Cryogenic Hydrogen Technology
Prof. Indranil Ghosh
Cryogenic Engineering Centre
Indian Institute of Technology Kharagpur
Week - 02
Lecture 06
Hydrogen Production - 1

Welcome to this lecture ah on cryogenic hydrogen technology. So, today we are going to start a new part of it that is the hydrogen production. So, here in this lecture we will start with ah I mean we will talk about hydrogen production mainly the using non-conventional energy ah sorry conventional energy resources. And ah these are the keywords partial I mean reforming partial oxidation and autothermal reforming. And then ah to start with ah let us first look at the basic ah of hydrogen production, but we have learnt earlier that there are two basic means from which we can get the hydrogen. That is ah hydrogen is when it is mixed in with oxygen it is water and abundantly available in nature.

There is other one when it is combined with the carbon and it is available in the form of hydrocarbon. So, ah if we try to you know I mean ah convert this hydrocarbon for generation of hydrogen we call it as fuel reprocessing or reforming. And then the other one if we are trying to you know get the hydrogen using water I mean that is the electrolysis process and from both this we can have the ah hydrogen. But we will talk about this ah hydrogen electrolysis production of um hydrogen using electrolysis separately.

But before that we will ah look into the reforming process and both these processes are quite matured process I mean both hydrocarbon I mean reforming generation of hydrogen from reforming process as well as you know electrolysis both are quite matured. So, we will try to look at them ah separately. And first of all, to start with ah let us you know start with the hydrocarbon. And we have in general three type of you know hydrocarbons say maybe it is coal or in the solid form, in the liquid form it is heavy oil or crude oil and in the gaseous form we also have the natural gas. And one of the major components of this natural gas is the methane depending on the ah well composition there can be higher hydrocarbons, but mainly it is ah based on the methane.

So, let us look into this ah as we have learned earlier or talked earlier that this coal is basically the one with which our industrialization started and we have ah very I mean matured or you know well established technologies with the associated with the coal. So, but all these three forms of energies ah you know be it coal, crude oil or natural gas these

are the fossil fuel. Now these are the some of the primary sources of energy. So, let us look into its ah in a different ah aspect ah I mean the generation of hydrogen using the non-renewable energy resources. So, this is the these are the primary energy resources as I told you that ah the natural gas or petroleum products, then we have the coal and then there is another third form of energy which we have not talked about so far that is the nuclear energy.

And this will come in picture later on when talking about the thermochemical processes and ah you know generation of hydrogen using thermochemical or high temperature thermochemical reactions. So, these primary sources of energy ah you know ah gives us the secondary source that is you know the electricity basically from this all is using all these resources in a primary resource we are generating the electricity. Again, electricity is something you know is ah not available freely it is again an energy factor derived from the primary energy resources. But unlike hydrogen this electricity I mean storage of electricity is bit challenging it can also be stored it is not like that we cannot store electricity. We need ah you know special devices superconducting magnets to store the electricity, but that is again another big challenge.

But if we are generating hydrogen ah you know from this primary and the secondary energy resources hydrogen can be stored in different means for a quite long time. Now, let us look into this secondary energy and from there we can look into the conversion techniques ah for generating the hydrogen. So, from natural gas and petroleum products we have ah 3 basic processes like partial oxidation steam reforming and auto thermal process. And from the coal there is again another process called gasification we will be talking about it later on. And from all this ah you know processes say this primary energy is used for ah generating the electricity and from electricity we can have you know the electrolysis of water.

And so basically this water will be used in all these 3 processes. So, maybe in the form of steam or in the form of say water or I mean in these 2 forms it will be used to generate hydrogen. So, these are the ah non-renewable energy-based hydrogen production. So, this non-renewable energy is you know quite ah I mean abundantly available for I mean still ah we have a quite a good reserve of coal, but that is a you know ah depleting quite fast in some of the regions or countries. And we have you know to as we have learned earlier that we need to look into the non-renewable energy resources that is ah let us look into that aspect.

So, what are the non-renewable or renewable energy resources we have to look into ah. So, renewable energy resources are the primary energy resources are the biomass and then

we have the solar and then the other ah like wind thermo hydraulic and geothermal. And there are some you know wave based or tidal generation ah tidal energy for generating generating the ah electricity. So, the secondary energy as we have learned that you know all these energy resources can be used to produce the electricity. So, if we are producing electricity again you know the conversion techniques as we have learned earlier that electricity can generate electrolysis using the water.

And this biomass can again be you know steam reformed and along with the gasification. And this ah solar energy can also produce I mean thermal ah you know it can be stored in the form of thermal energy to generate the bio photo electrolysis and a series of other you know photo catalytic thermolysis etcetera. But most of this you know processes are in the R and D level or research ah I mean no commercial generation of hydrogen ah in the commercial scale is not that much popular. So, all these ah energy resources ah I mean this conversion techniques are generate generally giving us the renewable ah you know hydrogen. So, using all these processes are again you know using water in the form of ah ordinary water or steam or hot water and we are getting the renewable hydrogen from ah these processes.

So, we have to look into this ah processes of course, ah you know these are ah the if hydrogen is to be used as a you know future fuel. We must look into the development of or maturing this techniques ah where this energy will be ah primary ah energy will be from the biomass solar or the wind or the hydro electricity. But ah at the same time we have to for immediate application ah of ah you know ah this ah hydrogen technology if we have to use ah in near future ah for hydrogen as the fuel ah future fuel ah in near future we must look into the non-renewable energy-based hydrogen. So, that is ah you know a primary component of non-renewable energy is ah basically the coal. So, what are the advantages of coal ah it may look bit odd that we are talking in favor of coal which you know produce so much of ah CO_2 that we have learnt, but there are certain positive aspects of this ah coal ah let us look into this.

Basically, this is a very low-cost energy resources and it is available in some of the regions and parts of this globe ah and that can sustain even up to it is estimated that you know for another 200 years ah it can be you know producing the energy. But another important part as we have ah talked earlier that ah since ah coal was the element with which you know this our industrialization started. So, there are technologies quite which are quite mature technologies and we have the technologies available with the vendors. So, we have ah you know quite ah bit of learning you know about the excavation of it or transportation of it because most of the time you will find that the coal based or the thermal ah power generation is located very close to the ah I mean coal mines and and or maybe you know

it is a within they are connected with the rails ah transportation. So, these infrastructures are already available with us and it can sustain or it can you know give us ah hydrogen production for for the the mid terms up to quite ah you know reasonable amount.

So, the production of ah this hydrogen is at this moment if we ah you know producing it using the coal it is the lowest. So, low production cost of you know hydrogen and as well as low coal cost is the I mean two attractive features for the generation of hydrogen using coal. And what are the technologies that are to be improved ah what are the limitations ah of this coal energy or this ah hydrogen generation using coal is also known to us. So, it is to be implemented ah if it can be considered. So, this can also be a good you know potential source of hydrogen energy.

So, it can have as I told you ah it can be a potential source of hydrogen generation in near future till we have you know quite compatible ah energy resources using the renewable energy ah based hydrogen production. But ah as we have ah already you know it is also known that there are quite a few you know negative features and one of them is the C02 generation. So, it is having the highest C02 emission ah among all the ah I mean ah non-conventional energy resources. And ah already we have learned about it that the carbon to hydrogen ah I mean is quite high with coal it is nearly about 2 to 2.5. So, when we are converting this ah ah I mean coal into generation of the hydrogen we need to produce the C02 that we will look how we know ah it can be curved or it can be you know captured. So, we need ah technology development associated with the C02 ah I mean capture as well as sequestration of CO2. But at this moment C02 emission with the hydrogen production associated with the coal is highest. Ah for in terms of say energy if we have to generate unit energy using coal ah nearly we need about 80 percent of more C02 generation as compared to the natural gas. If we have to generate same amount of ah energy out of coal and out of natural gas this coal will produce nearly 80 percent more CO2.

Nearly about ah you know for 1 kg of hydrogen if we have to produce we generate nearly 19 kg of hydrogen ah sorry 19 kg of C02 with the coal and ah compared to that you know ah if we have to generate 1 kg of hydrogen using natural gas then we ah you know it it is co-generation of ah C02 is about 10 kg. So, these are the kind of figures we have to keep it in mind at this moment that 1 kg of hydrogen will generate nearly about 10 kg of C02 with n g and natural gas and nearly 19 kg of C02 ah you know with the present technologies available with us it will give us of that sort of ah C02 generation. But it will also have ah the environmental ah I mean impacts like ah associated impacts like soil erosion would be there, land distribution disturbances would be there then you know dust and waste piles and abundant mines all these are ah you know ah creating problems with the environment. And ah these are I mean it is already there with the excavation of coal and we have to

definitely ah curb the use of coal in future. But so long as these other technologies are not getting matured we can probably think of using it with the ah you know C02 sequestration and capturing ok.

So, now ah before we try to understand the advantage of using coal and I mean what can be done you know ah or improvement that can be done with the ah use of coal in future. Ah let us look into the steam reforming as we have learned ah you know in the previous ah slides that there are quite a few processes ah when we are changing the hydrocarbon in from ah hydrocarbon to hydrogen. We have talked about the steam reforming and then we have talked about partial oxidation and orthothermal reactions. So, let us look into those reactions what exactly is happening in that ah processes. So, steam reforming reaction is basically you know meant for the I mean light feedstock like natural gas LPG naphtha etcetera.

So, ah the reaction if we look into the primary constituent of natural gas that is the methane and the reaction ah would be something like methane plus water it is not water it is the in the form of steam and it gives us ah the syngas. Syngas is basically a combination of CO plus hydrogen. So, it is called syngas because ah synthesis gas ah popularly known as syngas it ah is the basic of or basis of many ah I mean ah hydrocarbon or ah products which are produced in the chemical industries. So, this is what is syngas and this is ah basically and endothermic catalytic reaction. So, this catalytic reaction and quite ah you know bit endothermic.

So, you can ah see that the enthalpy of reaction enthalpy is nearly 2006 kilo Joule per mole and it is quite ah I mean ah high and we need to supply good amount of ah heat into this process. So, this endothermic process and catalytic process ah you know we need to have ah adequate ah precautions that we will talk about while talking about the process in details about the steam reforming reaction. So, we need to ah be careful about selection of the catalyst and pretreatment of the catalyst of the I mean feedstock. So, that you know some of this catalyst are very ah sensitive to some of the components in the feedstock ok. So, ah this is about the ah I mean primary constituent of natural gas that is methane, but with the higher hydrocarbons this would be like ah generalised reaction you can say in CnHm that will also give us the CO plus H2 and this is what is as we have learnt is the syngas.

There is a along with that I mean this is you have to as I told you that this is an ex endothermic reaction we have to supply energy in the presence of some catalyst and this you know this water that is in the form of ah steam and ah along with that in the bed there is a ah I mean another reaction side by side ah happening the actually this CO will also

react with ah you know the water. So, to produce CO2 and ah you know H2. So, this will of course, enhance the H2 concentration into the product, but there would be co-generation of CO2 and this reaction is ah basically slightly exothermic reaction. So, it can be understood from the sign of this ah reaction enthalpy this is minus 41 kilo Joule per mole whereas, you know since this reaction enthalpy is positive you know this is endothermic reaction this is exothermic reaction. So, this is an exothermic reaction it will slightly produce heat ah and we call it as water gas shift reaction.

So, this water gas shift reaction will generate you know hydrogen that will ah you know increase the quantity of hydrogen in that addition to this 3 H2 that has been ah you know ah producing the steam and ah I mean with the help of steam ah it is generating CO and H2 along with that we have the water gas shift reaction. So, the overall reaction would be something like you know CO plus CO2 and H2. So, H2 content will be higher. So, this is what is steam deforming reaction. Let us now look into the other one that is ah you called the partial oxidation.

So, in case of partial oxidation we you know we use the feedstock is basically the heavy oil pH or often you know it is the coal. So, with the ah partial oxidation we can use ah you know this is a generalized equation you can say that is ah with the higher hydrocarbons and it is producing CO and H2 again and this is again you can understand that this is the ah syngas or ah I mean basically it is the synthesis gas from there we call it as syngas. So, this syngas CO and ah you know H2 combination ah is produced ah as we have understood that this is coal or heavy oil or pitch and ah this is ah you know we have taken ah pure oxygen in this reaction. So, ah that means, you have to ah separate this oxygen from air ah this ah I think it is ah you know ah worthy to tell you that this O2 comes always most of the time ah you know from air and there we separate this air into it is component ah I mean 2 constituents oxygen and nitrogen ah and there is ah lot of cryogenics in it that is the cryogenic distillation is used to separate this ah air into it is constituent nitrogen and oxygen. So, that means, there you need additional you know energy or cost you know to generate this oxygen ah ah separating air into it is constituents, but there is an advantage we will talk later on about it.

So, if we are using ah oxygen ah purely ah I mean this can come from air itself and ah what I mean is that ah one can also use directly air and that air will be coming over here and it will be mixing with that inert N2 ah it along with that you know the product of CO and H2 ah you will have ah this N2 as you know in your ah it will be mixed with your final product. And if you need hydrogen eventually you have to you know separate the CO and also you need to ah separate nitrogen from this ah process ok. So, that is about ah the ah primary reaction ah that is happening ah with ah the partial oxidation and ah one can

also think of using ah what is called the ah methane here or the natural gas ah though it is ah said that you know the partial oxidation is mainly recommended for heavy oil or you know the coal one can also use the methane, but one has to compromise with ah the CO H2 I mean when someone needs ah or you know less amount of CO plus H2 and also ah one has ah ah the availability of oxygen ah you know then it can be thought of. So, here this reaction partial oxidation in contrast to that steam reforming process this is exothermic in react I mean in nature as well as this does not need any ah catalytic presence of any catalyst ok. So, that means, this is non-catalytic reaction and ah it is you know exothermic in nature and sometime of course, we as we have you know ah written here that steam addition is you know needed particularly with the liquid feedstock and it is atomization.

So, that is about ah this ah reaction and ah with the natural gas as I have ah told you that it needs ah oxygen and ah with this oxygen ah CH4 will generate ah CO and H2 and from the reaction enthalpy you can understand that it is exothermic in nature, but ah what happens if ah oxygen is used in excess. So, if it is you know oxygen in excess ah and if you are burning the coal or ah you know the heavy oil we will find it is generating the CO2 and H2, but there is no H2. So, that means, ah it is basically generating the CO2 and water, but there is no hydrogen in it. So, and this reaction is ah heavily exothermic in nature. So, this is about ah ah you know the partial oxidation when happening in excess of oxygen and this partial oxidation when it is having in presence of less oxygen it will generate of course, the hydrogen you can see that it is generating hydrogen, but there would be lot of soot formation.

So, ah basically ah we have not only that soot formation, but ah you know along with that we have the low outlet temperature at the exit of the ah I mean partial oxidation reaction. So, next is the autothermal ah process as you can understand that ah it is basically a combination of partial oxidation and steam reforming ah because if you look at this two reactions steam reforming is endothermic. Endothermic is basically where you need energy and partial oxidation as we have understood that this is exothermic. So, we are ah trying to combine this exothermic and endothermic reaction that means, initially this partial oxidation will generate ah the heat and that will be used to create this ah you know steam reforming and that is what is called the autothermal reforming process. So, we will talk about these three processes how ah you know they are happening and this is of course, this steam reforming is catalytic process this is non-catalytic process.

So, we will see how this autothermal reformers are made and these are the ah I mean some of the references and ah you can go through this ah literatures or read this book for this lecture. And so, let us try to conclude that we have non-renewable ah you know hydrogen generation we have talked mainly today and out of that you know we have talked about the

steam reforming partial oxidation and autothermal reforming. Whereas, the steam reforming process is catalytic process and endothermic process this ah partial partial oxidation is non-catalytic and it is exothermic. So, we have to take advantage of this and finally, the autothermal reforming is the combination of steam methane reforming and partial oxidation. So, thank you for your attention.