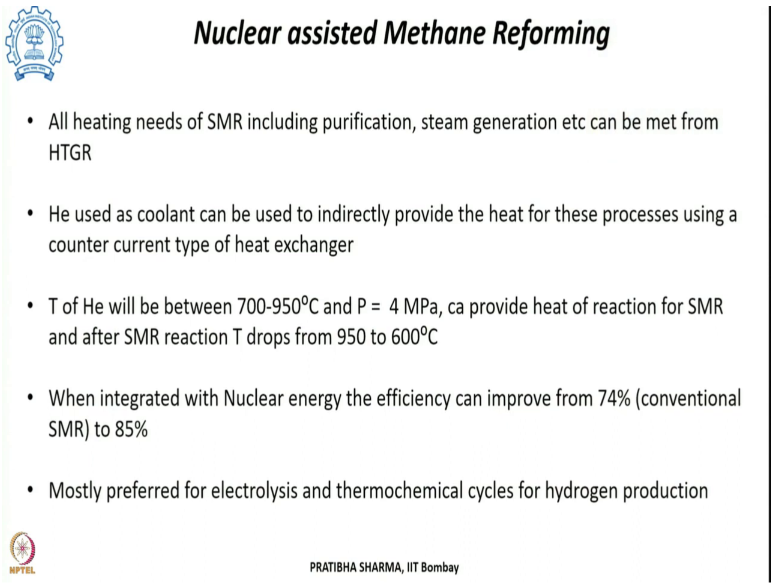

If we use the nuclear energy for the methane reforming all the energy input; in fact, the input energy for the reforming, reaction including the purification, steam generation can all be met using a high temperature gas cooled reactor. And high temperature gas cooled reactor, helium which is used as a coolant can be used for indirectly providing the heat of the reaction for the reforming and the other processes in the hydrogen production.

And this required heat can be provided using a counter current type of heat exchangers, helical coil type of heat exchanger passing through the catalyst bed having feed gas. And the temperature of the helium coolant that lies between 700 to 950 degree centigrade and a pressure of 4 mega pascal and that can provide the heat of the reaction for the steam methane reforming.

And in this process since SMR is an endothermic process. the temperature after the reforming it drops from 950 to 600 degree centigrade. Then such reactors are integrated with SMR process, then the efficiency which in a conventional SMR reformer is 74 percent max can increase to 85 percent. And besides reforming they are also preferred for electrolysis, for integration, or with the thermochemical cycles for hydrogen production.

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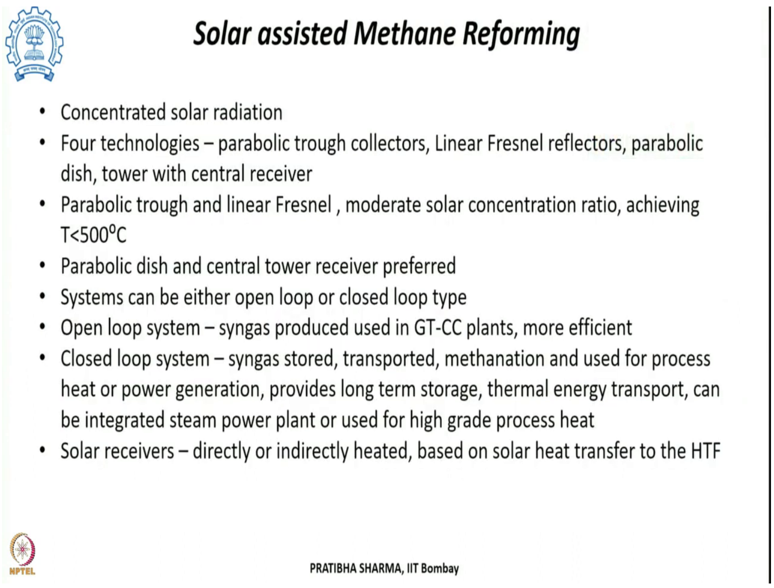

Not only the required energy can be fed by means of nuclear energy input, but the solar assisted methane reforming can also be carried out. Here in since, the reaction is highly endothermic; so, concentrated solar thermal energy would be required for performing the methane reforming. Now, we know that there are four different technologies which could be used either a parabolic trough collector, or a linear Fresnel reflector, or a parabolic dish type concentrator, or a tower with central receiver.

Out of these four the first two parabolic trough and linear Fresnel reflectors, they provide a sort of moderate solar concentration ratio and very high temperatures could not be achieved which are not favourable for the methane reforming. So, as such the last two technologies mentioned the parabolic dish and the tower with central receiver are in fact, preferred for reforming integration with the reformer.

Now, when such systems are to be integrated with a reformer there can be either a open loop system, or it could be a closed loop type of system. What do we mean by an open loop system? In an open loop system when a concentrated solar radiation falls onto a steam methane reformer, syngas is being produced.

The required temperature is supplied by the thermal energy. And that syngas which is being produced can be used in the gas turbine, it can be stored, it can be used for various industrial processes, it can be used in a combined cycle gas turbine plant.

And in this whole process not only upgradation of the hydrocarbon occurs, but at the same time syngas storage can also provide a means for storing the thermal energy. And then it can be utilized in a more effective and efficient manner. In a closed loop type of system through SMR; the syngas which is being produced can be stored, it can be transported over certain distances, and then when it is required it can again be converted into methane.

So, initially the methane is converted into syngas and that syngas can again undergo methanation process to convert it into methane and then it can be used for various processes. Whether it is process of heat generation, or power generation, in a gas turbine or it can be even stored for longer duration. So, thermal energy when it is converted into chemical form can be stored over a longer duration of time.

The thermal energy which is being converted into chemical energy can also be transported in this mode. And then later on whenever it is required can be either used to again convert back into methane, either in a gas turbine, or it can be integrated with a steam power plant or it can be used for high grade process heat.

So, this is a closed loop wherein we started with methane, converted into syngas again, converted into methane and used for various applications. Now, how this solar heat integration with the reformer will take place that can be by means of solar receivers which can be either directly or indirectly heating the reformer to get the required heat. Now, this depends upon whether the solar heat transfer to the working fluid or the heat transfer fluid occurs directly or indirectly in the process.

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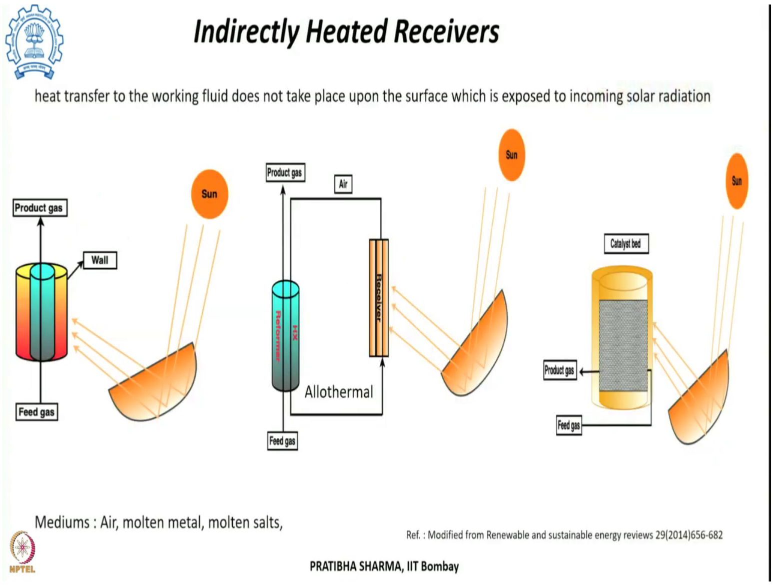

The indirectly heated receivers herein the heat transfer to the working fluid that does not take place exactly on the surface exposed to the incoming solar radiation. The solar radiation falls onto another surface this is a opaque wall, across this the heat is being conducted from the outer wall to the inner wall.

And from there it is being taken away by the working fluid or the heat transfer fluid. Such that the feed gas in this case the methane and steam when they react under these high temperature condition, they produce the product gas which is syngas.

Another method of indirectly heating is wherein again after concentration the heat is being carried to a different place and through a heat exchanger that amount of heat is being transferred into a catalytic bed or a reformer wherein the reaction takes place. So, the point where the heat is being absorbed and the utilization for the reaction chemical reaction is not the same. So, this method can also be called as allothermal.

A third method wherein again there is a catalytic bed, but it is not directly being heated. It is again indirect heating and opaque wall from where the heat transfer takes place to the catalytic bed and the feed gas being fed finally forms the product gas. Now, these mediums which are heating and which are providing the working fluid can be either in the form of air; it could be a molten metal, it could be a molten salt. So, these working fluids can be used for heat exchange.

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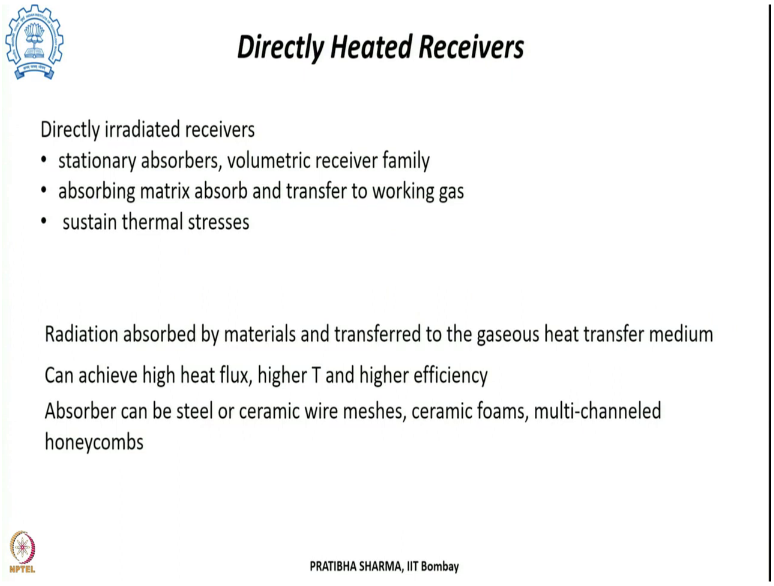

It is also possible to directly heat the reformer. So, directly irradiated receivers are there wherein there are stationary absorbers which absorb the radiations directly and this category of receivers are known as volumetric type of receivers. So, there is an absorber matrix which absorbs the solar radiations heat and then they transfer to the working gas.

So, this is a direct means of heating, but these absorbers needs to sustain the thermal stresses of repeated cycling of heating and cooling and they should be thermally stable and structurally stable under those operating conditions. When the radiation is being absorbed by the materials and these are transferred to the gaseous heat transfer medium then it is a direct type of transfer heat transfer.

And in using this particular method since it is a direct type of heat flow. So, high heat flux can be achieved in the process, even higher temperatures and better efficiencies can be achieved as compared to the indirectly heating. Now, these absorbers various configurations, various materials can be used for absorber and these are being directly getting solar radiations. So, these can be either steel or ceramic wire meshes, these could be ceramic foams, or multi-channel honeycomb type of structures.

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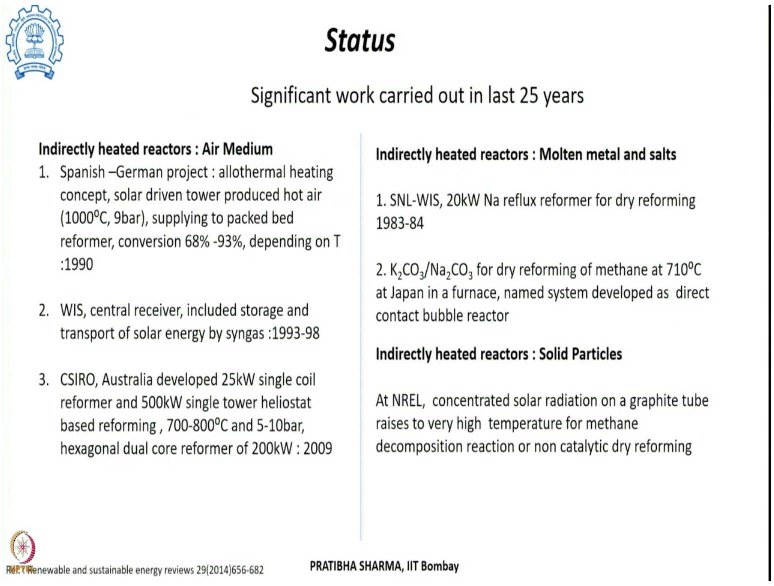

A significant amount of work has been carried out on solar based reforming like the some of the examples quoted here. Like the indirectly heated reactors wherein air is used as a medium, then the projects like Spanish German project wherein they have used this allothermal heating concept and have derived a solar tower that they produced. So, solar driven tower that produced hot air which was at 1000 degree centigrade and 9 bar and that supplied the required heat to the packed bed reformer.

Now, the reformer in various instances could be either a fluidized bed, or it could be a packed bed type of reformer. So, in this case like it is a packed bed reformer wherein they observed that a conversion of 68 percent to 93 percent could be achieved. Now, this is a wide range and that depends upon what is the temperature which is achieved at the reformer end and this was demonstrated as early as 1990.

Weizmann Institute of Science there they had a central receiver and they converted that into syngas in a reformer. They stored it they transported that converting the energy solar energy into syngas, and then they stored it they transported it over a distance. And this was again demonstration in between 1993 1998. So, there were several such projects being undertaken at Weizmann Institute.

Australia it is well placed in terms of renewables; so, CSIRO Australia they developed a 25 kilowatts single coil reformer as core and 500 kilowatts single tower heliostat-based reforming they have undertaken. And could get a temperature of 700 to 800 degree centigrade and 5 to 10 bar pressure.

Thereafter they have undertaken several such projects, another project was a hexagonal dual core reformer that was of 200 kilowatt and that was being executed in 2009. Among the indirectly heated reactors the various molten metals and molten salts have also been considered for heating as a working fluid. The sandia national lab along with Weizmann Institute of Science, they considered a sodium reflux reformer where sodium vapours were considered.

So, it is evaporation and condensation by that they have taken that amount of heat. So, this was a 20-kilowatt sodium reflux reformer. And this was used for performing dry reforming of methane and this was done as early as 1983 to 84. Potassium carbonate and sodium carbonate for dry reforming of methane at 710 degree centigrade was used in a furnace that was an IR furnace at Japan and they named that system as direct contact bubble reactor.

Among the other indirectly heated reactors was wherein the solid particles were used. So, at NREL concentrated solar radiation on a graphite tube was used and that raised the temperature to very high temperatures. So, the operational temperatures was about 17000 k here for methane decomposition and they could also carry out the non-catalytic dry reforming under those conditions.

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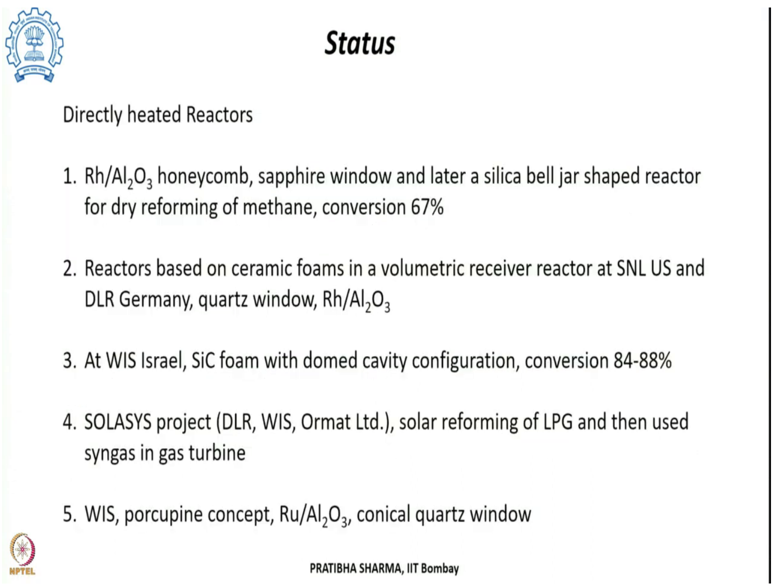

With the directly heated reactors, various catalyst like rhodium on alumina with honeycomb type of these structures and having a sapphire window for allowing the direct radiations falling onto the catalyst. And later on they upgraded it to a silica bell jar type of reactor, they used it for dry reforming of methane and could achieve 17 percent of conversion in this process.

In another reactor demonstration at DLR Germany along with Sandia National Lab US, reactors which were based on ceramic foams were demonstrated in a volumetric receiver type of reactor. They had a quartz window and used catalyst rhodium on alumina. At Weizmann Institute of Science Israel, they used silicon carbide foam with domed type of cavity configuration and could achieve very high conversions of methane 84 to 88 percent.

Similarly, like SOLASYS project which was jointly being carried out by DLR Germany Weizmann Institute and Ormat Limited. They performed solar reforming of LPG and then they use that syngas which was produced in a gas turbine. At same at the Weizmann Institute, they came up with a new concept porcupine type of concept. So, this was a different design that they came up with and they performed the reforming with ruthenium alumina catalyst and a conical quartz type of window was used.

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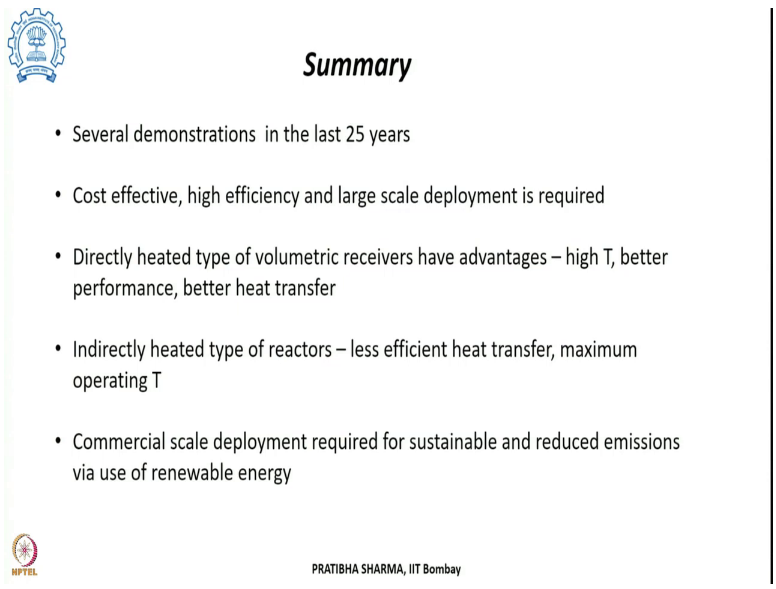

So, there were several demonstrations which were carried out and these demonstrations have shown that the method of solar assisted reforming can be deployed at a larger scale, it is cost effective and we can get high efficiencies. So, the directly heated type of volumetric receivers have the advantage of getting higher temperatures, better performance, and better heat transfer.

While the indirect heated type of reactors are comparatively less efficient in terms of heat transfer and the maximum operating temperature that could be achieved is also lower. So, a commercial scale development is required for the sustainable use of the solar assisted reforming and to reduce the emissions.

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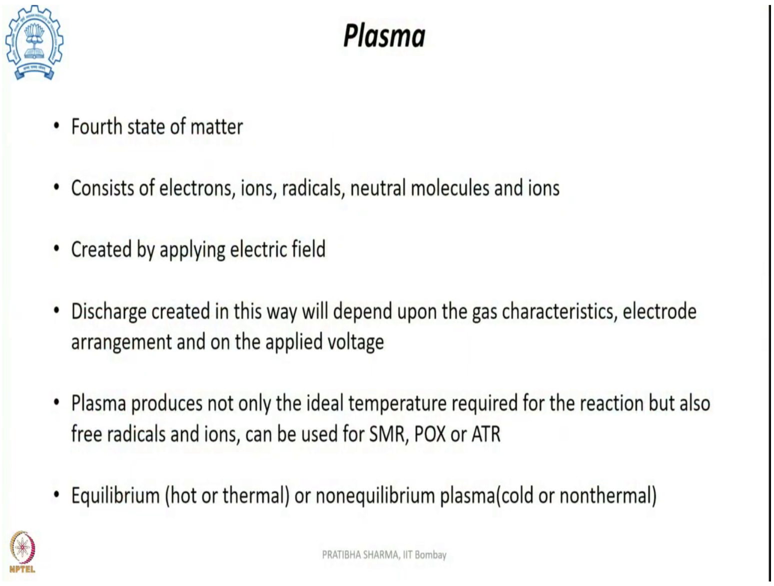

Now, another way of providing the required energy for the steam reforming is using plasma. So, plasma we know that it is the fourth state of matter and it consists of various ionized, species, radicals, neutral atoms, neutral molecules, atoms and electrons and this is created by applying electric field. Once we apply a potential difference a high electric field then the gas which was non-conductive in the beginning that electrons are either taken up or these are freed providing the energy which is higher than the binding energy of these electrons producing ions and electrons.

Now, these electrons they gain energy and they undergo several collisions, elastic and inelastic collisions producing more ions radicals and electrons in the entire process. In this way a discharge is created and that discharge effect will depend on several things like what is the gas characteristic, what is the electrode arrangement, and on the applied voltage. So, the plasma which is produced, produces not only the required temperature for the reforming in our case, but it also provides several free radicals and ions that can also be used for the reforming process.

Now, not only reforming various other hydrogen production methods can used the method of plasma reforming like partial oxidation or auto thermal reforming. This plasma which is generated depending upon whether the temperature of the electrons and heavy particles other than electrons ions, radicals, neutral molecules these are called heavy particles because they are higher in mass compared to the electrons.

Whether all of them they are having the same temperature then it is an equilibrium plasma, or a hot plasma, or a thermal plasma. If they are at a different temperature electrons are at a higher temperature compared to the other species, then it is known as non-equilibrium plasma also called cold or non-thermal plasma.

Now, thermal plasma are actually created at very high pressures and by applying a higher potential by applying a higher power. And that power could be provided by means of either a DC source, or a AC source, or an RF source.

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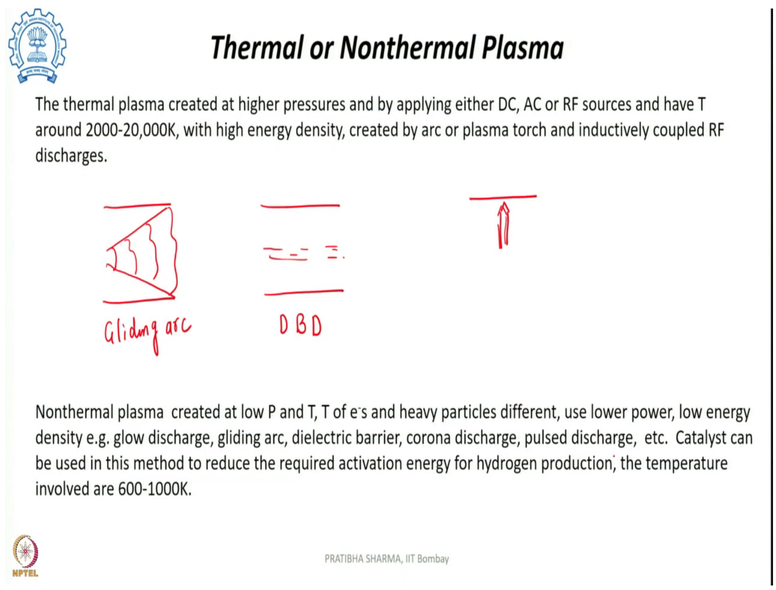

And temperatures that could be achieved in a thermal plasma are high about 2000 to 20000 kelvin. We could achieve very high energy density and these could be created by means of either an arc, or a plasma torch, or an inductive coupled RF discharge. While the non-thermal plasma are comparatively created at a lower pressure. Temperatures which are achieved are lower since it is a non-thermal, non equilibrium plasma; the temperature of electrons and heavy particles is different.

So, the temperature of electrons is higher than that of the heavy particles. The power required for creating non thermal plasma is lower, they have a lower energy density where there are various examples depending upon what is the electrode geometric configuration these can be either glow discharge type gliding arc type. So, if the electrodes they are separated oppositely and then they have a varying gap. So, the arc starts from the shortest distance and then it moves towards the largest distance and it dies down and then again starts.

So, this is a sort of gliding arc type of plasma or it could be dielectric barrier wherein between the two electrodes, there is a layer of dielectric this can be on one of the electrodes. So, dielectric barrier type of discharge or it could be a corona discharge where in one of the electrode is a sharp electrode. And another one either it could be a cylindrical surface and a pointed tip or it could be a pointed a sharp electrode and another electrode could be a planar electrode.

So, it could be a corona discharge; so, the discharge moves like a corona as such the name comes. Or it could be a pulse discharge, wherein a short pulses of high power are injected and all this type of plasma could be used for reducing hydrogen. But with the non-thermal plasma since the temperature which could be achieved are lower the energy densities are lower.

The heavy particles have a low temperature which is close to ambient on the electrons they are at a higher energy and high temperature and they perform the reaction. So, as such the conditions are such that a catalyst is required; so, as to induce the reaction. So, as to excite or to provide the required activation energy to the inert reactants of the reforming for hydrogen production. And the temperature in case of non thermal plasma lies in the range of 600 to 1000 kelvin.

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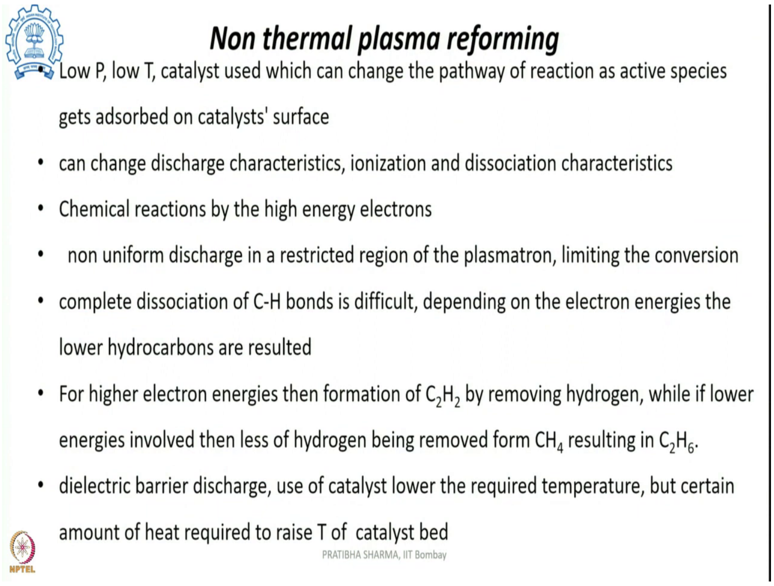

So, if you look at the non-thermal plasma these are the low pressure, low temperature and the catalyst for is always required with non-thermal plasma. So, that the temperature of the reaction could be achieved which can be reduced with the help of catalyst. But the presence of catalyst can also cause a change in the pathway of the reaction. Because the active species which will be created, they all get absorbed onto the catalyst surface.

And with the presence of catalyst, it can change even the discharge characteristics; like, the ionization and dissociation characteristics can get improved. And the actual chemical reactions that will take place will be by means of the energetic electrons.

As we have seen in the gliding arc plasma there is a non-uniform discharge which is created and that is also in a restricted region of the plasmatron. So, that in fact, limits the conversion process in the non thermal based plasma reforming. As such the complete conversion or breaking up of CH bond is difficult and that also depends upon what is the electron energy involved.

Like in spite of complete breaking up of the CH bond, it can even lead to formation of lower hydrocarbons and that depends upon electron energy. For example, if the electron energy is comparatively higher, then hydrogen could be removed such that it can lead to even formation of acetylene.

However, if there are lower energy involved then even that hydrogen could not be removed and then it can even result into formation of ethane. Certain amount of energy also goes in heating up the catalyst bed in the non-thermal plasma.

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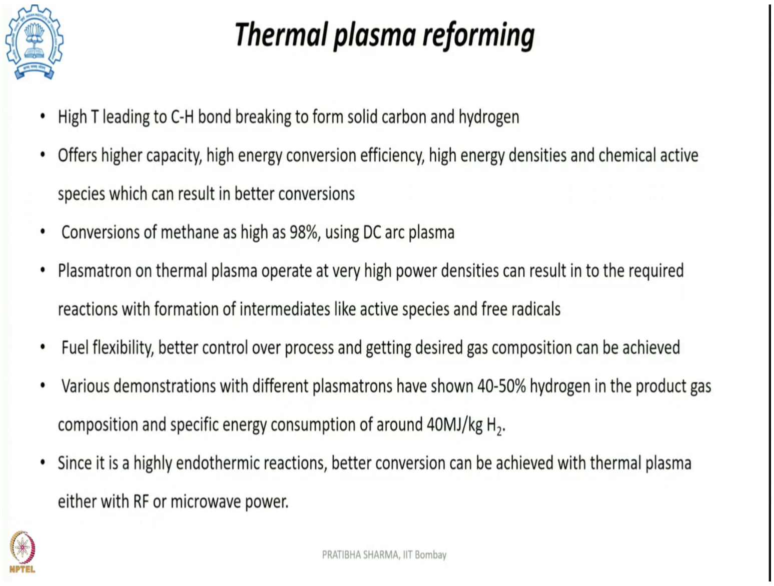

While in case of thermal plasma since the temperature involved in the process are high, the energy densities are high that can provide the sufficient energy for breaking up of CH bond. As such in the thermal plasma reforming, we can get solid carbon and hydrogen as the product.

So, the method of thermal plasma reforming that offers higher capacity, higher energy, conversion efficiencies, we can get high energy densities, and the chemical active species can result into better conversions of methane to produce the desired product which is hydrogen.

So, it has been observed that the convergence of methane could be achieved are as high as 98 percent using DC arc plasma. So, the plasmatron on thermal plasma since they operate at very high-power densities, they can result into the required reactions forming intermediates like active species and free radicals. With the use of thermal plasma, we can achieve fuel flexibility any kind of fuel from gaseous fuel to liquid fuels can be used.

And we can have a better control over the process getting the desired gas composition. There have been various demonstrations with different plasmatron and it has been observed that the 40 to 50 percent of hydrogen in the product gas composition could be achieved with a specific energy consumption of about 40 mega joule per kg. Since, this is reforming is a highly endothermic process. So, better conversion we can get with thermal plasma method compared to the non-thermal plasma and that also with RF or microwave power.

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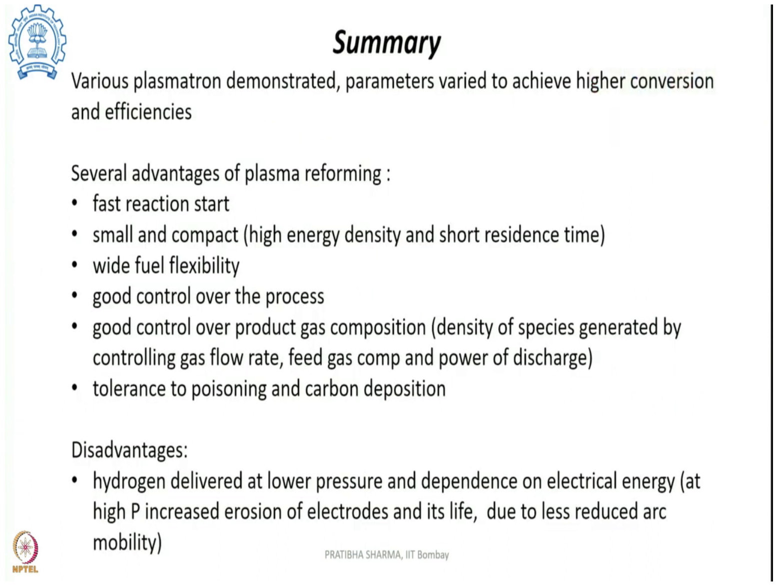

To summarize this part there are various plasmatron which have been demonstrated for plasma reforming of methane and other hydrocarbons. And there are certain parameters that needs to be varied to optimize and achieve higher conversions and get better efficiencies. With the plasma reforming there are several advantages compared to the conventional reforming like, we can achieve faster reaction.

So, the start time is less, the reactors reformers are smaller and compact because we can achieve higher energy density and even short residence time. Wide range of fuels can be used for reforming using plasma reforming, we can have a good control over the process because this is requiring an electrical energy input. At the same time we can get a good control over the output gas composition or the product gas composition.

Because the density of species generated can be controlled it can be controlled by gas flow rate, feed gas composition by the power of discharge. At the same time the poisoning of catalyst is less, the tolerance to poisoning in the plasma reforming is higher and that carbon deposition tolerance is also higher. However, there are certain associated disadvantages like we have to depend on electrical energy and the hydrogen which is produced at a lower pressure.

We can increase the pressure, but then there are challenges associated with the erosion of the electrodes and its life reduces because of the less reduced arc mobility. So, we have seen that how we can do steam reforming with the use of alternate energy sources like nuclear, or solar, or by means of electrical energy input using plasma reforming.

Thank you.