Cryogenic Hydrogen Technology
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Lecture 16
Hydrogen Storage: Overview

Welcome to this lecture on cryogenic hydrogen technology. We were talking about the hydrogen production so far. Now we will switch over to hydrogen storage that is another important aspect of this hydrogen technology. So, today's in today's lecture we will have ah hydrogen storage we will give an overview of the hydrogen storage system and the keywords are like on board hydrogen storage and then hydrogen density calculation we will look into and then we will finally, go to the Van der Waals gas equation in connection to this compressed hydrogen storage and this probably you are familiar with this kind of equations like ideal gas equation and real gas equation. So, we will also look into the generalized equation of state involving the compressibility factor. So, ah let us have a look into it.

So, we will just go back to our ah discussion on ah hydrogen infrastructure in that connection we have talked about three verticals like the hydrogen production then we have talked about the hydrogen storage and transportation finally, the utilization. And while talking about the utilization we have talked about ah mainly two things ah one is the the vehicular application and that includes light vehicle as well as heavy vehicle and there is a you know that is a aerial transportation or airplane. So, ah they have a different requirement of ah hydrogen if we want to switch over to the hydrogen fuel basically ah with on this hydrogen infrastructure ah part we have concluded that we need hydrogen as the fuel and we concentrated wanted to concentrate particularly on the vehicular aspect because ah it has been you know known that almost 25 percent or one quarter of the total energy consumption is related to this sector. So, in this ah lecture we will particularly comes I mean concentrate on the light vehicular one and to be very specific ah you know this will be involving ah I mean the the intention is to ah have a fuel cell-based vehicle and let us look into that details.

So, before we go ah to that ah discussion let us have what are the conventional fluids we have and their corresponding energy density or basically their density at part at this moment. So, we have we are familiar with ah the gasoline and then also we are familiar with the use of methane or the compressed ah CNG compressed ah natural gas ah basically that is the primary constituent of CNG is the the methane and let us look at ah this density ah it is not energy density it is the ordinary density. So, ah the density part ah if you look at we will find that it is not the energy density, but it is the ordinary density part and if we look at this ah I mean with respect to hydrogen we find that this gasoline is 55 times heavier in the gaseous form whereas, the liquid ah I mean with respect to this is about the liquid hydrogen density and with respect to liquid hydrogen density this ah gasoline is 700 I mean almost you know 10 times heavier. So, if this is 70.8 this is nearly 700 kg per meter cube. So, it is 10 times almost heavier and methane is liquid methane it will be about 6 times heavier than the liquid hydrogen. On the contrary in the in the gaseous form this hydrogen whose density is 0.08 kg per meter cube it is ah with respect to that gaseous hydrogen this methane is 8 times almost and this ah gasoline is 50 times 55 times heavier. So, we can understand that this hydrogen is it is already known that hydrogen is lighter in weight and also the liquid hydrogen is also lighter in weight. So, what are the problems ah if they are lighter in weight and ah let us look into that again say if in terms of energy density now if we look at we find that on this side we have the mass energy density that is given in terms of mega joule per kg and this is the energy density with respect to the volumetric energy density that is mega joule per unit meter cube.

So, in terms of methane gasoline and diesel if we look at we find that ah this with respect to hydrogen here you can see this is with respect to the compressed and liquid hydrogen and this is you know this is the mass based energy density this is with respect to the hydrogen ah again the mass based irrespective of obviously, liquid or gaseous mass, but volumetric mass is here the volumetric energy density you will find that the compressed hydrogen at 700 atmospheric pressure it gives this kind of ah I mean energy density and here with respect to this ah volumetric energy density both methane and gasoline or diesel they are way better, but with respect to the I mean mass energy density you can see that ah hydrogen is way above the methane or gasoline or the diesel. So, these are the positive with respect to the mass energy density it is ah definitely very attractive, but on the other hand it occupies lot of volume as compared to diesel or gasoline or methane. So, now let us look into the ah before we go I mean in the previous slide we have talked about this mega joule per kg of ah mass energy density and that is for hydrogen we have talked about 1 nearly 120 ah mega joule per kg and this is ah in volumetric energy density it is mega joule per meter cube. So, where from this number ah this numbers came ah you are familiar with this numbers, but just we need to ah introduce it in a different way. So, so far ah we have talked about the production of hydrogen from ah the liquid that means, we have water and we are putting energy.

So, we are getting you know the hydrogen and oxygen both in the form of paper or in the gaseous form. So, we spend energy and we got this ah you know we split water into hydrogen and oxygen. Now if we do the reverse thing that means, if we combine hydrogen and oxygen then we get the energy as well as we get the water as the product. So, here this energy that will be either in the form of electrical energy or it may be in the form of thermal energy. Exactly the similar way you know we have learned earlier that we put energy in the form of thermal energy or we put in the form of electrical energy to split it.

Now, when we combine them in a fuel cell or you know if we burn it in presence of oxygen we get either you know the electrical energy or we get ah in a electrical energy in the form of ah fuel cell in the fuel cell and thermal energy if we just burn it in presence of the oxygen gas. Now what is this energy that we obtained ah if we burn it or if we you know get it in the form of fuels in the form of fuel cell. So, let us have a look into that ah we are familiar with this ah you know, but here there is a difference that this water that may come in the form of liquid or it may so happen that ah you know depending on the temperature this water the product I mean the combination of hydrogen and oxygen when it is giving rise to water it can come in the form of vapor it can also come in the form of liquid. So, it is understandable that you are spending a part of this energy in order to vaporize this liquid into this vapor. So, that means, when you talk about this energy this will be higher and when you are getting or generating this ah vapor I mean water vapor then this energy will be slightly less. So, this is higher heating value and this is called the lower heating value. So, let us have a look into this numbers. So, you have you might you might remember that you know we have spent 285.83 kiloJoule per mole to break this ah you know water into hydrogen vapor and O2 vapor. So, that is the kind of ah you know ΔH that is necessary.

So, obviously, when we recombine it is a basically reversible ah reaction and when we put it in the form of liquid that is you know we started with the liquid that is water and if we are combining them into a liquid it will generate 285.83 kiloJoule per mole. So, we call it as the higher heating value. So, this is the higher heating value and the other one when you have this water in the form of vapor by you know spending some amount of energy and basically that will be the ah enthalpy of evaporation ok. So, that will give you 241.83 kiloJoule per mole that is the lower heating value. So, these two numbers we have to remember and many a times in terms of either kiloJoule per mole or it will be in kilowatt hour per kg or something like that. So, it will be I mean in appropriate unit it will be ah I mean used. So, this is what is the volumetric energy density. Now in terms of the mass energy density what we have to do is just we have to ah divide it this mole if we put it in terms of the gram or you know in terms of the kg then it will come as you know 199.716 for the lower heating value and the other one will be 141 from this number if you just divide it by this value that will give you the higher heating value, but this is the mass energy density. So, this mass energy density you know we have talked about in the earlier slide that when it is ah I mean it is nearly approximately 120 mega joule per kg ok. And then ah the other one was ah in terms of the volumetric energy density. Now when talking about the volumetric energy density ah you can easily ah convert this numbers mass energy density to volumetric energy density in terms of say mega joule per meter cube. So far, we have talked about kilo joule per mole we can also convert it into the mega joule per ah meter cube that is what that expression you have seen.

Now the moment we say that it is a mega joule per meter cube then we have to multiply it with the corresponding density of the liquid or the vapor ok or if it is in the gaseous form it will be in the form of gas. So, ah with respect to that let us have a look ah ah I mean we we we we can do that calculation ah if we just multiply it with the appropriate density we will do that later on. So, based on this ah background ah of the energy content of ah hydrogen the particularly with respect to the mass energy and the volumetric energy density. Now let us look at the onboard hydrogen storage target that has been set by the DOE of USA. And ah this particular requirement has been set ah for a particular vehicle I mean that is the mostly the fuel cell vehicle and this is meant for light duty vehicle.

So, let us now look at the different ah parameters and what is the target that they have set for 2025 in the near future and ultimately what should we achieve. So, there are 2 terms here ah I think there are 2 new terms for oops ah let us look at the terms we have this is the gravimetric storage capacity. That means, here what is the amount of hydrogen that can be stored per amount of or total system that means, if I have to store 5 kg of hydrogen and if I need x kg of the cylinder or etcetera I mean accessories then this x kg plus 5 kg of H 2 this will tell you what is the gravimetric storage capacity. So, that means, the kg of hydrogen divided by kg of the system plus the hydrogen including the hydrogen that gives you the gravimetric storage capacity. Similarly, the volumetric storage capacity in the volumetric storage capacity it is basically a ratio of the amount of hydrogen and the system volume in liter.

So, that is what I mean it would be 5 kg of hydrogen and this would be the volume of you know the system total volume of the system and that will include of course, the hydrogen and the volume of the cylinder etcetera and that ratio should be of this order. Along with that we have the dormancy time that means, this is particularly if the liquid is you know stored in a low temperature and if there is pressurization or self-pressurization because of you know stationary I mean if it is in a standing condition for long and that would you know. So, if it is getting pressurized we need to release that I mean pressure beyond a certain limit and that would be and between this that time is called the dormancy time and it should be about of the order of 10 to 14 ah I mean days. But in terms of the refueling that means, if we are going to ah filling station we should be able to get it filled within 3 to 5 minutes that is typically ah required in a gasoline or ah diesel fired I mean ah-based car. So, that is the kind of requirement or the storage parameters other than that there are plenty of other parameters one can have a look into this ah website they will be able to understand what is the exact requirement for set by the DOE for near future and ultimately for a particular I mean we have to keep it in mind that these all are I mean for meant for the fuel cell based light ah duty vehicle.

You can understand that the kind of storage options for this kind of vehicles will be one is the compressed hydrogen as we have talked about then we have the liquid hydrogen then there are two more options which may not be your familiar with is the ah cryosorption that means, you know we adsorb some of the hydrogen in carbonaceous material or porous material when it will be adsorbing this hydrogen and sometime it would be at low temperature. Then we have metal hydride some metals and some metal alloys we have and they can you know adsorb the hydrogen or chemisorb this hydrogen and we can store it in the form of this metal alloys also metal hydride in the form of metal hydride. So, let us have a look into this ah where we have different kind of ah I mean the storage options and where we are try trying to you know achieve something like you know which is achievable in terms of the tank volume and the tank weight for example. So, if we have to as I told you that some amount of the gasoline you are filling in and we can travel say 300 kilometer 400 kilometer depending on the size of the tank and the tank volume is you know we are familiar with a small tank which is there fitted with the car and the tank weight is about you know almost negligible with respect to the tank I mean the weight of the liquid. Now, if we have to carry hydrogen as we have learned that its density is very small.

So, we have to either compress it or liquefy it or you know we have to take it in the form of cryosorption or you know adsorbing alloy or basically they are metal hydrides. So, all these options you know will give you either will it will make the volume very large say for example, if we talk about the compressed hydrogen that is we are densifying the hydrogen, but still it has you know very large tank size it needs very large tank size. But when we talk about say metal hydride we find that its weight will be you know very high, but it will achieve you know very small tank volume we can store it in a very small volume, but we will have you know very large weight will be there. So, the tank weight restriction will be on this side on this side you know we have a large volume liquid hydrogen is of course, very close to this gasoline, but again it has its own problem like dormancy is a big problem with liquid hydrogen. So, all these things are I mean basically our target is to reach something like you know ah with the gasoline-based IC internal combustion engine based these cars and none of them are able to reach you know this kind of optimum solution in terms of tank volume or the tank weight.

So, we have the DOE ah targets and you know all over the world people are trying to achieve what is achieved already I mean we are familiar with this gasoline-based IC. So, so you can understand what we are now trying to look at. So, we will start with the compressed hydrogen and we will start with the density of gaseous hydrogen. So, to calculate the density of gaseous hydrogen as we have said that you know the density of gaseous hydrogen is 0.08 kg per meter cube how did you get it? So, the simplest equation of state is the ideal gas law and if we put P equals to say at 1 atmospheric pressure and say 298 Kelvin that is nearly around room temperature depending on the place.

So, here 1 atmosphere is basically 10^5 Pascal and $\bar{R}$ is the universal gas constant 8.314 Joule per mole per Kelvin. So, this is the first mole kiloJoule per kilo mole or say joule per mole per Kelvin. So, if we put this value ah we will have n by v equals to P by RT and if we put P equals to 1×10^5 P a and then if we divide it with 8.314 and then you know 298 this will give you this many 40 point something ah 40.36 mole per meter cube. So, the unit is ah mole per meter cube, but we can you know write 1 mole is equals to 1 mole is equals to 1 mole of hydrogen is equals to 2.02 into 10 to the power minus 3 kg and with that you know replacement if we put this 1 mole equals to this value then we will have n by v is equals to 0.0815 kg per meter cube. So, this is the density at ah 1 atmospheric pressure and 298 Kelvin. So, now if we want to ah calculate ah you know and pressurize it to very high pressure typically of the order of 300 to you know 350 to around 700 bar pressure.

$$\mathrm{PV} = \mathrm{n}\,\bar{\mathrm{R}}\mathrm{T}$$

So, ah can we use this ideal gas equation ah of course, you can use it, but it will give you an erroneous solution ah why because this P v equals to n $\bar{R}$ T that is basically ah based on certain idealization. This idealization is like that you know this P is not considering the intermolecular force between the atoms or I mean sorry the molecules and the v is neglecting the volume of the molecules, but all these molecules are having a finite volume. So, the volume that we are considering that it is inside a container, but we have to ah I mean take out the volume of the hard molecules of each one and then you know it will be slightly reduced and the pressure you know this gas are colliding with the wall and giving rise to some pressure, but we are neglecting the inter I mean molecular the force between the particles. So, if you include that that will enhance slightly the pressure part and we have ah one Van der Waals gas equation if we replace ok. So, first of all we will use the generalized gas equation with respect to the compressibility factor.

So, this compressibility factor chart will be available and it will be given in terms of the critical pressure and critical temperature, but these days most of the time we use the fluid property and there are the cool props then rip props they are the type of you know ah fluid property values we have available with us. So, we can have this compressibility factor ah taken from these charts. So, we can calculate it based on these values like we have this Z values given for different pressures and we can calculate the density based on that equation.

So, now, ah in terms of that earlier as we have talked. So, n by V would now become Z ah sorry P into Z into P by Z $\bar{R}$ T.

$$\frac{n}{V} = \frac{P}{Z\bar{R}T}$$

$$\rho = \frac{n}{V}$$

So, this is the pressure on the numerator part denominator part you will have that Z and then $\bar{R}$ and T. So, if you use ah this values say particularly say for we have given this discrete values for 0.1 MPa, 5 MPa, 10 MPa like that and for those pressures you can you know put this corresponding Z value and calculate the n by V and from there you can put it in it will give you in the mole per meter cube finally, you have to calculate it in terms of the mole per kg or sorry kg per meter cube. So, that would give you the density of the gaseous hydrogen in terms of the what is called a real gas equation. This is the real gas equation ah that is the generalized gas equation ah you know with respect to ah equation of state with the compressibility factor.

$$(P + n^2\frac{a}{V^2})(\frac{V}{n} - b) = \bar{R}T$$

So, there is another equation we are ah mostly familiar with that is the ah what is called the Van der Waals gas equation. So, here it takes care of that you know additional force that I was talking about and this is V by n is basically earlier we have talked about n by V that is equals to the density or the molar density and V by n is the molar volume. So, this is molar volume that gives you meter cube per mole. Now this equation you can slightly modify ah I mean this can be written as P by molar V plus n by V is you know rho square into a this a and b are the corresponding constants for the Van der Waals gas equation and for hydrogen they are ah basically 0.0244 and with this unit and this b is also given.

$$(P + \rho^2 a)(\frac{1}{\rho} - b) = \bar{R}T$$
$$(P + \rho^2 a)(1 - \rho b) = \rho\bar{R}T$$

So, this will be like this and multiplied by say 1 by rho minus b into $\bar{R}$ bar into T. So, now, if I multiply it with the rho on both sides what we will have is P into a plus rho square into 1 minus b into rho into rho $\bar{R}$ T. So, from here we can calculate the rho as P plus a rho square into rho $\bar{R}$ T. So, this will be 1 by 1 minus b into ah this rho equals to I am sorry this is 1 minus rho b.

So, this would be $\bar{R}$ into T. So, now, we are trying to calculate this rho and it is on the right-hand side you have this rho value again. So, that means, you need an iterative solution an iterative solution will be necessary and we can ah do it in different way ah. So, one way of doing it is ah given here ah we have this rho on the right-hand side and also, we try to calculate it on the I mean basically we calculate try to calculate this density and we have rho on both sides. So, we will start with a simplification maybe you know we can assume that this a and b are 0 and that is negligible. So, that will give you some density ah and basically that is the density achieved with the help of the ideal gas equation.

ah Now, if that would be the starting point and then we will move to the ah actual density calculation with the ah let us see how we doing it. So, let us have a look ah this is the here this is the pressure at one atmospheric pressure or one bar pressure we have the corresponding in terms of P a we can write it as you know 1×10^5 and density calculation we have done it using this ah expression where B4, B4 is basically the pressure in P A 8.314 and 298 as we have learned. So, this is the first assumption. Now, based on that assumption we are now trying to calculate the density where you will find that it is coming as ah if you look at this is the pressure part, this is the rho square part multiplied by a, this is a this value is given you know it is somewhere written over here ah sorry this value is basically ah that a value ok.

And this value is basically ah that a value ok and then ah this is ah dollar v is dollar v dollar 2 that is where you know a and b constants are given and then here comes ah and then you know divided by $\bar{R}$ and 298 Kelvin. So, that gives you the first approximation. Then ah based on this value we calculated the second one and you may find that there is no change even up to the 15th you know iteration that is because the pressure is low and there is almost no change whether it is the ah I mean it is ideal gas or the ah real gas. But the moment it comes to you know the higher density say how do we get that let us try to look into it let me delete it first then the next one is if we calculate it this plus 25 sorry plus ok. So, this is the first assumption A5. So, this if we just drag ah it will be equal to this. So, this is coming like this and then we have to drag it. So, that you know we can get the multiplied by one factor. So, now, what we will do is that we will simply drag it and it will give you the density calculation. This is up to the 14th step and if we just drag it one more time it will come as.

So, this is how we will do it. So, now, we will we calculated the density for using the Van der Waals gas equation then of course, we have calculated it with the help of ah this is with respect to the Van der Waals gas equation. This is with respect to the ideal gas equation as you can understand this is the linear graph and this is with respect to that generalized equation of state using the Z factor and this would be with respect to this Van der Waals gas equation. So, these are the graphs we have ah drawn with the help of different using the different gaseous equation and equation of state then let us go back. So, we have ah these are the kind of gaseous density and we have ah these are the kind of gaseous density and you can understand that at higher pressure this is quite different than the ah ah one which has been used with the help of basically the real gas equation and the. So, the real gas equation and this is with the ideal gas equation and these are with the real gas equation one is with the Van der Waals gas equation the other one is with the generalized equation of state using Z factor.

So, let us try to conclude ah these are the references you can look into and the erroneous density will be I mean if you are calculating the density with respect to the ideal gas equation you will find that they are giving a lot of errors and if it is a compressed hydrogen gas we have to use basically the real gas equation. So, that is all ah. Thank you for your attention.