Cryogenic Hydrogen Technology
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Week - 02
Lecture 09
Hydrogen Production

Welcome to this lecture on cryogenic hydrogen technology. You may remember that we were talking about the hydrogen production. So, far we had talked about the hydrogen production from ah conventional root in the conventional root using the fossil fuel. And you may remember that we have talked about ah the different processes like steam reforming, partial oxidation and then we have also talked about the autothermal processes. And the different kind of fossil fuels those are in use like ah you know starting from the coal, then natural gas, crude oil, naphtha, etcetera. And the different processes ah basically to produce ah the ah raw hydrogen or say the syngas then from the syngas we wanted to you know separate the raw hydrogen and from raw hydrogen it is to be purified to get the pure hydrogen.

So, that is what is the different those are the I mean different roots of generating hydrogen. So, this syngas generation is the common ah I mean industrial ah chemical engineering process ah which is I mean widely used and we have lot of experience. So, there is another you know way of generating this hydrogen now we will be talking about that and that you know is about the hydrogen production from coke oven gas. So, these are the ah I mean today in this lecture we will be talking about a process ah called Linde-Bronn process for separation of hydrogen from the coke oven gas.

So, ah I mean let us start ah. So, if we have to generate the hydrogen from coke oven gas first of all we need to know what is coke oven gas and before that ah what is coke. Coke is something ah like ah porous ah macro porous element and ah it is macro porous means is pore sizes are more than 500 angstrom. So, it is basically a carbonaceous material mainly ah a particular grade of coal or it is blend ah mostly it is made up from you know it comes from ah the bituminous coal and with a particular ah grade of coal ok. And it is utility is of course, ah in the steel making where this will be ah you know used for smelting of the iron core ah it comes both as fuel as well as the reducing agent.

So, the iron oxide will be reduced to iron and this ah you know carbon will take out that O2 in the form of CO2. So, that is where it is ah used ah I mean it is you know that the importance of steel in the modern ah societies and ah the use of coke is again I mean quite well known. So, this coke is generated from coal a special grade of coal and ah it is having I mean it should have like a low ash content then moisture and sulfur and etcetera. And ah obviously, there is a ah process of preparing this kind of coal ah or coke ah I mean it cannot come from all that all type of coals ok. There is some specific grade of coal as I told you along with that sometime we you know blend it different grades of coal I mean it is not like that everywhere this kind of special coals ah bituminous coal will be available.

And from those type of bituminous coal we try to get this coke and how do we prepare this coke it is basically ah ah you know ah produced in a coke oven and that is ah generally ah air less ah heating chamber and where it will be heated up nearly around 1400 degree centigrade it ranges between 1000 to 2000 degree centigrade. And when it is in absence of ah air basically there is no oxygen ah present in that atmosphere. So, all these volatile components which are there in the carbonaceous material ah or the coal ah it will come out. So, it will come out in the form of gas and ah the whatever is remaining is basically ah that is ah the carbonaceous material or the carbon that part will be remaining and that is the solid remain remnant is the coke. So, this gas or the which has been collected on the top of this coke that is what is called the coke oven gas.

So, you can understand the source of coke oven gas and typically ah this as I told you that ah coke oven gas is the volatile component we will see what are the things that are present in the next slide sometime. But typically, if we look at ah ah 1.3 to 1.7 tons of you know coal will produce a ton of coke and from there we can get nearly about 300 to 360 meter cube of coke oven gas. Now, this coke oven gas ah what does it do? I mean how it what it what it is ah comprising of ah.

So, this is ah I mean I get this composition from the Barron's book. Typically, if you look at we have hydrogen, nitrogen, carbon monoxide, some amount of oxygen, also carbon dioxide, methane, ethane heavier hydrocarbon and others. So, the majority or the main component of it is hydrogen. Then you have the methane and the other parts are like you know ah nitrogen and other components in ah carbon monoxide is also there and some amount of ethane ethylene etcetera will be there. And volume composition is also given ah and, but as I told you that this coke oven gas composition cannot be unique.

So, if you know some blend of coal or a particular grade of coal is used for generating this coke we will find certain composition of the coke oven gas. Whereas, if some other sources of coal is used then you know this composition you will obviously, change ah and say another so ah kind of you know composition I have received from this paper ah. Here it is telling that there is a hydrogen in the I mean the volumetric composition of hydrogen in this coke oven gas is between 55 to 60 percent. And the second major component is obviously, the methane ah there is no ah I mean difference between these 2 ah like this the majority part I mean or the main component is hydrogen and the other is you know methane. And rest of it could be you know ah hydrogen sorry nitrogen and carbon monoxide etcetera other than ah the heavier ah hydrocarbons.

Sometimes this ah hydrogen sulfide will also be there in small quantity and the depending on again the composition of the coke oven gas. Now, let us look into once we have this ah composition known to us then we can look into the ah normal boiling point of all these components present. So, here this is the you know composition that I have shown you first. So, these are the normal boiling point of ah different components in ah I mean Kelvin. So, hydrogen is you know already you are familiar with this it is normal boiling point is 20.3 and nitrogen is 77.4. Carbon monoxide, then oxygen and methane is the among this is the highest ah ok not only the I mean highest, but there are other components. So, methane is the ah one which is having 111.7 and the heavier hydrocarbons will obviously, will have higher boiling point. So, like you know if we have ah this propylene, ethane and ethylene. So, they have ah boiling normal boiling point like 226, 184.5 and 169.5 respectively. So, these are the typical boiling point of the different constituents or components of this coke oven gas.

So, what is ah you know let us look into the other one here also I mean there is the similar kind of ah ethylene is only ah added part here 169.5 and ethane is 184.5. So, these are the kind of normal boiling points of the liquid ah sorry of the gases or the composition of this you know coke oven gas. And ah you can see that there is a large difference between say ah this whole range with this you know hydrogen.

So, the normal boiling point of hydrogen is widely different from all these components other components. So, we can take advantage of this ah it you know to separate out this. So, ah obviously, for separating out into ah you know ah it is different compositions or different components we need to ah you know ah cool it cryogenically. So, one such process that we will be talking today is ah basically the Linde-Bronn process which has been ah invented long back sometime in 1924. And ah that has been in use ah for a different completely different ah reason ah that is basically to produce the ammonia.

So, in ammonia you know that ah it is ah composition is ah NH3. So, it is in NH3 we have you know one part of nitrogen combining with three part of hydrogen. So, it should be the composition should be you know ah finally, the product that should come out should have one part of nitrogen combining with the three part of hydrogen. So, that is the kind of composition this Linde-Bronn process is supposed to have. But finally, if we want ah this ah it is not of course, making the ammonia, but it is making a composition or gaseous composition of one part of ah nitrogen and three parts of hydrogen.

So, from there we can also you know separate it out this hydrogen from nitrogen. So, we will see to that initially we what we will try is to you know separate this nitrogen and hydrogen from this gas. And then we will go to the different ah what is called I mean the process let us see and then we will try to ah separate out this nitrogen and ah hydrogen. So, first of all this coke open gas is pressurized to nearly 1.3 MPa or nearly about 13 bar in a compressor.

So, once we compress it then we first of all you know ah cool it with the help of ah liquid I mean ammonia refrigerant. So, then so, it is like this we will be connecting ah this ah you know this compressed gas will come over here, then it will pass through this two-stream exchanger. And from here it is coming and then we will take it to another this is the three-stream exchanger. We will try to identify all the streams later on. So, this is how it is coming from ah the compressor to the first exchanger.

And this is this exchanger you know in the first exchanger as I told you that it is cooled with the ammonia. So, we are using ammonia to cool this ah incoming high-pressure coke oven gas, then it will come to a three-stream heat exchanger from this three-stream exchanger you know it will be cooling partially ah this coke oven gas. So, that we can take out some a a part of the propylene for example, ok. Say the propylene will be coming out from here and then ah you know it will the other part ah this is basically you know it is coming to a this is called a phase separator. Ah this phase separator you know will separate out the liquid portion and the gaseous portion will come as it is fine.

So, the coke oven gas is ah I mean whatever propylene was there is you know getting condensed and it is coming out this rest of the components are coming out ah you know in the compressed condition. So, then it comes to ah another heat exchanger here this will be say if it is ah getting cooled to nearly 45 degree centigrade this will be cooled to nearly about minus a 100 degree centigrade in this three-stream exchanger. And then it will be coming to this third heat exchanger where it will be cooled to minus 145 degree centigrade when you will find that ah some of the ah ethylene and you know is getting condensed ah and if small portion of methane will also be condensed. So, here this is coming over here ah then again you have the ah phase separator from where as I told you that ethylene will come out, ok. So, once this ethylene is getting separated the rest of the gas I mean compressed gas will come and from here it will come through this four-stream exchanger then it will come to a condenser evaporator.

So, what is that condenser evaporator ah here up to this part you know it will be cooled to nearly about minus 180 degree centigrade. So, at minus 180 degree centigrade you will find that ah it is not it it is ah you know condensing some of the methane, but ah you know methane will not be condensed completely that we have to you know you know ah condense it in ah what is called condenser evaporator. So, from here this high-pressure ah you know methane and I mean ah I mean the other components say hydrogen, nitrogen, CO and the methane all are coming over here. So, this is basically a tube assembly and connected ah on the top we will see later on about the detail structure of this condenser evaporator. So, you can see that this is coming to the tube side and this tube side it will be you know getting cooled the tubes will be cooled with the help of ah some you know refrigerant.

So, ah let us have a look into the refrigerant that we can you know provide one such refrigerant would be the liquid nitrogen. So, if we have ln 2 here this liquid nitrogen will come and that will be you know coming over here to this and it will be coming through ah you know expanded this ah you know this is called J T expansion after this J T expansion this will be provided over here. So, on this side on that you know cell side ah I mean on the tubes outside part you know it will be ah it it will be cooled with liquid nitrogen. So, we are providing liquid nitrogen. So, obviously, some amount of gaseous nitrogen will also I mean this nitrogen will evaporate.

So, this will you know come out like this ah this is the ah vapor nitrogen that is coming out. So, what is happening here these tubes will be cooled with liquid nitrogen to nearly about say minus 190 degree centigrade in this condenser evaporator. So, here at this point what we have is ah as we told that it is comprising of hydrogen, nitrogen and some amount of methane will be getting condensed and it will be stored over here and there is also some amount of nitrogen in it ok. So, this part ah which is getting collected on top it is basically the hydrogen plus some amount of nitrogen and CO and the methane is getting condensed over here. So, from here we will you know take out this mixture this will not be only the methane, methane will be mixed at the primary component will be of course, methane then along with that you know 70 percent 74 percent say methane would be there and there would be some amount of CO about 10 percent of CO would be present in it.

And from there this will be taken back ah to through this heat exchanger it will go back you know from here and this will go back finally, to and it will you know cool the incoming high-pressure gas ok. So, this is what is the the methane when it is coming out this is methane gas, but when it was coming out from this condenser evaporator you know it was in the form of liquid methane. So, that is about ah methane and what we are left with here on the top of this ah vapor you know this dome this is basically the nitrogen hydrogen and CO. So, you see that our vapor our target was to get hydrogen and nitrogen mixture ah with a ratio of ah nitrogen 1 and hydrogen 3. So, that we have obtained with the you know and with an additional component CO.

So, this can be ah you know we we can get rid of this CO ah with the help of CO scrubber. So, this is what is the CO scrubber and it is basically ah this component this mixture will be coming at this bottom ah and it will be as if you know we want to wash it with ah the liquid ah hydrogen sorry liquid nitrogen. So, here you may remember that earlier we have you know provided some refrigeration with the help of this liquid nitrogen. So, this liquid nitrogen a part of that liquid nitrogen is now coming into this CO scrubber where this will you know scrub this CO part ok it will be dissolved in that ah you know along with this hydrogen and nitrogen those will be collected on the top this will be hydrogen plus nitrogen and this is the product that we are looking for. So, finally, so, we will be you know taking this product from here ah you know this N2 plus H2 from this point and that will come over here and then it will come as a product from you know this part and while coming out you know it will be ah cooling the incoming high-pressure coke oven gas which we have you know shown earlier.

Now, at the bottom of it ah as we have understood that this again ah this ah some portion of this CO mainly it would be CO and you are washing it with the nitrogen. So, this CO N2 and a small portion of this ah CH4 will also be present here. So, this is CH4 is about ah you know 7 percent N2 would be about ah you know majority 73 percent and CO would be about 18 percent. So, these are the kind of composition we will have at the bottom of this CO scrubber and ah this is at low temperature definitely before we you know throw it out we want to ah you know take out its ah you know cold part from here and then we will you know put it in this heat exchanger. So, that will provide its refrigeration and this will come out from here and this will come out finally, as N2 and CO mixture in the gaseous form it was in the form of liquid at this point and ah it it is a it is a cold part has been retrieved all the way and ah there is another stream you know we have ah produced some kind of ah ethylene we have said and this ethylene will be ah finally, you know pushed through this ah 4 stream heat exchanger.

So, we have couple of ah heat exchangers along with that we have ah this condenser evaporator along with that we have a CO scrubber and most importantly we have this coolant ah liquid nitrogen. So, that we know we have to ah supply it in this process of ah in the lead bond process that is ah again has to be supplied along with ah other you know ah this coke open gas. So, now what we have obtained is basically this ah a mixture of hydrogen and nitrogen basically this process was meant for as I told you that for ammonia you know ah mixture ah ammonia ah you know gaseous mixture. So, so, ah so that means, we have this H2 plus N2 and now if we want to have this ah H2 out of this mixture ah again ah I mean that is the question how do we do that. So, let us look ah how we can finally, do that ah what could be the possibilities.

So, ah if we have again liquid nitrogen with us we will have this you know mixture with us ah that is nitrogen and 3 parts of hydrogen. So, what we will try to do is that we will ah use another condenser evaporator. So, what we will do is that we will take this mixture and ah we will put it on this side. So, here you know we will have the again liquid nitrogen and this would be the gaseous nitrogen that gaseous nitrogen will you know come out it will evaporate and from here you are supposed to get the hydrogen which will be collected on this doom part and here this is you know this is again LN2. This nitrogen is getting condensed over here and with the help of this liquid nitrogen that you have supplied here on this tube side and this is what is the gaseous nitrogen that is coming out of this system.

So, that is about ah this condenser evaporator part to produce the pure nitrogen ah you know from the coke oven gas ah. So, this complete process which I have you know drawn with the lines you can ah you know have a look into it. The thing is that here we had you know the pre-coolant ammonia and it was this coke oven gas which was coming here it was cooled initially with the ammonia then there is a 3-stream exchanger, two 3-stream exchangers are there here some amount of propylene was ah you know extracted then you know we have the ethylene that has come out from here. Then we have ah this 4-stream exchanger ah it will come over here and this will come into this evaporator and condenser. Similarly, this is the mixture of ah N2, H2 and H2, N2 plus CO and this CO we get rid of you know using the CO scrubber.

Here we have LN2 supply this LN 2 is also you know fed into this CO scrubber where this CO ah you know part will be ah scrubbed out or washed out from this in this CO scrubber part and from the top of it that has been taken out ok fine. So, from this part you know we have ah taken out this ah N2 and H2 ah from here this is what is that H2 plus N2 which will be taken as the product and that will come out from here. So, that is about this ah Linde-Bronn process. So, you can cross check it if I have drawn anything wrong in the earlier process this is the complete ah you know circuitry for the process diagram for the Linde-Bronn process. So, ah let us ah I mean have a look into this ah again ah I mean ah these are the references we have and to conclude with ah we have that we have identified that this coke oven gas is a potential source of hydrogen and that can be you know ah ah I mean Linde-Bronn process where liquid nitrogen is used as the coolant can be you know used to separate out this ah all this components of ah ah I mean coke oven gas and from there we can separate out this hydrogen. So, thank you very much for your attention.