Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 01
Properties of Hydrogen

Welcome to the course on Hydrogen Energy. In this first lecture, we will look at the different Properties of Hydrogen.

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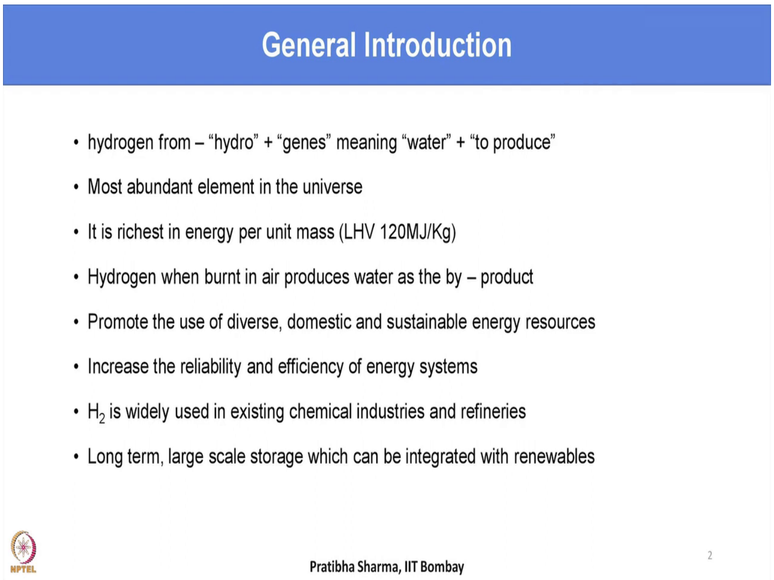

We will begin with a general introduction. Hydrogen was first discovered in 16th century. This was when Paracelsus, he accidentally poured iron fillings on to sulphuric acid; however, Henry Cavendish he identified this as a separate element. It was in 1780s that Anton Lavoisier, he gave the name hydrogen. The origin of this name hydrogen is from hydro and genes.

Hydro means water and genes means to produce; so, water producer. Hydrogen is the most abundant element in the universe, about 75 percent by mass of the universe is made up of hydrogen and 90 percent by volume; however, in the earth's atmosphere the quantity of hydrogen is very small. This is because of very high diffusivity of the hydrogen. It is richest in terms of energy per unit mass; when it is burnt in air it produce clean exhaust and the by-product obtained is water.

And thus it has great potential towards decarbonisation at the point of usage. Hydrogen is a versatile fuel, it can be produced from a wide variety of sources. It can be produced from whatever local feedstock is available and thus it can promote the use of diverse domestic and sustainable energy resources. With the use of the local feedstock available we can produce hydrogen and then it can be utilized for various applications.

And, thus we can reduce our dependence on fossil fuels and on the imports of fossil fuel. From the point of production to the point of consumption, if the production is also green we can reduce greenhouse gas emissions. At the same time the hydrogen conversion devices and the technologies where hydrogen is being used are reliable and more efficient as such the entire energy systems with the use of hydrogen can be made more reliable and efficient.

Hydrogen usage is not new in the energy sector. It was actually also being used earlier. Hydrogen was used in various chemical industries as well as refineries. This can also serve as an option for long term large scale storage when integrated with renewables.

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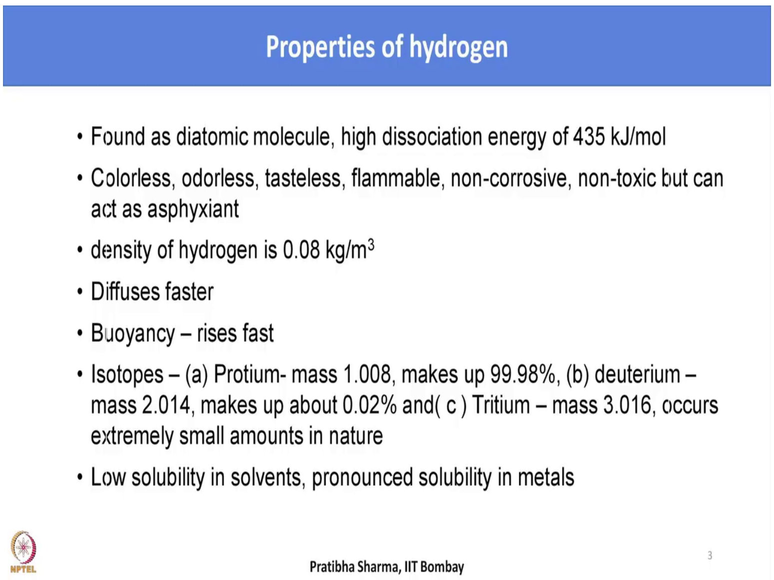

Starting with the properties of hydrogen, hydrogen is the simplest element and the first one in the periodic table. It is the lightest element having one proton and one electron in atomic form. Due to this arrangement, it is very reactive and not found as atomic hydrogen; rather it combines with the various other elements forming either water or different hydrocarbons or organic compounds.

Atomic hydrogen does not exist. It exists in the form of a diatomic molecule and this molecule if to be dissociated to form atomic hydrogen requires a high dissociation energy of 435 kilo joule per mole. Hydrogen as such is a colourless, odourless, tasteless gas, flammable, non–corrosive, non-toxic in nature, but it can act as an asphyxiant. If hydrogen is in confined spaces then it can displace oxygen, reducing the oxygen level and thereby can cause breathlessness.

If it reduces the oxygen level below a certain level say 12 percent by volume in that case it can lead to severe health challenges, unconsciousness and others. Hydrogen has a very low density of 0.08 kg per meter cube. It is 14 times lighter than air. It has a very high diffusivity and buoyancy. Hydrogen exist in three different isotopic forms protium wherein there is one proton and the mass of it is 1.008.

It makes up the relative abundance of it is high 99.98 percent; deuterium it has mass of 2.014 and a abundance of 0.02 percent; tritium having a mass of 3.016, but it occurs in extremely small amount and can be produced during nuclear reactions. Hydrogen has a very low solubility in solvents but it has a very high solubility in metals.

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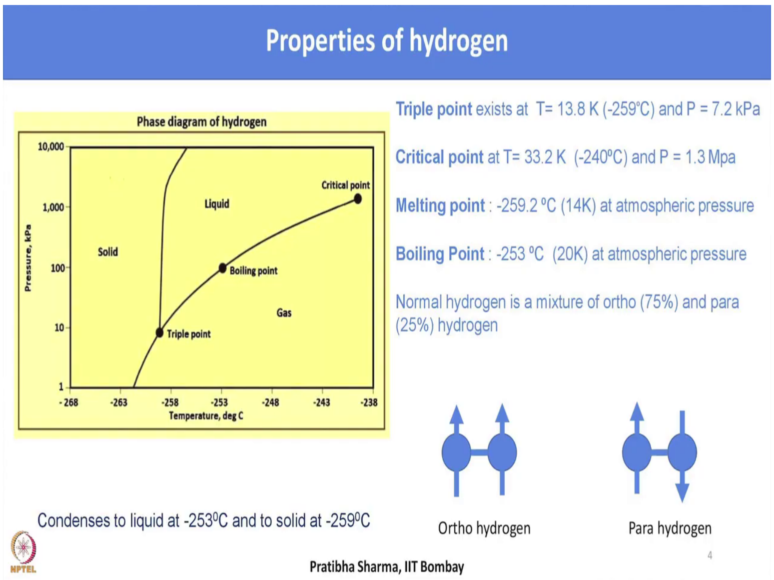

If you look at the phase diagram of hydrogen there are different regions wherein hydrogen exist in the form of solid, liquid and gas. Triple point of hydrogen wherein all the three phases coexist is at 13.8 K that is minus 259 degree centigrade and a pressure of 7.2 kilo pascal which is very low. Hydrogen's boiling point is at minus 253 degree centigrade that is 20K at atmospheric pressure.

However, this boiling point can be increased, hydrogen can still be liquefied at higher pressures up to a maximum of minus 240 degree centigrade or 33.2 K at a pressure of 1.3 Mpa which is the critical point; beyond which it cannot be liquefied by simply increasing the pressure. Hydrogen can be obtained in solid form at a temperature of minus 259.2 degree centigrade that is 14K at atmospheric pressure.

Under normal conditions, liquid hydrogen is a mixture of ortho and para hydrogen. At NTP, this is a mix of 75 percent of ortho hydrogen and 25 percent of para hydrogen. The difference between these two stages of hydrogen is, the nuclear spins are parallel in case of ortho hydrogen and anti parallel in case of para hydrogen. When hydrogen is to be liquefied, the 75 percent of ortho needs to be converted into para hydrogen because, that is a lower energy state; and that process is slightly exothermic reaction and a slow process as such requires catalyst.

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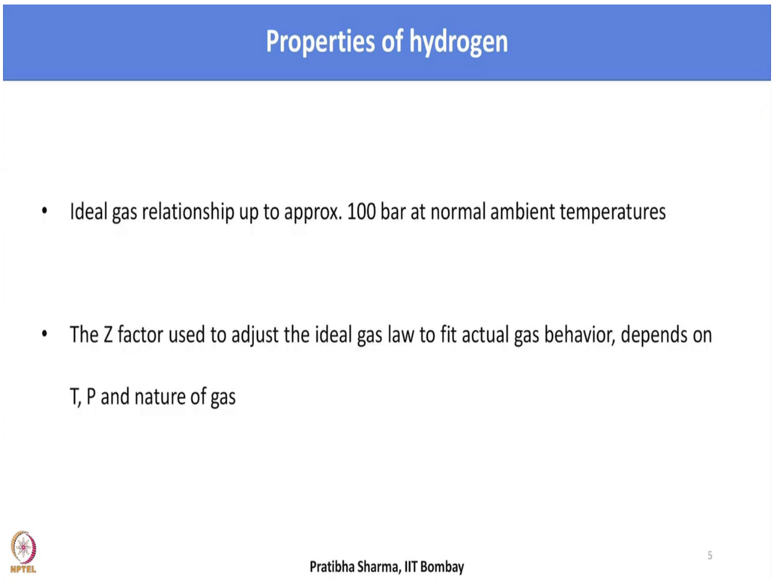

If we look at hydrogen, in that case the ideal gas relationship holds till a particular pressure under ambient temperature till say 100 bars; however, the deviation from the ideal gas behaviour occurs and this can be accounted for by the use of a factor which is known as compressibility factor.

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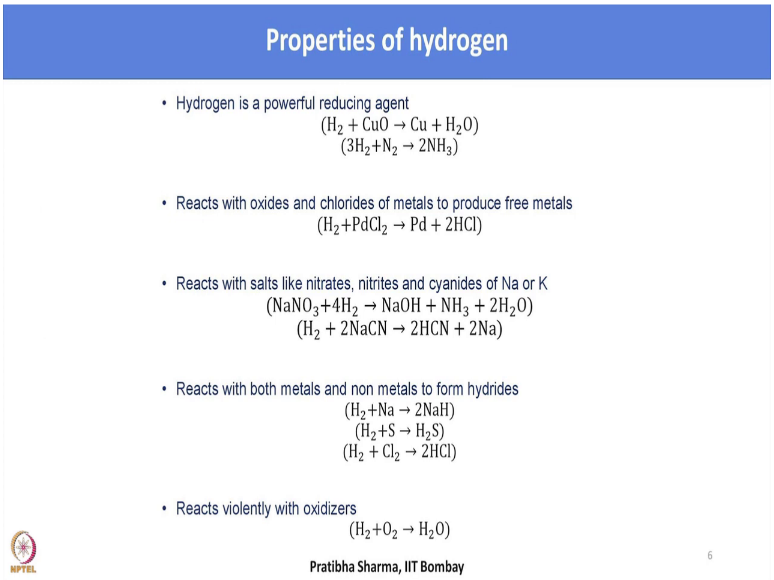

If you look at the chemical properties of hydrogen, we know that hydrogen is a powerful reducing agent. And it can react with large number of salts, oxides, chlorides then nitrates, nitride, cyanides to convert it into free metal. It can react with most of the elements in the periodic table both metals and non metals to form hydrides. It can react with various oxidizers producing a lot of heat. It reacts violently with these oxidizers.

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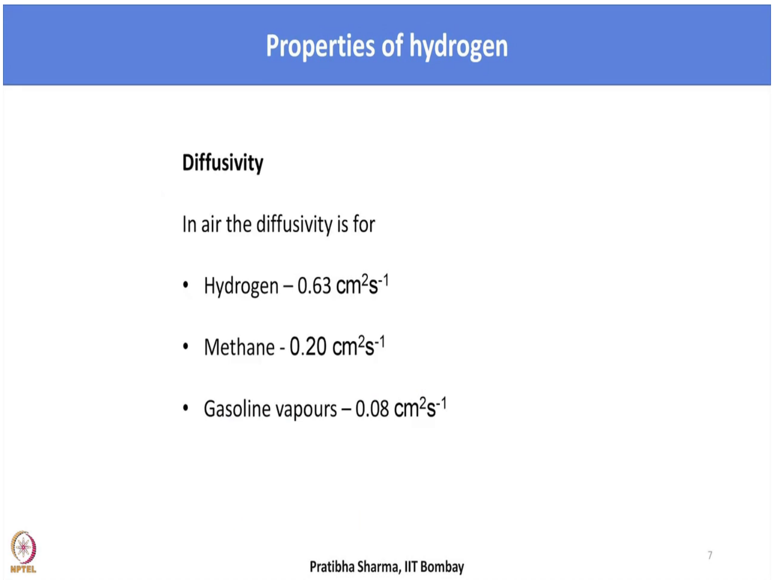

If you look at the fuel properties of hydrogen, hydrogen has a very high diffusivity in air. If we look at these numbers, hydrogen diffusivity is 0.63 cm^2/s. This is 3 times that of natural gas. It is an order of magnitude higher than that of the gasoline vapour.

Now, this diffusivity has both an advantage as well as a disadvantage. Since we know that molecule of hydrogen is very small as compared to any of the other gases, it can diffuse very fast. It can diffuse through airtight or impermeable materials as well and as such this becomes very difficult to contain hydrogen unlike the other gases, but this high diffusivity along with high buoyancy has an advantage in the sense if there is a hydrogen leak.

Then because of high buoyancy that rises and it diffuses very fast so that it dilutes very quickly along with air, forming a dilute mixture, especially when it is an unconfined space. Even if there is an ignition source in that case the flames which are produced because of hydrogen these are vertical, these will be a localized flame and these will be vertical flames in case of hydrogen.

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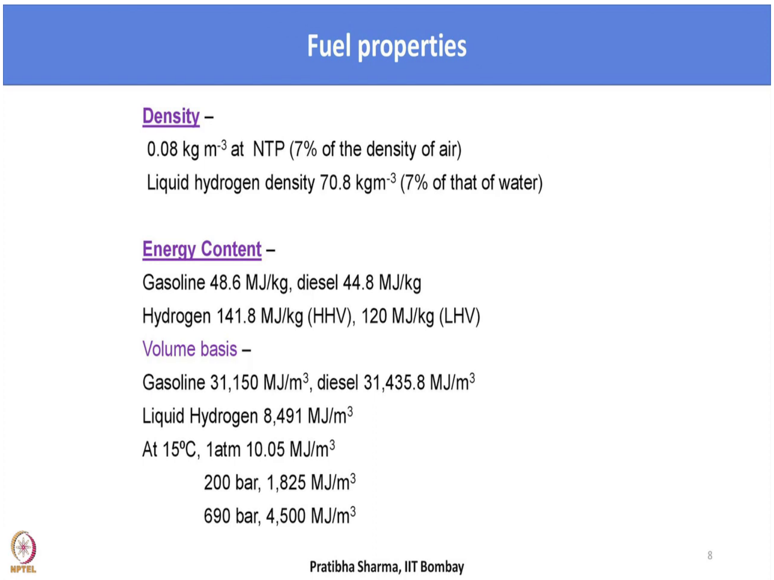

Density of hydrogen is very low. density we know depends on temperature and pressure. For hydrogen at NTP, this is 0.0899 kg/m^3. When we compare it let us say when we see what is the specific gravity that is defined with respect to a reference material; if it is gaseous then with respect to air if it is liquid then it is with respect to water.

So, the density of hydrogen is 7 percent of that of air; however, liquid hydrogen which has a density of 70.8 kg/m^3 this is 7 percent of that of water. If we talk about the energy content which is the amount of energy which is contained in a fuel that could be per unit on a mass basis or on a volume basis.

We can also define it as the amount of energy which is released on complete combustion of a unit mass of fuel. So, if we look at these numbers for hydrogen the higher heating value is 141.8 MJ/kg, lower heating value is 120 MJ/kg as against that of gasoline which is 48.6 MJ/kg. So, hydrogen contains approximately 3 times that much of energy per unit weight as that carried by gasoline or diesel.

That means large it has highest energy content on mass basis, but the situation is different when we consider on the volume basis. The amount of energy contained in a given volume of fuel energy density, this is very low for hydrogen. For hydrogen at temperature of 15 degree centigrade 1 atmosphere this value is 10.05 MJ/m^3. However, for gasoline this is 31,150 MJ/m^3. Liquid hydrogen has a higher density this is 8,491 MJ/m^3.

Now, these are very low numbers as against the conventional fossil fuel tells us that in order to store appreciable amount of hydrogen very large volume is required. These amounts also tells how compactly we can pack the molecules together in a given volume. So, that means, the volume that will be required to store hydrogen will be very high until and unless these are compressed to very high pressure.

Even when it is compressed to pressures like 690 bar, the energy density still it is 4500 MJ/m^3 which is appreciably lower than that of gasoline.

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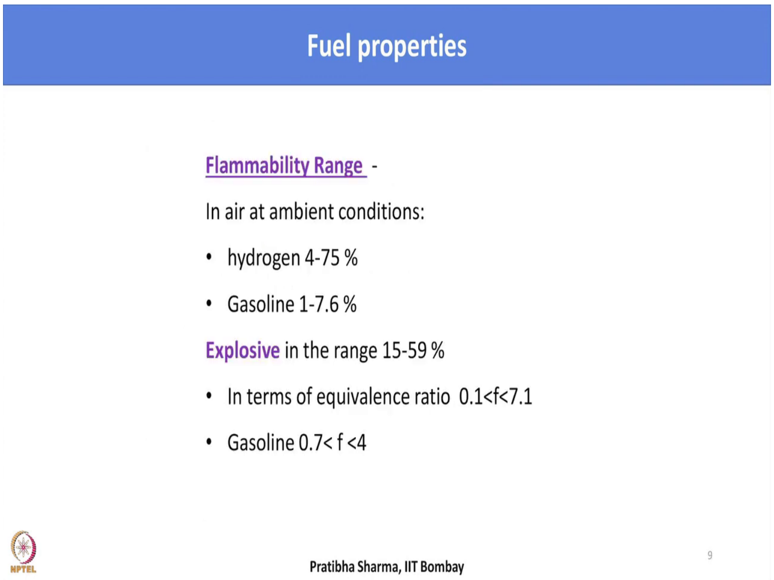

flammability limit which we define as the concentration range in which the combustible mixture supports a self propagating flame when ignited. There is a lower flammability limit which is the lowest concentration which can support a self-propagating flame when mixed with an oxidant and ignited. Below the lower flammability limit the mixture of air and fuel is leaner in fuel so that it cannot be combusted.

On the other hand, the upper flammability limit is defined as the concentration which can support self propagating flame when it is mixed with oxidant and ignited. Beyond this upper flammability limit, the combustion cannot sustain because the concentration of oxidant in the combustible mixture is low. For hydrogen this flammability range is very wide 4 to 75 percent by volume so concentration percent; for gasoline this is 1 to 7.6 percent.

Similarly, we can define the explosive limit which is defined as the range of concentration which will cause explosion when it is mixed with air and ignited. However, there is a difference between fire and explosion. for explosion the containment is required. So, when a combustible mixture is contained and then it is within the explosive limit and ignited then temperatures and pressures increase in such a manner that it gets sufficient enough to violently release from the confinement and leading to explosion.

For hydrogen this explosive range is from 15 to 59 percent. When we talk about engines, we define equivalence ratio which is for hydrogen lies in the range of 0.1 to 7.1. This is also defined as the actual fuel to air ratio by the stoichiometric fuel to air ratio. For gasoline;

however, this is lying in the range of 0.7 to 4. Thus for hydrogen this is quite wide. This wide flammability limit has both advantage as well as disadvantage.

Advantage in the sense when used hydrogen is used as a fuel in hydrogen IC engines, it can even dilute mixtures that can combust, it can result into stable operations, the ease of start better combustion could be possible with reduced emissions. At the same time this is a disadvantage that if there is a leak even very dilute mixture or even a concentrated mixture both can ignite and can result into fire or explosion. Ignition energy this is the minimum energy that is required to ignite a hydrogen and oxidant mixture under a given set of conditions.

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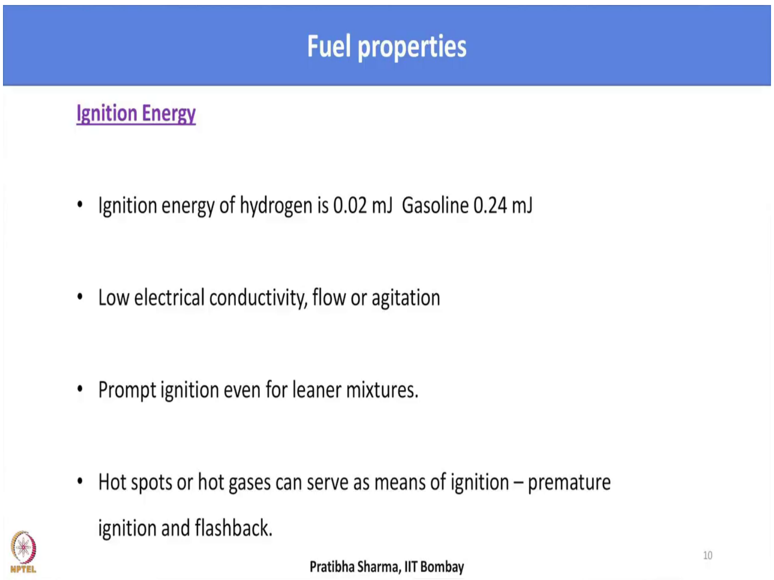

For hydrogen, if we see this ignition energy is very low 0.02 mJ which is an order of magnitude lower than that of gasoline. For gasoline, this value is 0.24 mJ; that means, very small amount of energy is required to cause ignition. This ignition source can be either a spark, it could be a flame or it could be a short circuit in an electrical device that could lead to ignition of a combustible mixture with hydrogen. The electrical conductivity of hydrogen is poor.

So, any flow or agitation in case of gaseous or liquid hydrogen can result into electrostatic charges leading to spark and causing an ignition as such whenever hydrogen is contained those vessels are usually containment devices they are usually grounded. Now, this small ignition energy again has an advantage in the sense that it can result into prompt ignition when used in IC engines; even leaner mixture can cause ignition.

But at the same time the major challenge is even the hot spot or hot gases they can also serve as a mean for ignition. And it can also result into premature ignition and flashback. Autoignition temperature which is defined as the minimum temperature, which is required to initiate self sustained combustion in a combustible fuel mixture in the absence of any external ignition.

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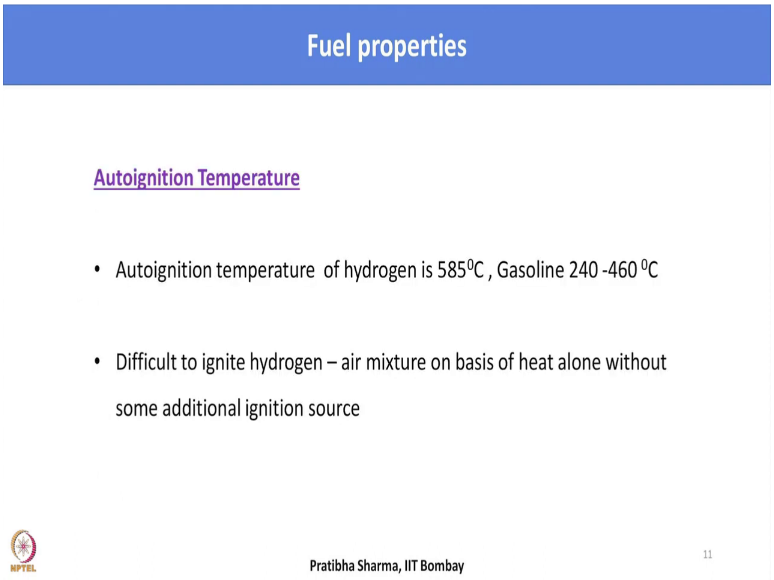

For hydrogen this auto ignition temperature is 585 degree centigrade; however, for gasoline this is lying in the range of 240 to 460 degree centigrade. Now, this higher auto ignition temperature makes it difficult to ignite a hydrogen air mixture, it is difficult to ignite on the basis of heat alone; that means, you require an additional ignition source to initiate combustion. Now, this is an advantage in the sense that in engines where a higher compression ratio is required.

So, as to have a better efficiency we can achieve a higher compression ratio using hydrogen, but at the same time even on higher compressions the ignition will not take place on its own. So, an external ignition source or a spark is required. So, ideally it will be bit fuel for a spark ignition engine.

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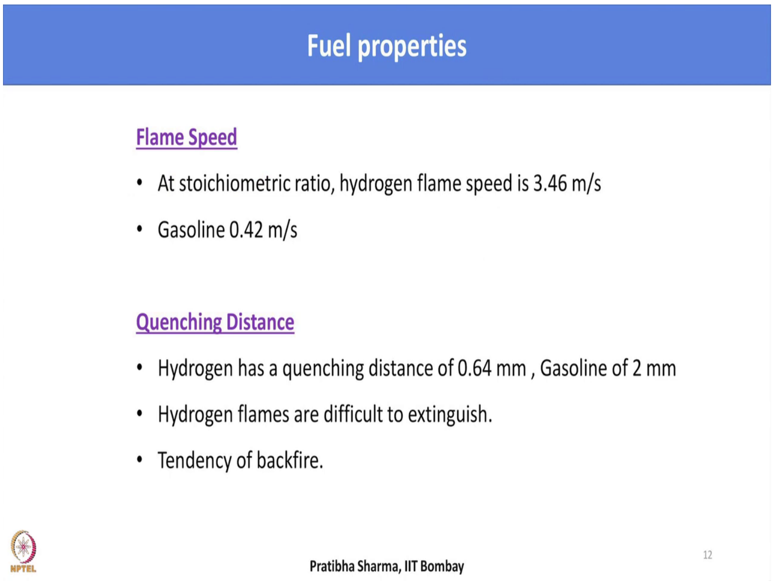

Flame speed, it is the distance travelled by hydrogen flame per unit time. If it is in the stoichiometric ratio hydrogen flame speed is 3.46 m/s which is again an order of magnitude higher than that of the gasoline. For gasoline, it is 0.42 m/s; that means, hydrogen flame travels much faster than that of the other fuels. It can allow hydrogen engine to more closely approach the thermodynamic cycle.

For any flame, for any fire the required things are an oxidant, a fuel and an ignition source. The quenching distance which describes a flame extinguishing property of fuel which is also related to the distance from the cylinder wall that the flame extinguishes because of heat losses. [FL], this is in the case of hydrogen travels very close to the cylinder and thus makes it very difficult to quench. For hydrogen this distance is 0.64 mm.

However, for gasoline it is 2 mm. So, hydrogen flame are very difficult to extinguish; at the same time they have a tendency of backfire. When materials are exposed to hydrogen over a longer period of time that can result into certain changes inside the material.

It can cause changes in the mechanical properties of the material, it can cause changes in the crystallinity of the material, material can change from its can lose its ductile behaviour and can become brittle. So, that all these fact, all these changes can result into failure of the material and leading to catastrophic events.

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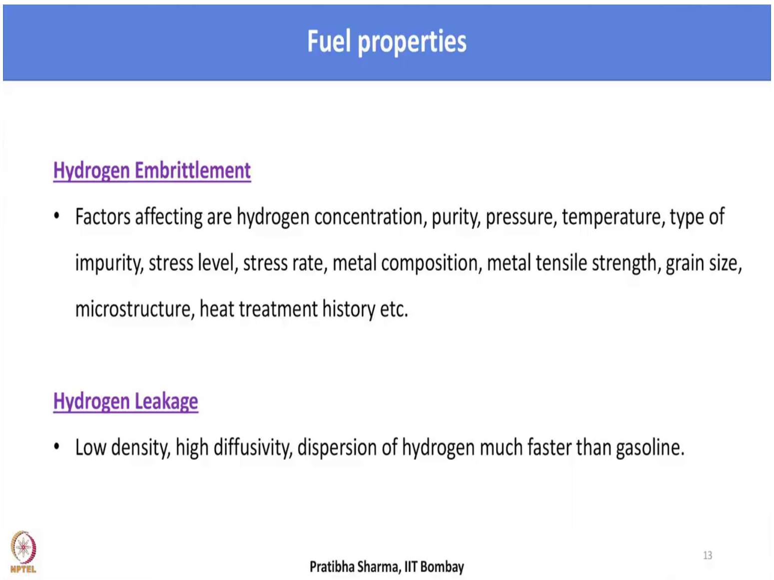

However, the embrittlement depends on various factors which are like hydrogen concentration, purity of hydrogen, pressure, temperature, the type of impurities present in the gas and in the material, the stress level, stress rate, metal composition, metal tensile strength, grain size, micro structure, the heat treatment history of the material.

If there is a leakage of hydrogen because of the low density of hydrogen high diffusivity hydrogen diffuse disperses very fast much faster than gasoline. Because of high buoyancy and dispersion diffusivity the hydrogen gets diluted, mixing up with air and rises up very fast. So, even if there is a leak and if it is much more safer than any of the other fuel even if there is a gasoline or diesel leakage in that case it takes some time to evaporate.

And then because of the lower diffusivity lower buoyancy compared to hydrogen it moves laterally, as such the leakage of hydrogen is much more safer as compared to that of gasoline.

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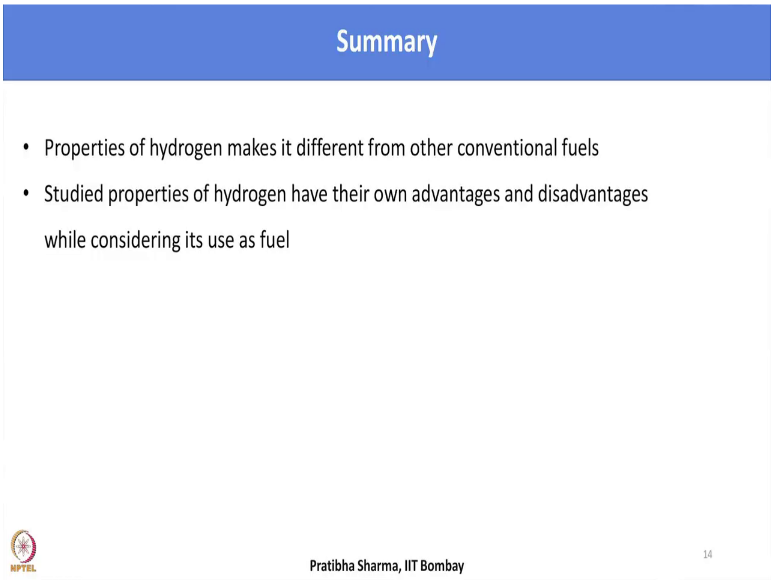

To summarize, we have seen the various properties of hydrogen and we have seen that how these properties of hydrogen are different from conventional fuels having a quite distinct characteristics. We have also seen that many of these properties have their own advantages and disadvantages if we are considering to use hydrogen as a fuel.

Thank you.