Cryogenic Hydrogen Technology

Prof. Indranil Ghosh
Cryogenic Engineering Centre
Indian Institute of Technology Kharagpur

Week - 02

Lecture 07

Hydrogen Production - 2

Welcome to this lecture on cryogenic hydrogen technology. So today this is in continuation to our earlier discussion on cryogenic hydrogen production I mean hydrogen production in particular. And in the last class we have talked about certain ah I mean hydrogen production technique mostly those are based on the conventional energy resources. And we have talked about the ah steam deforming, then we have talked about the partial oxidation and autothermal process. So, today we will again look into those aspects in detail. So, let us go through this.

So, this is ah as I told this is in continuation to our earlier lecture on hydrogen production. And this is of course, ah based on the conventional techniques. And the keywords are steam reforming, partial oxidation and autothermal reforming. So, if you remember ah in the last class we have talked about the reaction where steam deforming was taking place we have said that if the light feed stocks are there. And ah maybe it may be ah the methane or it may be ah I mean ah light oil and naphtha like that. And if it is ah I mean the methane that is the natural gas one of the primary components of natural gas is methane. So, when methane is passed over heated catalytic bed ah this is basically ah catalytic reaction and it is endothermic in nature. So, we need to supply energy from outside or add heat from outside. So, this is the reaction is followed by the water gas shift reaction where you will find that the CO and H2O are basically not in the form of ah ordinary water it is in the form of steam.

And this will give us you know CO2 and H2O. So, ah the overall reaction you will find that we are starting with the the methane and ah you know the steam at elevated temperature and it is a catalytic reaction we have said. So, ah the catalyst is nickel and if we are you know starting with say the methane and steam and finally, we are getting ah CO and H2. So, that is ah hydrogen and CO that is the carbon monoxide this mixture will be obtained basically this CO H2 mixture is called the syngas. So, the first reaction ah we have already learned that this is ah endothermic.

So, we need to supply energy whereas, this is you know exothermic and it does not need any energy rather energy will be evolved from here. But the point is that it needs a catalyst and the catalyst is a nickel that is a commonly used one of the I mean ah popular catalyst for this reaction. Now, this nickel is basically ah I mean ah it is susceptible to certain ah you know ah gases or you know components which may be detrimental for nickel. So, the feedstock being natural gas LPG or naphtha etcetera and this ah I mean this is a natural component and it may always have some ah what is called sulphur sulphur and chlorides ok. So, this mercaptans and thiophenes are the common ah you know the sulphur contents in this ah I mean in this ah feedstock and ah this sulphur content or chloride contents are you know not good for this nickel.

So, they are not in good harmony. So, we have to first do the feed treatment ah pretreatment of the feed is necessary before we start this you know steam deforming reaction. So, this nickel catalyst is sensible to this ah sulphur and chlorides. So, we have to keep it in mind that before we start this reaction we must get rid of this feedstock I mean this sulphur and chlorides. So, I mean we need ah to ah clean this fluid ah you know from sulphur and chloride.

So, let us ah look into this how it is done ah. So, in the process ah diagram. So, here is the feed and the feed pretreatment is done ah let us look into this pretreatment. So, this nickel catalyst ah you know will be subjected to ah hydrogen. So, hydrogenation of this thiophene or the marcaptans will result in a formation of hydrogen sulfide and basically this mixture of hydrogen and the feed will be passing over the cobalt molybdenum ah catalyst caloritic bed and this will generate the H2S.

Finally, this H2S will be removed ah with the help of zinc oxide ZnO and that will produce finally, the zinc sulfate and H2. So, this is how we ah remove the ah ah the hydrogen sorry the sulphur contents from the feed or this is called the feed pretreatment particularly necessary for the steam deforming. So, this will ah you know generate the treated feed and this treated feed will be again now taken into the reaction. So, this is ah as we have learned that we need certain amount of hydrogen for feed pretreatment. So, we have to later on see where from this hydrogen is coming.

So, we have done the feed treatment and pretreatment and then it is coming to the reformer. So, this reformer as we have understood that you know ah this needs some amount of thermal energy. So, this thermal energy will be given in the form of you know fuel burning and not only that we also need steam. So, the steam has to come ah you know to this process and this is coming from the demineralized water, but this demineralized water you know we will try to ah you know initially ah I mean do some waste heat recovery that we will see how it is generating and that demineralized water will be you know forming as I am forming steam using the waste heat that is generated you know from this ah reformer. And finally, this flue gas basically this reformer will generate certain amount of flue gas you know that flue gas being you know at high temperature we will try to utilize that and produce the steam using that energy waste heat energy.

So, from the reformer what we get is ah the steam gas basically a combination of you know CO and H_2. At the same time ah at the exit or at the outlet of this reformer there would be parallelly water gas shift reaction. So, where you see the water or the steam H 2 and CO will be ah further reacting to generate CO_2 and H_2. So, basically that will enhance the H_2 content in the ah overall reaction. So, water gas shift reaction will take place and finally, that will come you know into you know here what we have is basically CO plus H 2 this combination would be there along with that some amount of feed will also you know be carried over as well as CO 2 will be there into in this ah reaction.

So, all these things you know finally, what we are looking for is basically you know from here this is the hydrogen that if we want you know for our hydrogen production. Please note that you know this CO is again ah important for the chemical plants and, but particularly for this application here we are looking for the hydrogen. So, we need to get it ah you know and this is PSA is something which is called pressure swing adsorption you know where this hydrogen will be separated and we get you know finally, the hydrogen product. And as we have learned earlier that the free pre-treatment you know is ah needing some amount of hydrogen. So, that hydrogen will come from here and ah you know ah this feed treatment will be done initially using this ah final product a part of it will be delivered to I mean diverted to the ah I mean feed treatment.

So, this is ah the ah I mean this is the ah I mean one of the or rather you know ah the process diagram for steam reforming there are other ah modifications or modified versions of this will be available depending on the feed and it is a you know ah the CO H_2 content. So, here ah if we look back we will find that the overall reaction for this ah I mean CH_4 plus ah H_2O that is steam that is generating some amount of CO plus H_2 that is the I mean ah what is called reforming reaction. So, this is ah this is steam and this is carbon. So, the steam to carbon ratio or the stoichiometry is basically 1. So, we have one carbon and for which you know we are giving one steam, but in reality, what we will find that this ratio goes as I has you know 3.3 to 3.5 and you know the higher the ratio we will have more you know ah it will be shifting towards more hydrogen generation. So, if we are looking for more hydrogen. So, we will try to you know put more you know steam in it, but at the cost of definitely ah more you know firing or the heat input ah to the system. So, ah we need to keep this in mind that ah we are putting additional amount of steam into the system and that will ah basically help us you know to generate more hydrogen, but if it is so that you need ah this CO content stored and, in that case, you know this will be ah I mean the steam content will be slightly less in quantity. So, this is what we have to keep it in mind fine.

So, this is ah the the trailing gas part ah here you can see that ah you know we have obtained this ah cleaned version of the gas is coming from here. So, this is ah the PSA system and this PSA system has ah finally, you know generated this hydrogen, but at the same time this is called the PSA tail gas this will have some you know content of H_2 CH_4 which we have not separated or I mean it is basically kind of forming a mixture, but it is having some calorific value. So, we will you know add it with the fuel and that will be used ah as you know ah fuel gas basically that will be combined with the fuel and it will try to heat up the system. So, that is about the steam reforming ah in short. So, now let us look into the reformer ah how it looks like basically as we have understood that this is having some catalytic bed let us look into this ah the radiation zone what is called.

So, here we have the you know the catalytic bed through which CO and H_2O that is steam that is flowing in and here we are you know these are the burners these are the top fired ah radiation zone and this ah reformer or reforming zone ah where you know this catalytic bed is formed you know inside this tube and generally this CH_4 I am sorry this is not CO, CH_4 will be flowing in along with the H_2O. So, that will generate ah CH_4 plus H_2O will come in and it will form the CO and H_2 that will be the product. So, here we have CH_4 plus steam and we are adding heat using the burners. So, ah this is the top fired one then we have the bottom fired and the you know ah again side I mean fired one and there are different geometry those are possible, but ah this methane generally we try to put it under pressure because that will give us this H_2 under I mean under pressurized condition though ah the thermodynamics will tell that this ah methane at low pressure would have been better. But finally, as we understand that this hydrogen ah it has to be stored in an ah you know compression-based condition or it has to be liquefied. So, preferably we try to put it in under pressure and that will you know generate the hydrogen under pressure and ah, but there there is a limit to which you know we can ah put it under pressure because this tubes are the tube has to understand withstand the high pressure at elevated temperature. And typically, if we look at the temperature at this point will be around I am sorry this is not visible here. So, this is ah coming out at around you know from the radiation zone is the convective zone. So, this is 850. So, I am sorry this is an 850 to ah 920 is the typical ah temperature at which they are coming.

So, this is at that temperature this ah gas is going out or the reactants are coming out. Finally, ah this is the kind of several I mean this is only one tube has been shown. So, in reality we will find such a multiple tube are in use and we will be able to get ah the ah I mean CO and H_2 under pressure and of course, at elevated temperature. So, this ah temperature as I told you that they are at high temperature around 850 to 920 degree centigrade. So, obviously, you know they are to be cooled and of course, that CO2 is to be separated ah which is coming from the water gas shift reaction.

So, those high temperature separation of CO2 and you know finally, separating out this H2 ah you know needs certain amount of you know cooling and there this ah cooling of this gases finally, will be ah I mean done by some waste gas recovery where you will find that we are trying to cool them down using the water and that water will eventually you know be used useful ah for you know generating the steam. So, that is how you know we try to ah reduce the temperature of this gases whenever necessary and use it ah for generating the steam. So, now, let us ah look into the partial oxidation reaction. So, we have also ah talked about it and this is the summary of that ah partial oxidation reaction where we have seen that this is the salient features of it is that it is a non-catalytic reaction and this is exothermic in reaction that means, we need not ah supply additional heat from outside, but what we need to supply is ah you know the oxygen. So, here this is the oxygen that we have to supply and ah the feed stock is basically one of them could be you know it is not necessarily restricted to the coal, but ah we can also use natural gas as well as coal and heavy you know oil ok.

So, we have to be careful about the use of less oxygen in the system which may you know result you know ah from you know soot formation and it is handling. So, but importantly what we understand is that ah we need some O2 ah can we not use air the answer is yes. So, we can use air instead of ah O2 because this is the finally, this is the oxygen that is being used here will be you know separated from air only. So, it contains in the you know air contains N2 and O2 and from this O2 only it will be separated maybe you know by ah say membrane separation or cryogenic separation and that oxygen will be ah you know used in the reaction. But ah the problem with the air is that ah if we are using air this nitrogen will be staying with this reaction and here you know whatever ah in addition to this ah what is called the partial oxidation reaction if there is any additional you know ah CO or water gas shift reaction is there taking place because some amount of ah you know water will also be added to this system.

So, that will you know cause ah in in N2 will be added with that system. Finally, if we want to remove any CO2 from the system and ah along with that this nitrogen will be there at high pressure or you know NOx formation will also be you know ah more in ah quantity. So, that means, ah later on if we have to at all you know ah separate this NOx or N2 it is better if we separate this ah you know air initially and put it in the form of O2 in the reaction that will be ah you know advantageous. So, let us now look how it ah actually this process is taking into action.

So, this is partial oxidation. So, here we have another important part is that there is no catalyst catalyst are in use. So, non-catalytic reaction. So, there is no initial ah pre-treatment is necessary. So, here we have heavy oil and we are putting O_2 and that is the partial oxidation is taking place in that reaction zone and from the reaction zone it is the syngas that is coming ah this reaction is exothermic in in nature. So, it is the temperature would be a quite high.

So, nearly it will go as high as 1200 to 1400 degree centigrade and there we will find that it needs a you know quenching of the syngas. So, once we ah try to you know quench it ah it is again you know ah we try to use the demineralized water to generate ah the steam. This steam will be useful ah later on ok for different purposes ok. So, this ah finally, this syngas has to be again in CO_2 and H_2 will be ah removed and this CO_2 concentrated CO_2 will be coming from here and it is ah you know most of the ah time you know it is ah removed from here and this H_2S that is being ah you know separated from here we try to generate the sulphur from here and that sulphur you know often is used for producing the sulphuric acid another important component in the chemical industries. So, finally, ah what we do is that ah we try to condense it and generate ah the ah what is called again it will be subjected to PSA to generate the hydrogen.

So, this take this process takes place around as I told you that this partial oxidation ah you know it will be around 1200 to 1400 when it is coming out from this reaction zone. Now, we have talked about in both the processes in something called pressure swing adsorption PSA. Now, let us have a look into what is this PSA ah or pressure swing adsorption ah. This pressure swing adsorption is basically ah this PSA pressure swing adsorption is ah something where you can understand that pressure swing adsorption. There is another process called absorption, but here what we have written is adsorption.

So, adsorption means you know there are adsorbents which will ah adsorb some of the gases selectively adsorbent like ah most common adsorbent if you are familiar with maybe you know the silica gel. Silica gel is ah some adsorbent which you are familiar with ah when you buy some ah you know ah you know costly ah instrument. You will find there is a small such if and it is ah having some salt like structure basically that is ah very often you know it is silica gel to absorb the moisture. So, there ah after sometime they will adsorb the moisture or retain the moisture, but after sometime this internal pore basically these are porous material these adsorbents. So, these pores will be saturated with ah you know ah the what is called if it is ah for H_2O or moisture ah this will be adsorbing this moisture and finally, it will be saturated.

So, after sometime you need to regenerate it you need to reactivate it and one way of reactivating it is basically to enhance it is temperature. So, that is what is called the temperature swing adsorption where you are you know at some point it is at low temperature or at room temperature they are adsorbing the moisture or the you know the adsorbate they are adsorbing and later on they are also ah you know ah they are I mean they are ah releasing it by change in the temperature. So, that is what is called the thermal swing adsorption, but in contrast to that we have the pressure swing adsorption. So, at some point the adsorbent bed will be pressurized you know this I mean this gas from here this is the mixture this is called the raw hydrogen will be coming from here and this raw hydrogen will pass through that adsorbent bed many a times this is an activated carbon or you know some other adsorbent would be there depending on the impurities which is there in it. So, this bed will be finally, saturated with those impurities and that bed will be again you know reactivated by depressurizing it.

So, that means, it is an ah intermittent process where you will find the successive pressurization and depressurization is you know trying to ah purify this ah raw hydrogen and from there we are getting the pure hydrogen. So, that is about the partial oxidation and now ah as we have ah learned the third one that is the part autothermal reforming ah where we will find that the natural gas and steam may be top it sometime you know we add this two and finally, this O2 or air is getting mixed with it and they are you know coming to this combustion zone. So, this is where you can understand that this is basically ah the process is PO or partial oxidation that is happening because here we do not need any additional heat input, but whereas, here we have the catalytic bed and this mixture is coming over here and here that you know steam reforming is taking place and that steam along with that ah what is called that you know reactants of PO will be forming the finally, CO plus H2 combination and this same gas will be coming out at moderate temperature since we are not adding any heat from outside you will find that the resulting temperature will be something like 900 to 1100. So, ah that is about these three processes for let us try to have a comparison of these three processes that we have learned so far that is steam reforming partial oxidation and autothermal. So, what is the advantages of this steam reforming process? So, it is having you know ah it is extensively in ah use in the industrial scale and we have ah lot of experience of handling it in the industries and of course, there is no O2 requirement in the steam reforming process, but it is you know ah we need a catalytic bed.

So, that is a basically will come under ah disadvantage part and relatively lower temperature among this three you know processes that we have seen and it is it gives you the best H2 CO ah ratio. So, if it is for the hydrogen production definitely it is giving us the added benefit. On the other side this is the highest air emissions you know it will have and on the you know other part I mean if we talk about the partial oxidation we have you know decreased desulphurization that is you know the free treatment initially is not needed and there is no catalyst of course, but ah this partial oxidation will you know need ah the oxygen supply and relatively you know ah on the ah disadvantage part we find that it has a low H2 by CO ratio and of course, as we have learned that it is a temperature is quite high nearly about 1200 to 1400 degree centigrade and here on the advantage part is that we have written you know the low ah methane slip. That means, ah methane content in the reactant or in in in the final product will be much less. In autothermal process of course, on the other part you know the soot formation and soot formation and it is handling is an disadvantage on the partial oxidation part.

In the autothermal process we see that that is low temperature low relatively low process temperature and it is also having the advantage of low methane slip, but on the other side you know it needs O2 which we have also said in case of ah you know partial oxidation because ah that will you know additionally cost the I mean separation of air will be coming in play. So, that is about ah this ah is I mean salient features of these 3 ah technologies for generating hydrogen and ah the references are like this ah we have this industrial gas processing by edited by Haring and A Leon for hydrogen technology and this is a journal paper you can refer to. So, the conclusion we have learned about the ah so called you know conventional techniques ah the process ah features of this steam reforming autothermal and you know partial oxidation. So, in future whenever needed we will talk about this process. So, you have to keep it in mind the typical temperature range and the ah I mean what are the basic needs of this kind of ah processes.

So, that is about this ah hydrogen production at the moment. Thank you for your attention.