Skills for Hydrogen Safety

Erasmus+ KA202 - Strategic Partnerships for vocational education and training

Hydrogen Storage

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-------- BLOCK 1 --------

1.1. The Atomic Structure of Hydrogen

Hydrogen is by far the most plentiful element in the universe, making up 75% of the mass of all visible matter in stars and galaxies. Hydrogen is the simplest of all elements. You can visualize a hydrogen atom as a dense central nucleus with a single orbiting electron, much like a single planet in orbit around the sun. Scientists prefer to describe the electron as occupying a **"probability cloud"** that surrounds the nucleus some-what like a fuzzy, spherical shell.

The shared pair of electrons is shown as two dots in between the two HH symbols (H:H)(H:H). This is called a "**single covalent bond"**, when two atoms are joined by the sharing of one pair of electrons. The single covalent bond can also be shown by a dash in between the two symbols (H−H)(H−H).

A single hydrogen atom **H** with one electron is on the left and an $\mathbf{H_2}$ molecule showing the electron cloud overlap is on the right as given in below diagram. The structures of molecules that are seized collectively by covalent bonds can be depicted by "Lewis electron-dot structures".

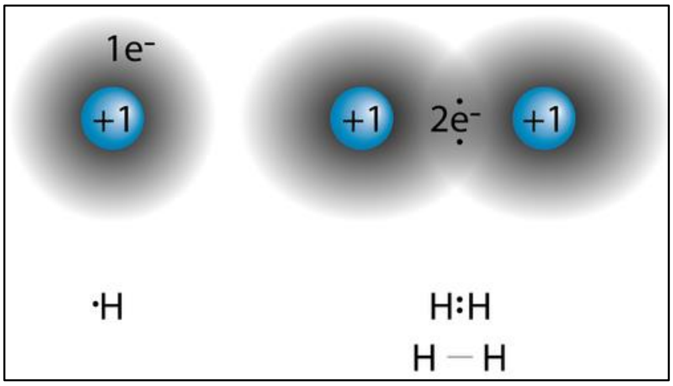


Figure 1. Hydrogen Molecule

Figure Link - https://chem.libretexts.org/Bookshelves/Introductory_Chemistry/Book%3A_Introductory_Chemistry_(CK-12)/09%3A_Covalent_Bonding/9.02%3A_Lewis_Electron-Dot_Structures

1.1.1. Isotopes of Hydrogen

Individual hydrogen atoms are electrically neutral. Hydrogen atoms naturally combine into molecular pairs (H^2 instead of H) due to their high reactivity. Each proton in a hydrogen pair has a field associated with it that can be visualized and described mathematically as a "spin".

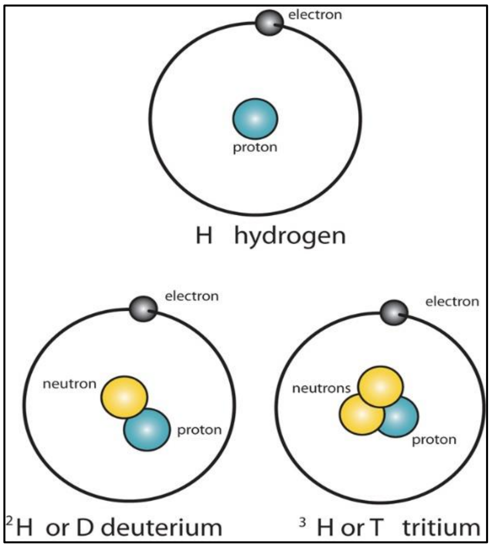


Figure 2. Hydrogen Molecule

In most hydrogen atoms, the nucleus consists of a single proton, although a rare form (or "isotope") of hydrogen contains both a proton and a neutron. This form of hydrogen is called deuterium or heavy hydrogen. Other isotopes of hydrogen also exist, such as tritium with two neutrons and one proton, but these isotopes are unstable and decay radioactively.

1.1.2. Ortho- and Para-Hydrogen

Molecules in which both protons have the same spin are known as **"ortho-hydrogen"**. Over 75% of normal hydrogen at room temperature is ortho-hydrogen. Molecules in which the protons have opposite spins are known as **"para-hydrogen"**. At very low temperatures, orthohydrogen becomes unstable and changes to the more stable parahydrogen arrangement, releasing heat in the process. This heat can complicate low temperature hydrogen processes, particularly liquefaction.

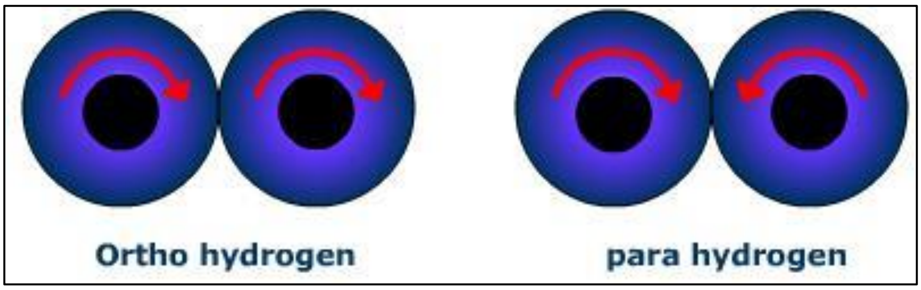


Figure 3. Ortho- and Para-Hydrogen

1.1.3. Composition of Other Fuels

Methane is 84 times more potent than CO_2 in the short term. Other common hydrocarbons are ethane (C^2H^6), propane (C^3H^8) and butane (C^4H^{10}). These are all considered light hydrocarbons since they contain less than five carbon atoms per molecule and therefore have low molecular weight (a carbon atom is almost 12 times as heavy as a hydrogen atom).
Gasoline is composed of a mixture of many different hydro-carbons, but an important constituent is heptane (C^7H^{16}).

The lightest hydrocarbons are gases at normal atmospheric pressure and temperature. Heavier hydrocarbons, with 5 to 18 carbon atoms per compound, are liquid at ambient conditions and have increasing viscosity with molecular weight.

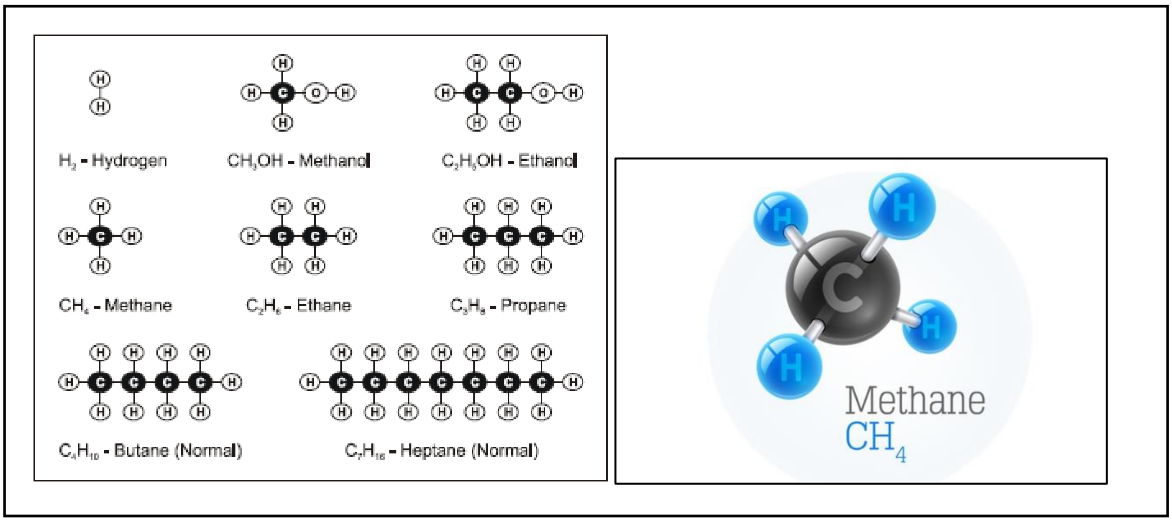


Figure 4. Fuel compositions

1.2. The Physical and Chemical Properties of Hydrogen

Each substance has a characteristic boiling temperature and freezing temperature (at a given pressure). The process of condensation is also known as liquefaction and the process of freezing is also known as solidification. Obviously, these temperatures are extremely low. Temperatures below –100 ºF (200 K; –73 ºC) are collectively known as cryogenic temperatures, and liquids at these temperatures are known as cryogenic liquids.

Boiling and freezing temperatures are most meaningfully compared relative to **"absolute zero".** Absolute zero (0 ºR; 0 K; –273.15 ºC) is the lowest temperature in the universe at which all molecular motion stops.

Hydrogen has the second lowest boiling point and melting points of all substances, second only to helium. Hydrogen is a liquid below its **boiling point of 20 K** (–253 ºC) and a solid below its **melting point of 14 K** (–259 ºC) and atmospheric pressure. Unfortunately, hydrogen's boiling point can only be increased to a maximum of (–240 ºC) through the application of approximately 195 psig (13 barg), beyond which additional pressure has no beneficial effect. Hydrogen as a vehicle fuel can be stored either as a high-pressure gas or as a cryogenic liquid.

1.2.1. Odor, Color, Taste and Toxicity

Pure hydrogen is odorless, colorless and tasteless. Compounds such as mercaptans and thiophanes that are used to scent natural gas may not be added to hydrogen for fuel cell use as they contain sulfur that would poison the fuel cells. Hydrogen that derives from reforming other fossil fuels is typically accompanied by nitrogen, carbon dioxide, carbon monoxide and other trace gases. In general, all of these gases are also odorless, colorless and tasteless. It is non-toxic but can act as a simple asphyxiant.

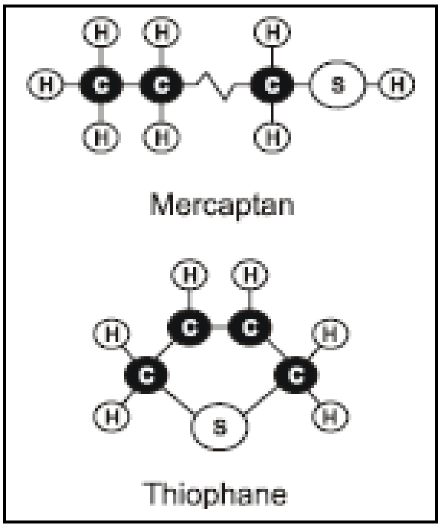


Figure 5. Mercaptans and Thiophanes compounds

1.2.2. Asphyxiation

Oxygen levels below 19.5% are biologically inactive for humans. Effects of oxygen deficiency may include rapid breathing, diminished mental alertness, impaired muscular coordination, faulty judgement, depression of all sensations, emotional instability and fatigue.

As asphyxiation progresses, dizziness, nausea, vomiting, prostration and loss of consciousness may result, eventually leading to convulsions, coma and death. At concentrations below 12%, immediate unconsciousness may occur with no prior warning symptoms.

In an enclosed area, small leaks pose little danger of asphyxiation whereas large leaks can be a serious problem since the hydrogen diffuses quickly to fill the volume. The potential for asphyxiation in unconfined areas is almost negligible due to the high buoyancy and diffusivity of hydrogen.

- Inhaled hydrogen can result in a flammable mixture within the body.
- Inhaling hydrogen can lead to unconsciousness and asphyxiation.

1.2.3. Density and Related Measures

Hydrogen has lowest atomic weight of any substance and therefore has very low density both as a gas and a liquid. Density is measured as the amount of mass contained per unit volume. Density values only have meaning at a specified temperature and pressure since both of these parameters affect the compactness of the molecular arrangement, especially in a gas. The density of a gas is called its vapor density, and the density of a liquid is called its liquid density. A common way of expressing relative density is as specific gravity. Specific gravity is the ratio of the density of one substance to that of a reference substance, both at the same temperature and pressure.

Table 1. Density and related measures for distinct substances

Substance	Vapor Density (at 20 ºC, 1 atm)	Liquid Density (at normal boiling point, 1 atm)
Hydrogen	0.08376 kg/m^3 (approximately 7% the density of air)	70.8 kg/m^3 (7% the density of water, *Specific Gravity*)
Methane	0.65 kg/m^3	422.8 kg/m^3
Gasoline	4.4 kg/m^3	700 kg/m^3

- 1kg/ 0.08376 kg/m^3 = 11,93 m^3
  Meaning: 1 kg of gaseous hydrogen at STP occupies nearly 12 cubic meters of volume

1.2.4. Expansion Ratio

Hydrogen’s expansion ratio from liquid to gas is **1:848**. Never trap liquid hydrogen in a system. Always install pressure relief valves/devices where liquid hydrogen could get trapped.

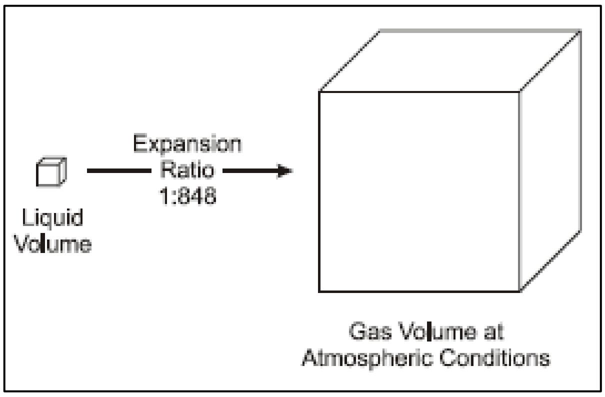


Figure 6. Hydrogen’s expansion ratio

1.2.5. Leakage

The molecules of hydrogen gas are smaller than all other gases, and it can diffuse through many materials considered airtight or impermeable to other gases. This property makes hydrogen more difficult to contain than other gases. Leaks of liquid hydrogen evaporate very quickly since the boiling point of liquid hydrogen is so extremely low.

When used as vehicle fuel, the propensity for hydrogen to leak necessitates special care in the design of the fuel system to **ensure that any leaks can disperse** with minimum hindrance, and the **use of dedicated leak detection equipment** on the vehicle and within the maintenance facility.

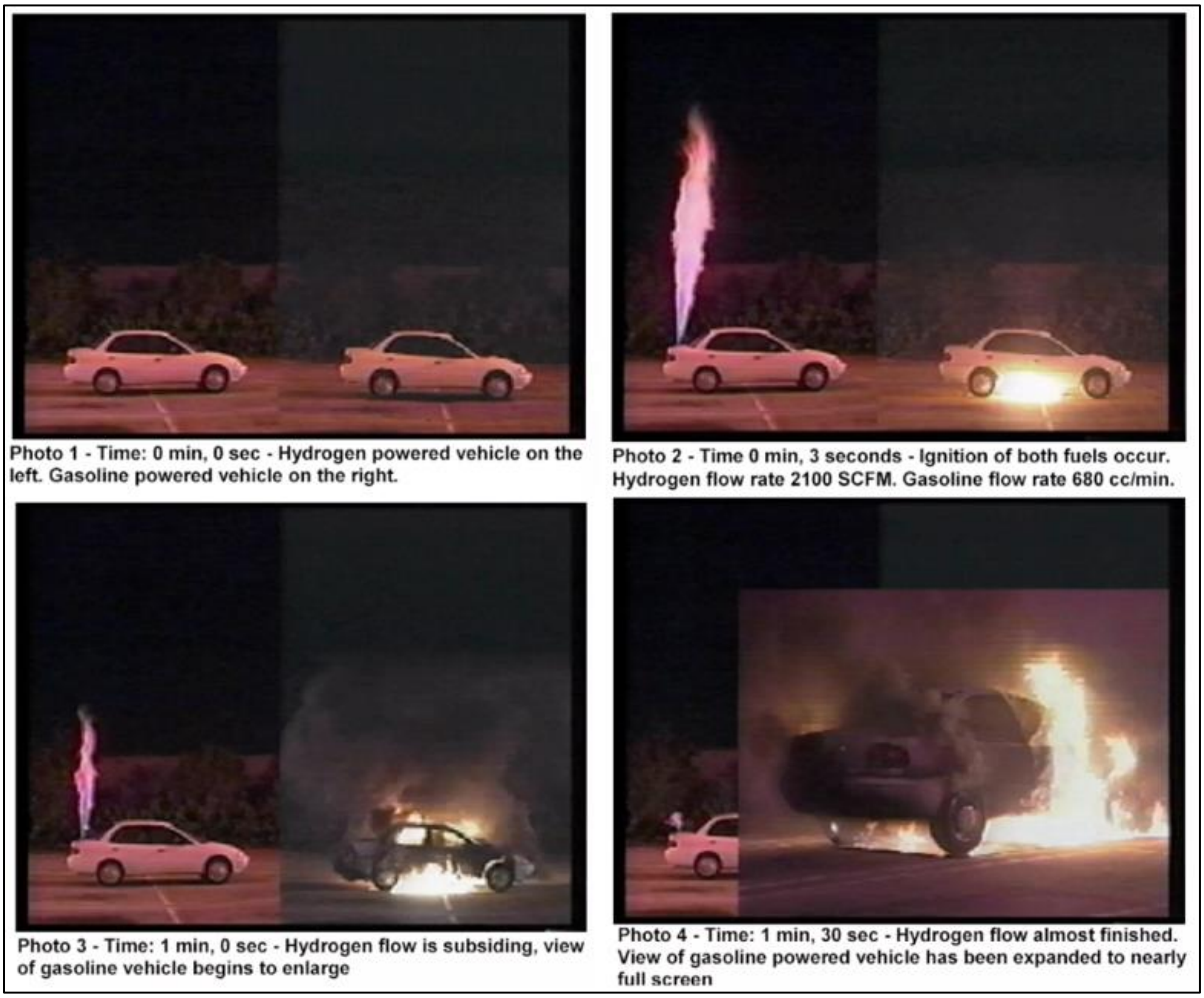


Photo 1 - Time: 0 min, 0 sec - Hydrogen powered vehicle on the left. Gasoline powered vehicle on the right.

Photo 2 - Time 0 min, 3 seconds - Ignition of both fuels occur. Hydrogen flow rate 2100 SCFM. Gasoline flow rate 680 cc/min.

Photo 3 - Time: 1 min, 0 sec - Hydrogen flow is subsiding, view of gasoline vehicle begins to enlarge

Photo 4 - Time: 1 min, 30 sec - Hydrogen flow almost finished. View of gasoline powered vehicle has been expanded to nearly full screen

Figure 7. Hydrogen and gasoline Leakage when used as a vehicle fuel

Hydrogen leaks are dangerous in that they pose a risk of fire where they mix with air. However, the small molecule size that increases the likelihood of a leak also results in very high buoyancy and diffusivity, so leaked hydrogen rises and becomes diluted quickly, especially out-doors. This results in a very localized region of flammability that disperses quickly. As the hydrogen dilutes with distance from the leakage site, the buoyancy declines and the tendency for the hydrogen to continue to rise decreases. Very cold hydrogen, resulting from a liquid hydrogen leak, becomes buoyant soon after is evaporates.

In contrast, leaking gasoline or diesel spreads laterally and evaporates slowly resulting in a widespread, lingering fire hazard. Propane gas is denser than air so it accumulates in low spots and disperses slowly, resulting in a protracted fire or explosion hazard. Heavy vapors can also form vapor clouds or plumes that travel as they are pushed by breezes. Methane gas is lighter than air, but not nearly as buoyant as hydrogen, so it disperses rapidly, but not as rapidly as hydrogen.

For small hydrogen leaks, buoyancy and diffusion effects in air are often overshadowed by the presence of air currents from a slight ambient wind, very slow vehicle motion or the radiator fan. In general, these currents serve to disperse leaked hydrogen even more quickly with a further reduction of any associated fire hazard.

1.2.6. Reactivity

High reactivity is characteristic of all chemical fuels. In each case, a chemical reaction occurs when the fuel molecules form bonds with oxygen (from air) so that the final, reacted molecules are at a lower energy state than the initial, unreacted molecules. The change in chemical energy state is accompanied by a corresponding release of energy that we can exploit to do useful work. Chemical reactions of this type often require a small amount of activation energy to get started, but then the energy released by the reaction feeds further reaction in a domino effect. The water-forming reaction of hydrogen and oxygen is reversible. This is the principle behind hydrogen production through electrolysis.

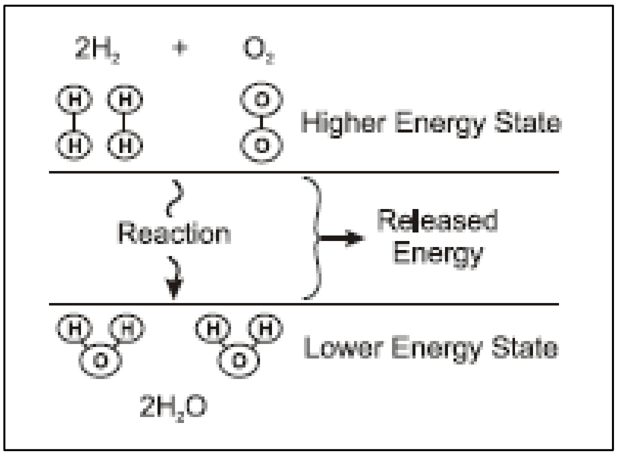


Figure 8. Chemical reactions

1.3. Chemical By-Products of Fuel Reactions

All of the atoms present at the start of a reaction are present at the end of the reaction although they may be reorganized into different molecules. Oxygen reacts with carbon to form carbon monoxide (CO) and carbon dioxide (CO^2). Oxygen reacts with nitrogen to form oxides of nitrogen (NOx). Oxygen reacts with sulphur to form oxides of sulphur (SOx).

Hydrocarbon emissions pass into the atmosphere through incomplete combustion and evaporation. Hydrogen is a nearly ideal fuel in terms of smog reduction when combusted. Hydrogen contains no carbon or sulphur, so no CO, CO^2 or SOx or soot is produced during combustion. Hydrogen is an ideal fuel in terms of smog reduction when used electrochemically in a fuel cell, rather than combusted.

Discussion →

CONTINUOUS ASSESSMENT 1:

-------- End of Block 1 --------

-------- BLOCK 2 --------

2.1. How Hydrogen Compares to Hydrocarbon Fuels in Terms of Energy, Flammability and Safety

2.1.1. Energy Content

Every fuel can liberate a fixed amount of energy when it reacts completely with oxygen to form water. This energy content is measured experimentally and is quantified by a fuel's higher heating value (HHV) and lower heating value (LHV). The difference between the HHV and the LHV is the "heat of vaporization" and represents the amount of energy required to vaporize a liquid fuel into a gaseous fuel, as well as the energy used to convert water to steam.

- Hydrogen has the highest energy-to-weight ratio of any fuel since hydrogen is the lightest element and has no heavy carbon atoms. It is for this reason that hydrogen has been used extensively in the space pro-gram where weight is crucial.
- Specifically, the amount of energy liberated during the reaction of hydrogen, on a mass basis, is about 2.5 times the heat of combustion of common hydrocarbon fuels (gasoline, diesel, methane, propane, etc.) Therefore, for a given load duty, the mass of hydrogen required is only about a third of the mass of hydrocarbon fuel needed.
- The high energy content of hydrogen also implies that:
    - The energy of a hydrogen gas explosion is about 2.5 times that of common hydrocarbon fuels.
    - Thus, on an equal mass hydrogen gas explosions are more destructive and carry further.
    - However, the duration of a conflagration tends to be inversely proportional to the combustive energy, so that hydrogen fires subside much more quickly than hydrocarbon fires.

Table 2. Energy content Details with comparison to Gasoline

Fuel	HHV (at 25 ºC and 1 atm)	Comparison to Gasoline	LHV (at 25 ºC and 1 atm)	Comparison to Gasoline
Hydrogen	**141.86 kJ/g**	**2.99**	**119.93 kJ/g**	**2.70**
Methane	55.53 kJ/g	1.17	50.02 kJ/g	1.12

Propane	50.36 kJ/g	1.06	45.6 kJ/g	1.02
Gasoline	**47.5 kJ/g**	**1**	**44.5 kJ/g**	**1**
Diesel	44.8 kJ/g	0.94	42.5 kJ/g	0.96

2.1.2. Energy Density

Energy density is the product of the energy content (LHV in our case) and the density of a given fuel (Energy content x density of fuel). The energy density is really a measure of how compactly hydrogen atoms are packed in a fuel. It follows that hydrocarbons of increasing complexity (with more and more hydrogen atoms per molecule) have increasing energy density. At the same time, hydrocarbons of increasing complexity have more and more carbon atoms in each molecule so that these fuels are heavier and heavier in absolute terms. On this basis, hydrogen's energy density is poor (since it has such low density) although its energy to weight ratio is the best of all fuels (because it is so light). The energy density of a lead acid battery is approximately 8700 Btu/ft3 (324,000 kJ/m3).

- The energy density of a fuel is also affected by whether the fuel is stored as a liquid or as a gas, and if a gas, at what pressure.
- To put it into perspective: a (500-L) diesel tank containing (400 kg) of fuel is equivalent on an energy basis to a (8000 L) volume of hydrogen gas at (250 barg). This is a 16 times increase in volume, although the weight of the hydrogen is only (150 kg), representing a decrease in fuel weight by a factor of about 2.8.
- The same diesel tank is equivalent to a (2100-L) tank of liquid hydrogen. This is a 4.2 times increase in volume.
- If hydrogen is stored as a metal hydride, every kilogram of diesel fuel is replaced by approximately 4.5 kg of metal hydride to maintain the same hydrogen/diesel energy equivalence.
- Thus, the same (500 L) diesel tank containing (400 kg) of fuel would have to be re-placed with a hydride tank containing (1725 kg) of "fuel" mass.
- The energy density of comparative fuels, based on the LHV, is indicated in Table next slide.

Table 3. Energy density details

Fuel	Energy Density (LHV)
Hydrogen	(10,050 kJ/m3); gas at 1 atm and (15 ºC)

	(1,825,000 kJ/m3); gas at (200 barg) and (15 ºC) (4,500,000 kJ/m3); gas at (690 barg) and (15 ºC) (8,491,000 kJ/m3); liquid
Methane	(32,560 kJ/m3); gas at 1 atm and (15 ºC) (6,860,300 kJ/m3); gas at (200 barg) and (15 ºC) (20,920,400 kJ/m3); liquid
Propane	(86,670 kJ/m3); gas at 1 atm and (15 ºC) (23,488,800 kJ/m3); liquid
Gasoline	(31,150,000 kJ/m3); liquid
Diesel	(31,435,800 kJ/m3) minimum; liquid
Methanol	(15,800,100 kJ/m3); liquid

2.1.3. The Flashpoint

All fuels burn only in a gaseous or vapor state. Fuels like hydrogen and methane are already gases at atmospheric conditions, whereas other fuels like gasoline or diesel that are liquids must convert to a vapor before they will burn. The characteristic that describes how easily these fuels can be converted to a vapor is the flashpoint.

The flashpoint is defined as the temperature at which the fuel produces enough vapors to form an ignitable mixture with air at its surface. If the temperature of the fuel is below its flashpoint, it can-not produce enough vapors to burn since its evaporation rate is too slow. Whenever a fuel is at or above its flashpoint, vapors are present.

The flashpoint is not the temperature at which the fuel bursts into flames; that is the autoignition temperature. The flashpoint is always lower than the boiling point. For fuels that are gases at atmospheric conditions (like hydrogen, methane and propane), the flashpoint is far below ambient temperature and has little relevance since the fuel is already fully vaporized. For fuels that are liquids at atmospheric conditions (such as gasoline or methanol), the flash-point acts as a lower flammability temperature limit.

Table 4. The flashpoint details

Fuel	Flashpoint

Hydrogen	(< –253 ºC; 20 K)
Methane	(–188 ºC; 85 K)
Propane	(–104 ºC; 169 K)
Gasoline	Approximately (–43 ºC; 230 K)
Methanol	(11 ºC; 284 K)

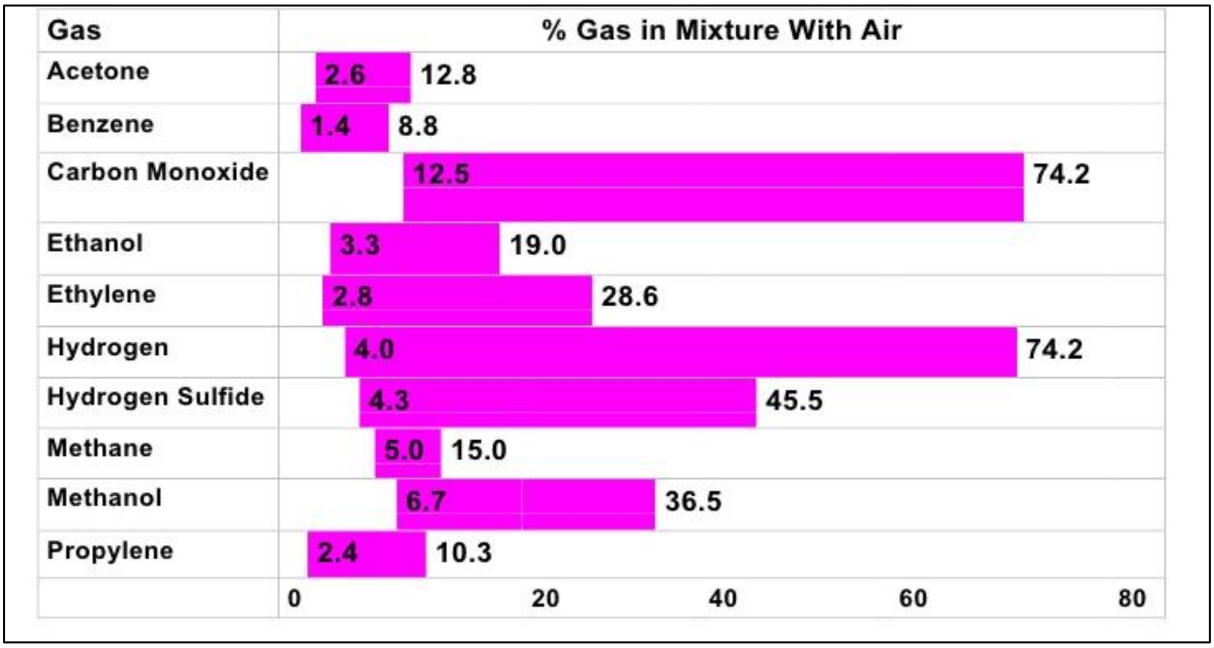
2.1.4. The Flammability Range

The flammability range of a gas is defined in terms of its lower flammability limit (LFL) and its upper flammability limit (UFL). The LFL of a gas is the lowest gas concentration that will support a self-propagating flame when mixed with air and ignited. Below the LFL, there is not enough fuel present to support combustion; the fuel/air mixture is too lean. The UFL of a gas is the highest gas concentration that will support a self-propagating flame when mixed with air and ignited. Above the UFL, there is not enough oxygen present to support combustion; the fuel/air mixture is too rich. Between the two limits is the flammable range in which the gas and air are in the right proportions to burn when ignited.

A stoichiometric mixture occurs when oxygen and hydrogen molecules are present in the exact ratio needed to complete the combustion reaction. If more hydrogen is available than oxygen, the mixture is rich so that some of the fuel will remain unreacted although all of the oxygen will be consumed. If less hydrogen is available than oxygen, the mixture is lean so that all the fuel will be consumed but some oxygen will remain.

Practical internal combustion and fuel cell systems typically operate lean since this situation promotes the complete reaction of all available fuel. One consequence of the UFL is that stored hydrogen (whether gaseous or liquid) is not flammable while stored due to the absence of oxygen in the cylinders. The fuel only becomes flammable in the peripheral areas of a leak where the fuel mixes with the air in sufficient proportions.

Table 5. The flammability range of distinct gases



The flammability limits increase with temperature. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion.

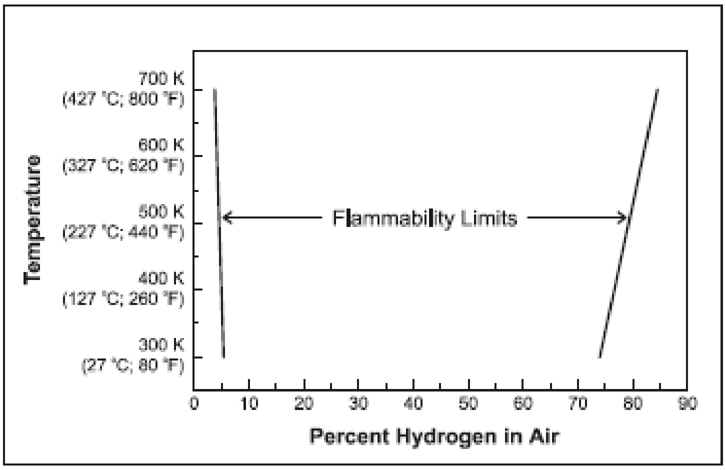


Figure 9. The flammability limits graph

2.1.5. Explosive Limit

Two related concepts are the lower explosive limit (LEL) and the upper explosive limit (UEL). The LEL is the lowest gas concentration that will support an explosion when mixed with air, contained and ignited. Similarly, the UEL is the highest gas concentration that will support an explosion when mixed with air, contained and ignited.

An explosion is different from a fire in that for an explosion, the combustion must be contained, allowing the pressure and temperature to rise to levels sufficient to violently destroy the containment. For this reason, it is far more dangerous to release hydrogen into an enclosed area (such as a building) than to release it directly outdoors.

Hydrogen is flammable over a very wide range of concentrations in air (4 – 75%) and it is explosive over a wide range of concentrations (15 – 59%) at standard atmospheric temperature.

The flammability limits increase with temperature as illustrated in next figure. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion. Mixtures of hydrogen and air are potentially flammable or explosive.

2.1.6. Autoignition Temperature

The autoignition temperature is the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. In other words, the fuel is heated until it bursts into flame.

Each fuel has a unique ignition temperature. For hydrogen, the autoignition temperature is relatively high at 1085 ºF (585 ºC). This makes it difficult to ignite a hydrogen/air mixture on the basis of heat alone without some additional ignition source.

Table 6. The autoignition temperature

Fuel	Autoignition Temperature
Hydrogen	(585 ºC)
Methane	(540 ºC)
Propane	(490 ºC)
Methanol	(385 ºC)
Gasoline	(230 to 480 ºC)

2.1.7. Octane Number

The octane number describes the anti-knock properties of a fuel when used in an internal combustion engine. Knock is a secondary detonation that occurs after fuel ignition due to heat buildup in some other part of the combustion chamber. When the local temperature exceeds the auto-ignition temperature, knock occurs.

The performance of the hydrocarbon octane is used as a standard to measure resistance to knock and is assigned a relative octane rating of 100. Fuels with an octane number over 100 have more resistance to auto-ignition than octane itself. Hydrogen has a very high research octane number and is therefore resistant to knock even when combusted under very lean conditions. The octane number has no specific relevance for use with fuel cells.

Table 7. The autoignition temperature

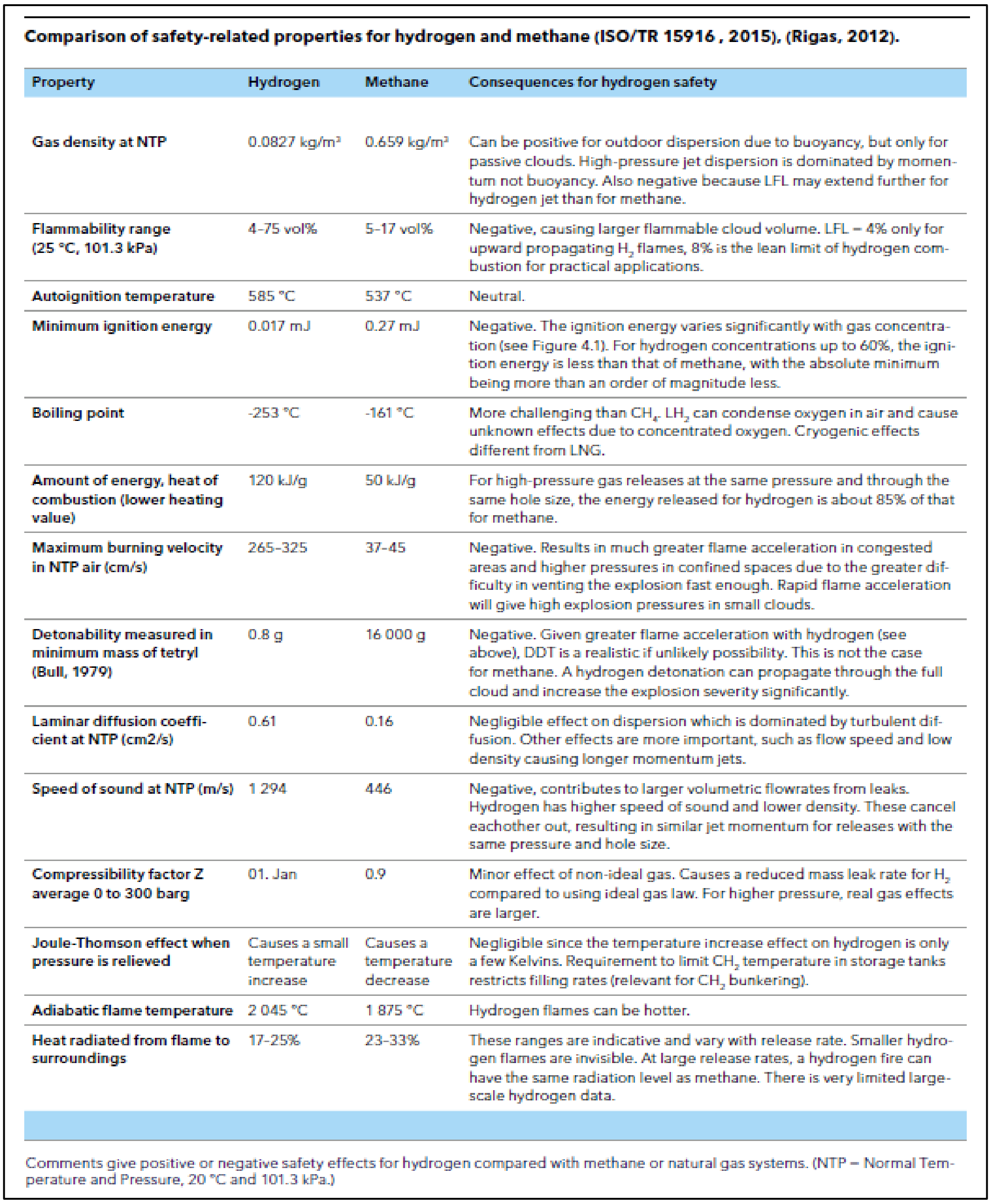
Fuel	Octane Number
Hydrogen	130+ (lean burn)
Methane	125
Propane	105
Octane	100
Gasoline	87
Diesel	30

2.1.8. Ignition Energy

Ignition energy is the amount of external energy that must be applied in order to ignite a combustible fuel mixture. Although hydrogen has a higher autoignition temperature than methane, propane or gasoline, its ignition energy at (0.02 mJ) is about an order of magnitude lower and is therefore more easily ignitable.

Hydrogen has the added property of low electro-conductivity so that the flow or agitation of hydrogen gas or liquid may generate electrostatic charges that result in sparks. For this reason, all hydrogen conveying equipment must be thoroughly grounded. Flammable mixtures of hydrogen and air can be easily ignited.

Table 8. Comparison of safety-related properties for hydrogen and methane



Comparison of safety-related properties for hydrogen and methane (ISO/TR 15916 , 2015), (Rigas, 2012).

Property	Hydrogen	Methane	Consequences for hydrogen safety
Gas density at NTP	0.0827 kg/m³	0.659 kg/m³	Can be positive for outdoor dispersion due to buoyancy, but only for passive clouds. High-pressure jet dispersion is dominated by momentum not buoyancy. Also negative because LFL may extend further for hydrogen jet than for methane.
Flammability range (25 °C, 101.3 kPa)	4-75 vol%	5-17 vol%	Negative, causing larger flammable cloud volume. LFL = 4% only for upward propagating H_2 flames, 8% is the lean limit of hydrogen combustion for practical applications.
Autoignition temperature	585 °C	537 °C	Neutral.
Minimum ignition energy	0.017 mJ	0.27 mJ	Negative. The ignition energy varies significantly with gas concentration (see Figure 4.1). For hydrogen concentrations up to 60%, the ignition energy is less than that of methane, with the absolute minimum being more than an order of magnitude less.
Boiling point	-253 °C	-161 °C	More challenging than CH_4. LH_2 can condense oxygen in air and cause unknown effects due to concentrated oxygen. Cryogenic effects different from LNG.
Amount of energy, heat of combustion (lower heating value)	120 kJ/g	50 kJ/g	For high-pressure gas releases at the same pressure and through the same hole size, the energy released for hydrogen is about 85% of that for methane.
Maximum burning velocity in NTP air (cm/s)	265-325	37-45	Negative. Results in much greater flame acceleration in congested areas and higher pressures in confined spaces due to the greater difficulty in venting the explosion fast enough. Rapid flame acceleration will give high explosion pressures in small clouds.
Detonability measured in minimum mass of tetryl (Bull, 1979)	0.8 g	16 000 g	Negative. Given greater flame acceleration with hydrogen (see above), DDT is a realistic if unlikely possibility. This is not the case for methane. A hydrogen detonation can propagate through the full cloud and increase the explosion severity significantly.
Laminar diffusion coefficient at NTP (cm2/s)	0.61	0.16	Negligible effect on dispersion which is dominated by turbulent diffusion. Other effects are more important, such as flow speed and low density causing longer momentum jets.
Speed of sound at NTP (m/s)	1 294	446	Negative, contributes to larger volumetric flowrates from leaks. Hydrogen has higher speed of sound and lower density. These cancel eachother out, resulting in similar jet momentum for releases with the same pressure and hole size.
Compressibility factor Z average 0 to 300 barg	01. Jan	0.9	Minor effect of non-ideal gas. Causes a reduced mass leak rate for H_2 compared to using ideal gas law. For higher pressure, real gas effects are larger.
Joule-Thomson effect when pressure is relieved	Causes a small temperature increase	Causes a temperature decrease	Negligible since the temperature increase effect on hydrogen is only a few Kelvins. Requirement to limit CH_4 temperature in storage tanks restricts filling rates (relevant for CH_4 bunkering).
Adiabatic flame temperature	2 045 °C	1 875 °C	Hydrogen flames can be hotter.
Heat radiated from flame to surroundings	17-25%	23-33%	These ranges are indicative and vary with release rate. Smaller hydrogen flames are invisible. At large release rates, a hydrogen fire can have the same radiation level as methane. There is very limited large-scale hydrogen data.

Comments give positive or negative safety effects for hydrogen compared with methane or natural gas systems. (NTP = Normal Temperature and Pressure, 20 °C and 101.3 kPa.)

2.1.9. Flame Characteristics

Hydrogen flames are almost invisible in daylight. Corn brooms are used by emergency personnel to detect hydrogen flames.

Figure 10. Visual upshot of hydrogen flame

Hydrogen fires can only exist in the region of a leak where pure hydrogen mixes with air at sufficient concentrations. For turbulent leaks, air reaches the centerline of the leakage jet within about five diameters of a leakage hole, and the hydrogen is diluted to nearly the composition of air within roughly 500 to 1000 diameters.

In many respects, hydrogen fires are safer than gasoline fires. Hydrogen gas rises quickly due to its high buoyancy and diffusivity. Consequently hydrogen fires are vertical and highly localized. When a car hydrogen cylinder ruptures and is ignited, the fire burns away from the car and the interior typically does not get very hot.

Courtesy Michael Swain/U.S. DOT

Figure 11. Visual upshot of fire coming from hydrogen cylinder car

2.1.10. Hydrogen Embrittlement

Constant exposure to hydrogen causes a phenomenon known as hydrogen embrittlement in many materials. Hydrogen embrittlement can lead to leakage or catastrophic failures in metal and non-metallic components. There are many factors that influence the rate and severity of hydrogen embrittlement.

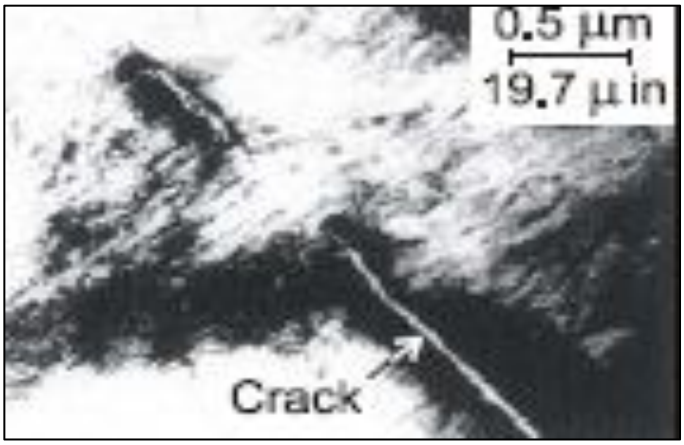


Figure 11. Image of hydrogen embrittlement

2.1.11. Flammability of Hydrogen in Air

With 4%-75% hydrogen, very little energy is required to ignite hydrogen. The speed of a hydrogen fire is ten feet per second to 4600 mph.

- 4% Barely burn and even then only upward
- 5% Fire starts burning sideways
- 18% Fire will now burn faster than the speed of sound
- 45% Burning at 4600 mph-including shock wave
- 74% Barely burn 75% Will not burn-no air

Oxygen and hydrogen mixed-speed approximately 8000 mph. The speed of sound is 1050 feet per second.

2.1.12. Flammability Safety Precautions

- Eliminate ignition sources
- NO SMOKING! NO OPEN FLAMES!
- Use only non-sparking tools
- No synthetic clothing (nylon, etc.)
- Electrical equipment-explosion proof, intrinsically safe or purged

- Bonding and grounding

2.1.13. Hydrogen Fires

A hydrogen flame is invisible under many conditions Hydrogen flames cause little damage from radiation Hydrogen flames can burn in a strong wind and be stretched out away from its source a number of feet. Any venting should be done carefully to prevent accumulation in pockets which may cause an explosive mixture

2.1.14. Hydrogen Fire Fighting

The following cares should be taken to avoid or to control the hydrogen fire situation.

- Shut off the source and allow the fire to burn out
- Daylight fires can be detected by heat waves or a broom
- If the fire is extinguished before all the gas burns off, watch for pockets which may suddenly re- ignite
- Very small fires can be controlled with carbon dioxide and water spray
- Larger fires may be controlled with steam and/or nitrogen
- Tanks containing hydrogen should be cooled with water if near a fire
- Hydrogen vent stack fires can be extinguished by shutting off the source and snuffing the fire with nitrogen or helium gas
- WATER SHOULD NEVER BE SPRAYED ON OR NEAR A VENT STACK!!!
- Make sure nitrogen or steam line is attached securely

2.2. Hydrogen Production Pathways

Nearly all of the hydrogen used in the United States (95 percent) is produced through a process called steam methane reforming. This process breaks down methane (CH4), a hydrocarbon, into hydrogen and carbon dioxide (CO2).

The methane in natural gas is reacted with water (in the form of high-temperature steam) to produce carbon monoxide and hydrogen. These gases are reacted with water again, in a process called a water shift reaction, to produce more hydrogen and CO2.

2.2.1. Gasification

Gasification processes include a series of chemical reactions in which coal or biomass is “gasified” (i.e., converted into gaseous components) using heat and steam. A series of chemical reactions is then used to produce a synthesis gas (a gas mixture that contains varying amounts of carbon monoxide and hydrogen), which is reacted with steam to produce more hydrogen.

Producing hydrogen via coal gasification is significantly more efficient than burning coal to produce electricity that is then used in electrolysis. Although gasification technology is commercially available, the challenge is lowering the amount of CO2 emitted from the process to decrease upstream emissions from the use of FCEVs.

Coal gasification with carbon capture and sequestration (CCS) or biomass gasification can produce hydrogen with very low or no net GHG emissions, although both these technologies are only in the early stages of commercial-scale deployment.

2.2.2. Electrolysis

In electrolysis, an electric current is used to split water into hydrogen and oxygen. Electrolysis is in advanced stages of technological development and could play an important role in the near to midterm. Net GHG emissions from electrolysis for hydrogen production depend on the source of the electricity used. If powered by electricity from low-carbon sources (i.e., renewable technologies, nuclear, power, or fossil fuels coupled with CCS), the process generates little to no GHG emissions.

With nuclear high-temperature electrolysis, the efficiency of the process increases. In this type of electrolysis, the heat from the nuclear reactor is used to increase the water temperature and thereby reduce the amount of electricity needed for electrolysis.

2.2.3. High-Temperature Thermochemical Water-Splitting

This is another water-splitting method that uses high temperatures from nuclear reactors or from solar concentrators (lenses that focus and intensity sunlight) to generate a series of chemical reactions that split water, producing hydrogen.

The process is in the early stages of development but considered a potential long-term technology, since it is powered by non-GHG emitting technologies and yields a very low-carbon hydrogen fuel.

2.2.4. Photobiological and Photoelectrochemical Processes

These processes use energy from sunlight to produce hydrogen, although both are currently in early stages of research. Photobiological processes use microbes, such as green algae and cyanobacteria. When these microbes consume water in the presence of sunlight, hydrogen is produced as a byproduct of their metabolic processes. Using special semiconductors and sunlight, photoelectrochemical systems produce hydrogen from water as well.

2.3. Hydrogen Distribution

Currently, there is no infrastructure for distributing hydrogen, like that for fossil fuels. Because hydrogen has less energy per unit volume, distribution costs are higher than those for gasoline or diesel. Most hydrogen is produced either on-site or near where it is used, usually at large industrial sites. It is then distributed by pipeline, high-pressure tube trailers, or liquefied hydrogen tankers. Pipeline is the least expensive way to distribute hydrogen; the last two, while more expensive, can be transported using different modes of transportation – truck, railcar, ship, or barge.

Building network of pipelines and filling stations for FCVs would require high initial capital costs. One potential solution is to produce hydrogen regionally or locally to limit issues with distribution.

A second is to use a phased approach: At first, hydrogen distribution (and sales of FCVs) could be concentrated in a few key areas. The next phase would expand the distribution sales network by targeting geographic corridors and then gradually expand to other regions. This phased approach would remove the need for stations all across the nation at the outset, and allow for a slower and affordable build-up in the number of stations and areas served over time.

Suggested Reading and Discussion →

CONTINUOUS ASSESSMENT 2:

-------- End of Block 2 --------

References

Industrial Metallurgists, L. (2016, SEPTEMBER 15). Hydrogen Embrittlement of Steel. Retrieved from imetllc.com: https://www.imetllc.com/hydrogen-embrittlement- steel/#:~:text=Hydrogen%20embrittlement%20is%20a%20metal's, yield%20strength%20of% 20the%20metal.

Pfeifer, M. (2022, January 24). An Introduction to Hydrogen Embrittlement. Retrieved from https://www.corrosionpedia.com/: https://www.corrosionpedia.com/an-introduction-to- hydrogen-embrittlement/2/2568

TZIMAS, E., FILIOU, C., PETEVES, S., & VEYRET, J. (2003). HYDROGEN STORAGE: STATE-OF-THE-ART AND FUTURE PERSPECTIVE. Luxembourg: Office for Official Publications of the European Communities.

Wikipedia. (2022, March 06). Hydrogen embrittlement. Retrieved from en.wikipedia.org: https://en.wikipedia.org/wiki/Hydrogen_embrittlement#cite_note-31

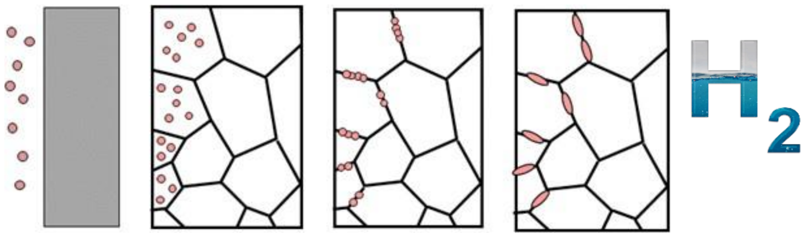
Figures and tables are referenced in caption when applicable.

-------- BLOCK 3 --------

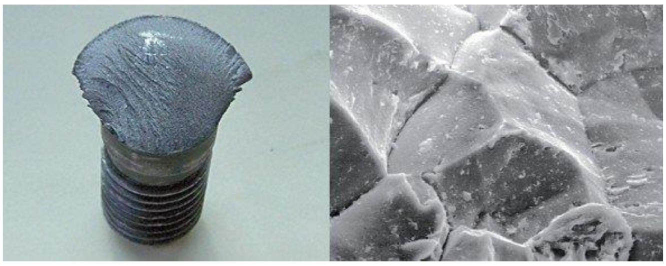
3.1. Hydrogen Embrittlement

Hydrogen embrittlement (HE) also known as hydrogen assisted cracking or hydrogen- induced cracking is the process a material goes through when it comes in contact with forms of hydrogen. This process causes the material to lose ductility, making the material brittle and prone to the propagation of fractures and cracks in the material. Hydrogen may degrade the mechanical behaviour of metallic materials used in the hydrogen infrastructure (e.g., storage tanks, pipelines, etc.) and lead them to failure.

These cracks may also allow hydrogen to pass through the material surface into the surrounding area posing potential safety risks as well as contamination in some systems.



(a) Image Link -https://www.imetllc.com/wp-content/uploads/2016/09/Hydrogen-embrittlement.png



(b) Image Link - https://www.imetllc.com/wp-content/uploads/2016/09/BoltAndFractureSurface.jpg

(C) Image Link - https://upload.wikimedia.org/wikipedia/commons/9/99/Steel-with-Hydrogen-Induced-Cracks-01.jpg

Figure 1. Hydrogen-embrittlement in (a), Bolt and Fracture Surface in (b), Steel-with-Hydrogen-Induced-Cracks in (c)

3.1.1. Hydrogen Embrittlement Issues

Hydrogen embrittlement has been recognized classically as being of two types:

- **Internal hydrogen embrittlement**: This occurs when the hydrogen enters molten metal which becomes supersaturated with hydrogen immediately after solidification.
- **Environmental hydrogen embrittlement**: This results from hydrogen being absorbed by solid metals. It can occur during elevated-temperature thermal treatments and in service during electroplating, contact with maintenance chemicals, corrosion reactions, cathodic protection, and operating in high-pressure hydrogen.

The material cracks allow hydrogen to pass through the material surface into the surrounding area posing potential safety risks as well as contamination in some systems.

In 2007, hydrogen explosion is noticed at the Muskingum River Power Plant. Due to a failed rupture disk on a storage vessel, a large quantity of hydrogen escaped and collected under a roof before it ignited, killing one and injuring 10 others.

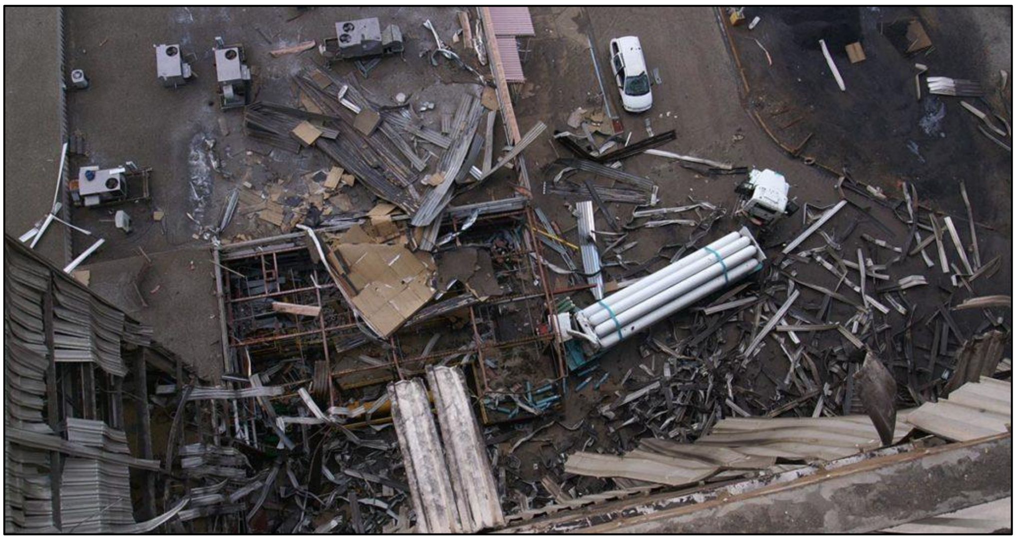


Image Link - https://wha-international.com/wp-content/uploads/2020/09/Muskungim-Power-Plant-Explosion-1024x536.jpg

Figure 2. Muskungim-Power-Plant-Explosion

3.1.2. Hydrogen Embrittlement Process

The reasons that cause it are still debated in the scientific community. In brief, the accumulation of hydrogen in a solid metal result in the reduction of its ductility thus increasing the probability of brittle fracture.

Hydrogen can cause embrittlement when present in a metal or alloy in its atomic form and not as a molecule. Solute hydrogen atoms in metals tend to concentrate in defects of the crystal structure (dislocations and grain boundaries among others), imposing a barrier to the movement of dislocations, effectively impeding the plastic flow of the material. As a result, the ductility of the metal decreases and the material becomes brittle.

An example of failure due to hydrogen embrittlement is shown in the figure below. In this figure, the left image shows a macroscopic view of a fractured, chromium-plated steel bolt and the right image shows a scanning electron microscope image of the fracture surface. The faceted appearance of the fracture surface is indicative of intergranular fracture. The bolt became embrittled during the chromium electroplating process.

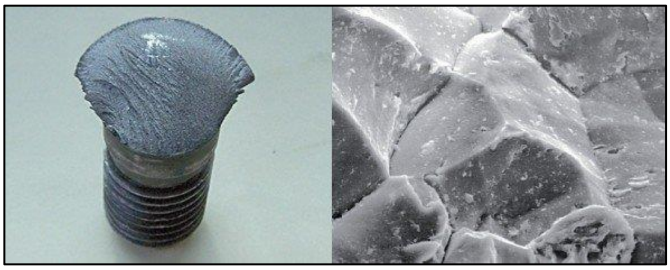


Image Link - https://www.imetllc.com/wp-content/uploads/2016/09/BoltAndFractureSurface.jpg

Figure 3. Bolt and Fracture Surface

3.1.3. Hydrogen Embrittlement Factors

Hydrogen embrittles a variety of metals including steel, aluminium (at high temperatures only), and titanium. Therefore, the embrittlement of materials used in hydrogen-related applications is a major practical issue.

High-strength carbon steel and low alloy steels are the alloys most vulnerable to hydrogen embrittlement. Steels with an ultimate tensile strength of less than 1000 MPa or hardness of less than 30 HRC are not generally considered susceptible to hydrogen embrittlement.

There are three required factors for failure due to hydrogen embrittlement:

- A susceptible material
- Exposure to an environment that contains hydrogen.
- The presence of tensile stress due to residual and/or applied stress.

3.2. Processes lead to Hydrogen Embrittlement

During manufacture, hydrogen can be dissolved into the component by processes such as phosphating, pickling, electroplating, casting, carbonizing, surface cleaning, electrochemical machining, welding, hot roll forming, and heat treatments. During use, hydrogen can be dissolved into the metal from wet corrosion, through misapplication of protection measures such as cathodic protection as well as chemical reactions of metal with acids, or with other chemicals.

Atomic hydrogen may enter the metal via several mechanisms:

- via dissolution during welding, while the metal melts locally dissolving hydrogen from water or other contaminants.
- via electrochemical processes, such as surface treating (e.g., electroplating or acid pickling) or aqueous corrosion, where molecular hydrogen dissociates into atoms that diffuse into the metal; or chemisorption, resulting from van der Waals forces between a metal surface and hydrogen molecules also resulting in the dissociation of the hydrogen molecules into atoms.

In the presence of hydrogen, stressed components may fail due to hydrogen- induced stress corrosion cracking, a type of damage understood as the formation of cracks by tensile stress in the presence of a corrosive hydrogen atmosphere.

3.3. Prevention of Hydrogen Embrittlement

Hydrogen embrittlement can be avoided or prevented through several methods, all of which are centred on minimizing contact between the metal and hydrogen:

- **Control of stress level (residual or load) and hardness.** For applications where there will be hydrogen absorption while a component is in service, the use of lower strength steels and reduction of residual and applied stress are ways to avoid fracture due to hydrogen embrittlement.
- **Avoiding the hydrogen source.** Understanding sources of hydrogen during manufacturing or service use is important in avoiding hydrogen dissolve into the material.
- **Baking (low hydrogen annealing) to remove hydrogen.** Hydrogen embrittlement of electroplated components can be prevented by baking them at 375 to 430 °F (190 to

220°C) within a few hours after the electroplating process. During baking, the hydrogen diffuses out of the metal.

- **Materials selection** is another way of preventing this problem. Certain metals or alloys are highly susceptible to this issue so choosing a material that is minimally affected while retaining the desired properties would also provide an optimal solution.

3.4. Evaluating for Hydrogen Embrittlement

Most analytical methods for hydrogen embrittlement involve evaluating the effects of internal hydrogen from production and/or external sources of hydrogen such as cathodic protection.

There are tests that can be performed to evaluate whether processing leads to hydrogen embrittlement:

- ➢ ASTM Standards. There are numerous ASTM standards for testing for hydrogen embrittlement such as ASTM F519 “Standard Test Method for Mechanical Hydrogen Embrittlement Evaluation of Plating Processes and Service Environments” or ASTM F1940 “Standard Test Method for Process Control Verification to Prevent Hydrogen Embrittlement in Plated or Coated Fasteners”.
- ➢ NACE TM0284-2003 (NACE International) Resistance to Hydrogen-Induced Cracking
- ➢ ISO 11114-4:2005 (ISO) Test methods for selecting metallic materials resistant to hydrogen embrittlement.

Discussion Tasks →

- Search for other methods preventing Hydrogen Embrittlement. Explain where are used and discuss their pros and cons.
- Explore other tests that can be performed to evaluate whether processing leads to hydrogen embrittlement.

CONTINUOUS ASSESSMENT 1:

-------- End of Block 1 --------

-------- BLOCK 4 --------

4.1. Properties of Hydrogen Compression

When hydrogen is utilised in a gaseous form it usually must be compressed to an elevated high-pressure level that can give satisfying energy densities. This process requires work to be done on the gas. Hydrogen compression is achieved by mechanical or non-mechanical compressors. Mechanical compressors are the most widespread type of compressors used nowadays and are based on the direct conversion of mechanical energy into gas energy.

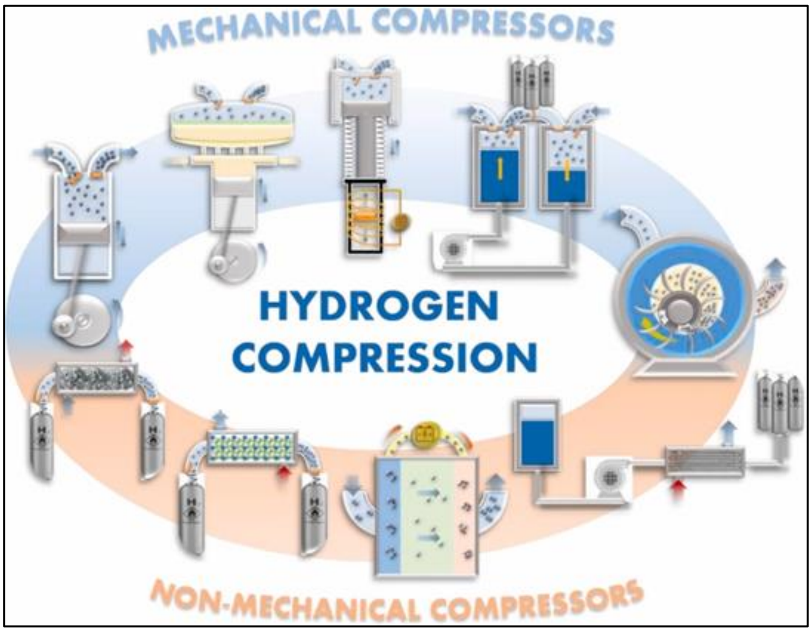


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Figure 4. Hydrogen compression via mechanical and non-mechanical processors

There are several types of hydrogen compressors available:

- Reciprocating piston compressor
- Ionic liquid piston compressor
- Electrochemical compressor
- Metal hydride hydrogen compressor
- Piston-metal diaphragm compressor
- Adsorption compressor

4.1.1. Reciprocating Compressors

A single-stage reciprocating compressor consists of a piston-cylinder system, equipped with two automatic valves – one for intake and one for delivery. The piston is linked to a crankshaft by a connecting rod, converting the rotary motion of the moving units into the almost linear motion of the piston. This movement is known as reciprocating motion. The energy necessary for the compression is provided by either an electrical or a thermal machine.

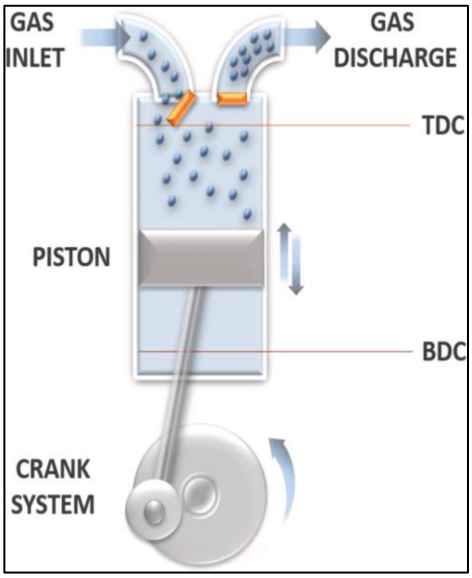

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Figure 5. Reciprocating compressor

The piston movement towards the upper side of the cylinder, i.e., the Top Dead Centre (TDC), creates a partial vacuum in the lower part of the cylinder itself, opening the intake valve and allowing the gas to enter. The consequent suction phase lasts until the piston reaches the Bottom Dead Centre (BDC), then the intake valve is closed. Moving again towards the TDC, the gas is compressed until the pressure reaches the desired level, then the delivery valve is opened to discharge the gas. A high-pressure compressed hydrogen can be achieved when a multistage configuration is used.

- **Reciprocating Compressors - Pros & Cons:**

Although reciprocating compressors are widely used for applications involving hydrogen, but they are not perfectly appropriate for this purpose. Several improvements have been achieved in reciprocating compressors’ design, like the upgrading to non-metallic ring and valves materials, the use of a tungsten carbide piston rod coating, and the implementation of continuous monitoring systems to predict possible failures. Table 1 given below summarise the main Pros & Cons of the reciprocating compressors.

Table 1. Pros & Cons of the reciprocating compressors

Advantages	Disadvantages
• Mature technology • Adaptability to a large range of flow rates • High discharge pressures	• Contamination by lube oils (if used) • Embrittlement phenomena • Several moving parts • Manufacturing complexity • Effective maintenance is difficult. • Difficulty in managing thermal transfer. • Presence of vibrations and noise

4.1.2. Diaphragm Compressors

The operation of diaphragm compressor is based on the reciprocating motion of a piston inside the cylinder. The gas is completely isolated from the piston, since its movement is transmitted to a hydraulic fluid, which in turn transmits the motion to a thin metal membrane called “diaphragm”, isolating hydrogen from the hydraulic part.

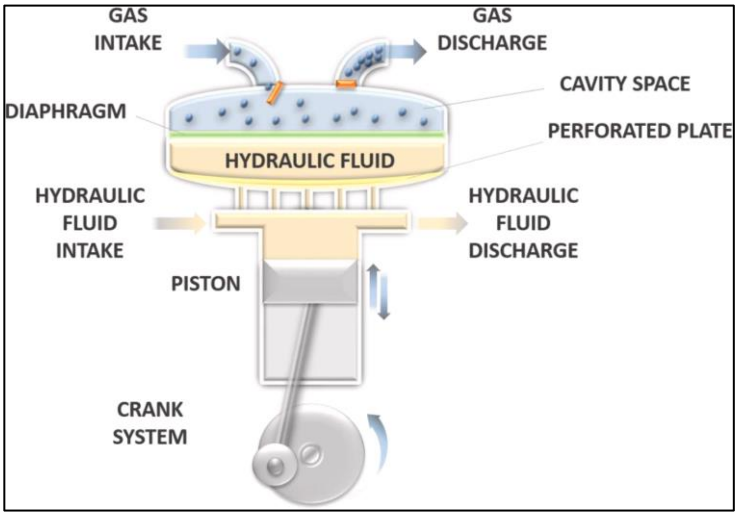

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Figure 6. Diaphragm compressor

The movement of the diaphragm into the cavity space, in which the gas is confined, reduces the available volume, thereby increasing the gas pressure.

- **Diaphragm Compressors - Pros & Cons:**

Although diaphragm compressors present several advantages, one of the most compelling goals remains the optimisation of the diaphragm design in order to reduce its risk of failure. Tables 2 below summarise the main Pros & Cons of the diaphragm compressors.

Table 2. Pros & Cons of the diaphragm compressors

Advantages	Disadvantages
• High throughput • Low power consumption • Low cooling requirement • Ideal for handling pure gases or explosives.	• Diaphragm failure • Complex design

4.1.3. Linear Compressors

Linear compressors are particularly used in cryogenic applications driven by Stirling cycle coolers and involving hydrogen and helium gas, as well as for domestic refrigeration.

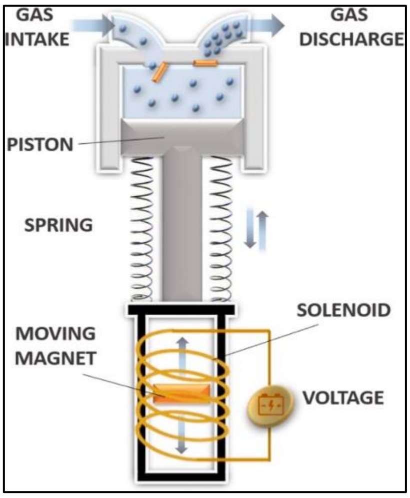

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Figure 7. Linear compressor

Compared to the former mechanical compressors, the piston is directly connected to a linear motor coupled with a resonating spring system, reducing the number of moving units because of the absence of a rod-crank assembly making it simpler with lower cost. The linear motors commonly used for driving the piston are magnetic-type and more specifically moving-coil and moving-magnet types. A clear advantage in using linear compressors is that the piston and the cylinder are separated by a gas bearing system.

- **Linear Compressors - Pros & Cons:**

Nowadays, linear compressors are especially used for cooling electronics because of their capacity to maintain low temperatures inside chips and miniature devices. Nevertheless, research is investigating a novel concept to enhance their applicability for high-scale hydrogen applications, consisting of driving a permanent magnet piston inside a hermetically sealed compressor cylinder through electromagnetic windings. Tables 3 given below summarise the main Pros & Cons of the linear compressors.

Table 3. Pros & Cons of the linear compressors

Advantages	Disadvantages
• Compactness • High reliability • High efficiency • Low vibration and low noise • Long operation life • Few moving parts	• Necessity to control the piston displacement. • Necessity to operate at resonant conditions. • Oscillating pressure

4.1.4. Liquid Piston Compressors

Liquid compressors are particularly suitable for hydrogen applications. They are positive displacement devices using liquids to directly compress a gas working in the absence of mechanical sliding seals.

More specifically, a column of liquid moves forth and back in a cylinder, compressing the gas introduced into its head. The liquid movement is driven by a pump which is connected to two cylinders in most applications and a compression step continually follows an expansion step. Internal liquid-spray cooling is often used in reciprocating compressors and can even be a valid alternative to further limit the temperature rising inside the compression chamber.
Moreover, liquid piston compressors benefit more than their reciprocating counterparts from this cooling method since the residue of the spray falls downwards to the liquid phase.

However, in order to obtain an effective increase of compression efficiency, an optimal spray profile still needs to be determined.

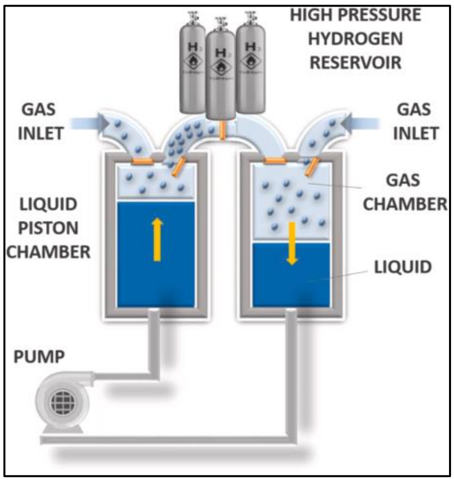

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Figure 8. Liquid piston compressor

4.1.5. Liquid Rotary Compressors

Liquid rotary compressors are particularly used to compress a gas with a high liquid content. This design features an impeller located eccentrically in a stator frame and made up of a series of blades extending radially from it. The impeller forces the liquid to move in an oscillatory manner overall, forming a ring compressing the gas introduced from a door placed in the rotor centre.

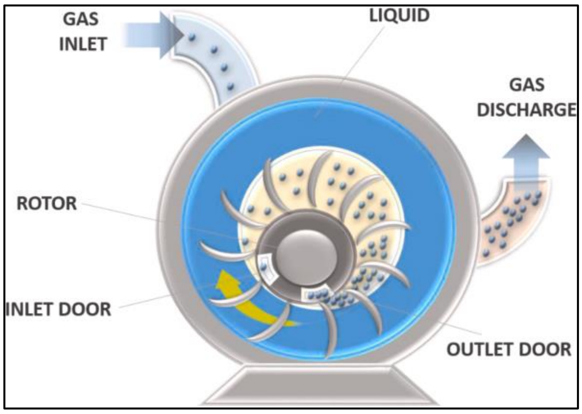

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Figure 9. Liquid rotary compressor

This kind of compressor particularly suits applications involving a vacuum or when saturated gases must be handled. However, they are not widely used because of their low overall efficiency of about 50%.

4.1.6. Ionic Liquid Compressors

The basic principle is the replacement of the conventional metal piston with an ionic liquid. Ionic liquid compressors were specifically developed to increase compression efficiency when hydrogen is used. Ionic liquids are low-melting point salts and are therefore in the molten state at room temperature. They exhibit good thermal and chemical stability, high ionic conductivity, fire retardance, moderate viscosity, high polarity, negligible volatility and have no negative effects on human health while also offering low compressibility and superior lubricating abilities especially for high-pressure applications.

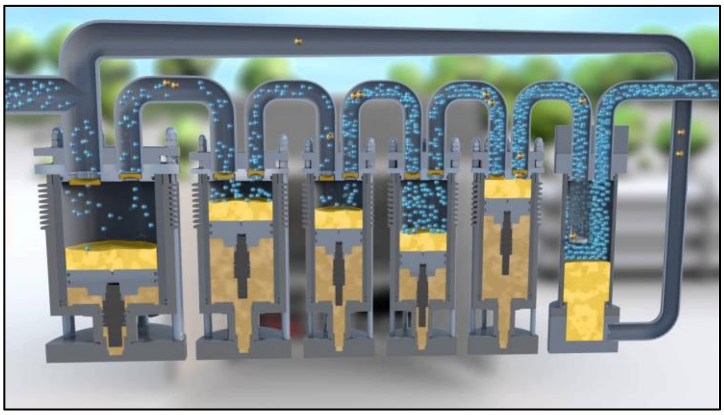

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Figure 10. Ionic liquid compressor

When used for compression applications, substituting the solid piston in a positive displacement device as well as in rotary configurations enables ionic liquids to achieve very good performances. Hydrogen solubility in many ionic liquids is negligibly low which means very high volumetric efficiencies and high compression ratios can be achieved. Ionic liquid compressors used in hydrogen fuelling stations have been proved to be a high-performance solution for the enhancement of the hydrogen value chain.

- **Ionic Liquid Compressors - Pros & Cons:**

  The use of ionic liquids for hydrogen compression also ensures low energy consumption, long service life, low material costs and low noise emission. Nevertheless, the risk of corrosion remains high, causing a decrease in overall efficiency by reducing the strength of the constituent materials and increasing the possibility of contamination by the corrosion products. Table 4 given below summarise the main Pros & Cons of the diaphragm compressors.

Table 4. Pros & Cons of the Ionic liquid compressors

Advantages	Disadvantages

• High efficiency • High compression factors • Low energy consumption • Reduced wear and long service life. • Low material costs • Low noise emission • Quite isothermal compression • No gas contamination • Very small number of moving parts	• Liquid leaks • Cavitation phenomena • Corrosion

4.2. Compression Work

When hydrogen is utilised in a gaseous form it usually has to be compressed to an elevated pressure, a process that requires significant amounts of energy to compress enough gas. The actual compression work carried out by a mechanical hydrogen compressor is almost one-third of the amount of energy stored in the resultant compressed gas. However, the precise calculation of the work of hydrogen compression requires the knowledge of an appropriate equation of state and of a calorific equation, information that is not widely available.

To simplify calculations, many investigators consider the compression of hydrogen as an isentropic (adiabatic) process, i.e., they assume that during compression there is no heat exchange between the compressor and the environment, and the process is reversible (ideal). The work required to increase the pressure of a gas, P, is: $W = \int_{V_1}^{V_2} PdV$ where V is the volume of the gas.

Based on the assumption that hydrogen behaves as an ideal gas, the work of isentropic (adiabatic) compression for 1 mole of hydrogen (or 2.02 g) from pressure P_1 to pressure P_2 ($P_1<P_2$) is given by: $W_{ideal} = \frac{\gamma}{\gamma-1} RT_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right]$ where T_1 is the temperature of hydrogen at P_1 and γ is the specific heat ratio of the gas that has the value of 1.4 and R is the universal gas constant.

Since the adiabatic compression of hydrogen is not a reversible process, deviation from the ideal behaviour is accounted for by introducing an isentropic compressor efficiency. where η is the isentropic efficiency of the process typically of the order of 75-85%.

4.3. Cryogenic Compression

Cryo-compression combines hydrogen liquefaction and compression with the benefits and challenges of both storage methods. It relies on the achievement of high pressures at very low temperatures. Instead of compressing hydrogen in the gaseous state, liquid hydrogen is pressurised and stored in cryo-compression systems consisting of a pressure vessel integrated in an insulated jacket to significantly reduce heat transfers between cold hydrogen and the exterior.

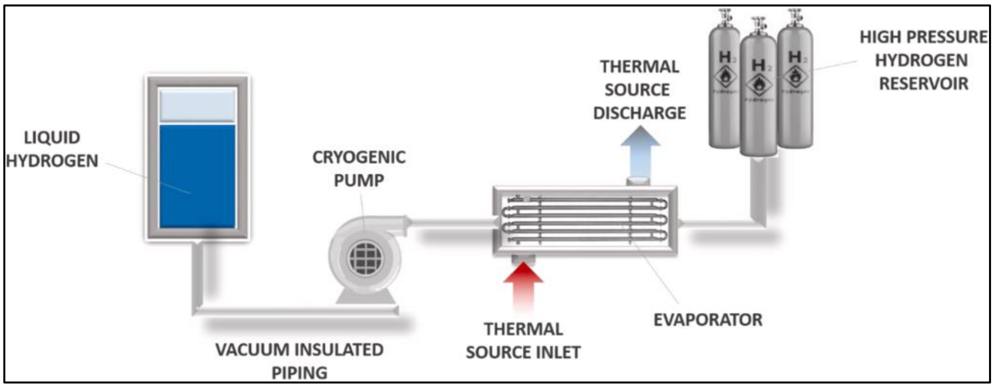

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Figure 11. Cryogenic compression

The design of such hydrogen-compressing systems is very sophisticated and consists of several sequentially-arranged modular elements – a tank storing liquid hydrogen at low pressure, a cryogenic pump and cryo-compressed vessels. Liquid hydrogen is fed into a cryogenic pump through vacuum-insulated piping and then the cryo-pump brings liquid hydrogen to the desired pressure value. Vaporisers can be used downstream of the cryogenic pump in order to obtain high-pressure gaseous hydrogen.

- **Cryogenic Compression - Pros & Cons:**

Despite the aforementioned advantages of hydrogen cryo-compression over traditional compression, it is well known that the energy cost necessary to liquefy hydrogen is a definite drawback since only 30% of the chemical energy is stored, based on the hydrogen lower heating value (LHV). Table 5 given below summarise the main Pros & Cons of the linear compressors.

Table 5. Pros & Cons of the cryogenic compression

Advantages	Disadvantages
• High hydrogen density • High volumetric efficiency • High gravimetric and volumetric capacities	• Low temperatures • Difficulty in managing thermal insulation. • Energy cost for liquefaction • Difficulties in vacuum stability

4.4. Metal Hydride Compressors

Metal hydride compressors ensure efficient hydrogen compression without any moving parts such as solid or liquid pistons or diaphragms. They are also commonly known as “thermally powered” compressors because they use the properties of hydride-forming metals, alloys or intermetallic compounds to absorb and desorb hydrogen simply by means of heat and mass transfer in the reaction system.

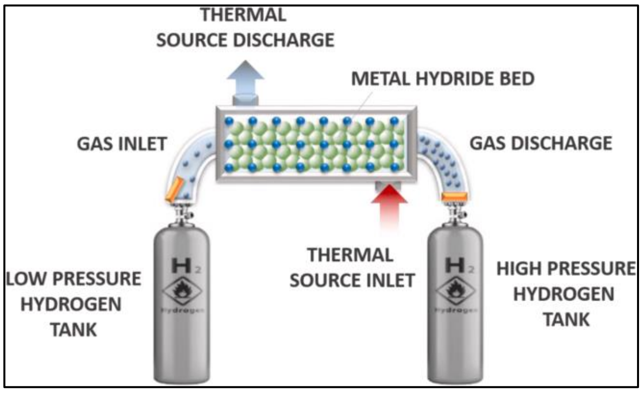

Image Link - https://ars.els-cdn.com/content/image/1-s2.0-S1364032118307822-gr10_lrg.jpg

Figure 12. Metal hydride compressor

A metal hydride is a binary combination of hydrogen and a metal (elemental metal, alloy or intermetallic compound) in which the latter reacts reversibly with hydrogen. It can be simply explained as - Hydrogen is first stored in the metal hydride at a low supply pressure and temperature; the hydrogen remains in the hydride until it is exposed due to an increase in temperature or pressure drop; then, the stored hydrogen exits the hydride. If the temperature increase is sufficient and the final storage volume is smaller than the supply volume, the hydrogen exits the metal hydride at pressures that range from approximately 3–10 times the original supply pressure.

- **Metal Hydride Compressors - Pros & Cons:**

The real advantage of metal hydride compressors is that the system can be powered using waste industrial heat instead of electricity or a renewable energy source, particularly solar energy. The efficiency of a hydrogen metal hydride compressor is generally below 25% at 423 K and strictly depends on the compression rate and amount of heat provided to the system; it can be defined as the ratio of compression work to heat input. Table 6 given below summarise the main pros & cons of the Metal Hydride compressors.

Table 6. Pros & Cons of the metal hydride compressor

Advantages	Disadvantages
Thermally driven compression	Limited heat transfer
Absence of moving parts	Necessity of using appropriate alloys
Compact design	Low efficiency
Safety	Weight
Absence of noise	Cost of container/ compression elements
High-purity hydrogen	

4.5. Electrochemical Hydrogen Compressors

An electrochemical hydrogen compressor, also known as "electrochemical hydrogen pump", is an innovative device that can be used to compress hydrogen with high recovery ratios of up to 95% and in applications requiring low gas quantities at very high pressures. It is based on the same basic principles as those of a proton-exchange membrane fuel cell (PEMFC).

Low-pressure hydrogen is fed into the anode of an electrochemical cell where it splits into protons and electrons according to the following reaction: $H_2 \rightarrow 2H^+ + 2e^-$. The protons flow electrochemically through a solid polymer electrolyte while the electrons follow an external path, which is the electrical circuit controlled by the potential differential supplied to the system. Once the protons and electrons reach the cathode, they recombine to form hydrogen molecules again with a resultant increased pressure: $2H^+ + 2e^- \rightarrow H_2$.

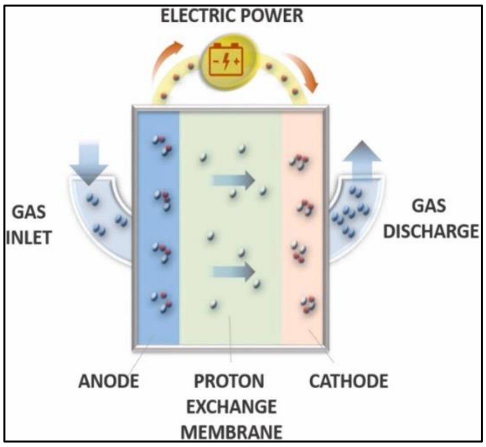

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Figure 13. Electrochemical hydrogen compressor

The membrane currently used in hydrogen electrochemical compressors is based on perfluorocarbon sulfonate polymers, e.g., Nafion® 117. In order to ensure optimum compression performances, a good hydration level of the membrane is required, since its protonic conductivity is enhanced when the membrane is saturated with water. A proper design of an electrochemical cell allows a long service life with high-pressure hydrogen storage, typically between 20 and 35 MPa.

- **Electrochemical Hydrogen Compressors - Pros & Cons:**

Hydrogen electrochemical compressors exhibit a high level of efficiency when the discharge pressure is moderate. As electrochemical compressors also require lower energy consumption at lower pressure range, they can be used at the outlet of an electrolyser to produce hydrogen at very high pressure thus enhancing the efficiency of the whole system. Table 7 given below summarise the main Pros & Cons of the Metal Hydride compressors.

Table 7. Pros & Cons of the electrochemical hydrogen compressor

Advantages	Disadvantages
• Low-cost operation • Production of high-purity hydrogen • No moving parts • Very high compression efficiency • Use as hydrogen purifier	• Difficulty in manufacturing the cell assembly. • Difficulty in realizing a perfect sealing. • High cell resistance • Hydrogen back diffusion

4.6. Adsorption Compressors

Adsorption compression is a new emerging technology for hydrogen compression which is based on adsorption and proceeds by means of changes in the system temperature, without any mechanical moving unit. A hydrogen adsorption compressor can be described as a thermodynamic engine in which compression is controlled by heat transfers between the compression reservoir and the system environment. Low-pressure hydrogen is fed into a closed tank filled with a solid bed consisting of a porous material with a high surface area and thus high adsorption potential. At specific temperature and pressure conditions, adsorption takes place exclusively on the surface of the porous material. After adsorption, heat is supplied to the system, resulting in an increase of temperature that produces hydrogen desorption.

As a direct consequence, the density of the hydrogen bulk phase increases and high-pressure hydrogen is obtained. This is due to the fact that hydrogen moves from the adsorbed phase, which is denser, to the bulk gas phase in a confined tank volume when the temperature increases. Hence, the potentially achievable pressure level depends strictly on the final temperature, on the volume available for the bulk gas phase inside the tank and on the mass of adsorbent.

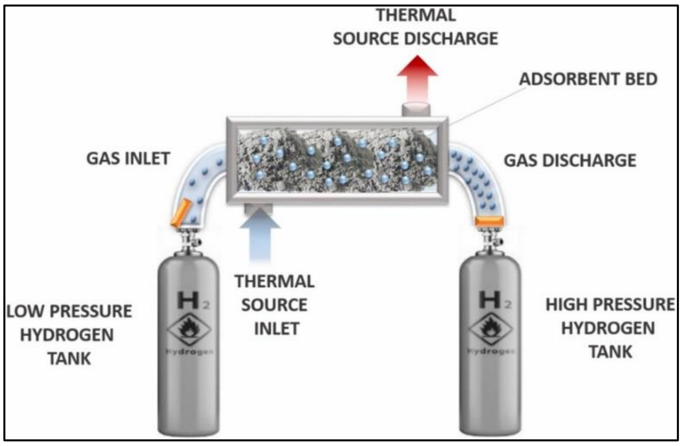

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Figure 14. Adsorption compressor

- **Adsorption Compressors - Pros & Cons:**

Important requirements for a well-driven adsorption process are the high surface area and developed porosity of the adsorbent, since the net adsorbed amount of hydrogen depends on the total bed surface area. Hydrogen adsorption compressors are affected by several thermal effects. Heat is generated during adsorption, whereas heat is needed in order to release hydrogen through desorption. Table 8 given below summarise the main pros & cons of the adsorption compressors.

Table 8. Pros & Cons of the Adsorption compressor

Advantages	Disadvantages
• Thermally driven compression • No moving parts, no vibration, no noise • No necessity for sealing • Low cost of adsorbent	• Low thermal conductivity of adsorbents • Difficulty in thermal management • Low-temperature operation

Discussion Tasks →

- Search for ways to overcome cons of each type of hydrogen compressors. Discuss these enhancements.

- Try to find which are most used hydrogen compressors. Discuss the reasons for that.
- Explore the hydrogen compressors used in automotive supply stations in Europe and specify their types.

CONTINUOUS ASSESSMENT 2

-------- End of Block 4 --------

-------- BLOCK 5 --------

5.1. Liquid Hydrogen

Liquid hydrogen (LH2 or LH_2) is the liquid state of the element hydrogen. As for any gas, storing hydrogen as liquid takes less space than storing it as a gas at normal temperature and pressure. To exist as a liquid, H2 must be cooled below its critical point of 33 K. However, for it to be in a fully liquid state at atmospheric pressure, H_2 needs to be cooled to 20.28 K (−252.87 °C; −423.17 °F). There are many different pathways that can be followed so that such low temperatures are achieved. Liquid hydrogen is typically used as a concentrated form of hydrogen storage. Once liquefied, it can be maintained as a liquid in pressurised and thermally insulated containers.

Image Link - https://en.wikipedia.org/wiki/Liquid_hydrogen#/media/File:Liquid_Hydrogen_pour.jpg

Figure 15. Pouring liquid hydrogen into a container in an enclosed environment

Image Link - https://h2stationmaps.com/sites/default/files/Linde-liquide-hydrogen-tank_edit.jpg

Figure 16. Liquid hydrogen storage tank

Image Link - https://ehs.princeton.edu/sites/g/files/toruqf5671/files/media_files/wysiwyg/liquid%20nitrogen%20cylinder.jpg

Figure 17. Liquid hydrogen cylinders

5.2. Cooling for Liquefaction

Cryogenic (icy cold) liquefiers are based on the thermodynamic concept that the cooling effect is obtained by expanding adiabatically a fluid from a proper initial condition. The adiabatic expansion can be executed either with or without mechanically extracting energy from the fluid being expanded. Expansion without energy extraction, which is an isenthalpic process, is realised by a throttling valve, while expansion with energy extraction, which is ideally an isentropic process, is realised by an expanding machine. Because liquefiers are based on the expansion of a fluid, they require a compression process to complete the cycle from the pressure perspective. This compression is executed at ambient temperature and, commonly, in an intercooled manner. Additionally, liquefiers require heat exchangers to complete the cycle from the temperature perspective.

In general, throttling of any fluid leads to an appreciable temperature change, either positive or negative. The theoretical background of liquefaction is reviewed in brief now, while the characteristics of the equipment required (compressors, expanders and heat exchangers) are discussed in Block 2.

5.3. The Joule-Thomson (J-T) Effect

In thermodynamics, the Joule–Thomson effect (also known as the Joule–Kelvin effect or Kelvin–Joule effect) describes the temperature change of a real gas or liquid when it is forced through a valve or porous plug while keeping it insulated so that no heat is exchanged with the environment. This procedure is called a throttling process or Joule–Thomson process.

In 1852, working with William Thomson (who would later become Lord Kelvin), Joule conducted an experiment in which they pumped gas at a steady rate through a lead pipe that was cinched to create a construction. On the upstream side of the constriction, the gas was at a higher pressure than on the downstream side of the constriction. Also, the temperature of the gas was carefully monitored on either side of the construction. They observed that the gas was cooling as it expanded from a high-pressure region to a lower pressure region. This experimental work was extremely important and lead to a common design of modern refrigerators.

It is also noticed that not all gases undergo a cooling effect upon expansion. Some gases, such as hydrogen and helium, will experience a warming effect upon expansion under conditions near room temperature and pressure. The direction of temperature change can be determined by measuring the Joule-Thomson coefficient, μ_{JT}. This coefficient has the definition:

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

T: Temperature K, p: Pressure Pa, and H: Enthalpy J/K

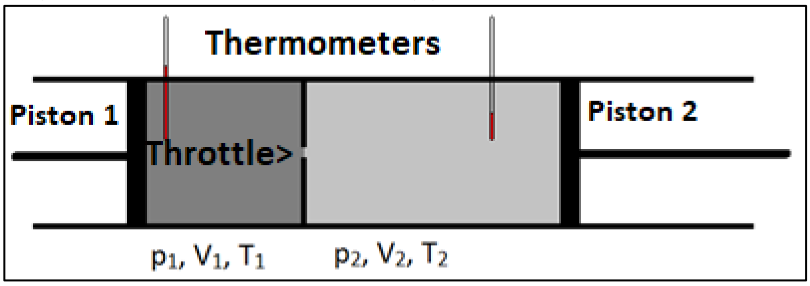

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Figure 18. Joule–Thomson process

Upstream of the throttle in the high-pressure region, the flow of the gas can be equated to work done on the gas by the conceptual piston at left against the resistance of the throttle. The force-distance work done by Piston 1 is equivalent to the pressure-volume product P_1V_1 of the gas.

Downstream of the throttle in the low-pressure region, the flow of the gas can be equated to work done by the gas against the resistance of the conceptual piston at right, which is under lower pressure (atmospheric pressure in the original Joule-Thomson experiment). The force-distance work done by Piston 2 is equivalent to the pressure-volume product P_2V_2 of the gas. The net work W done on the given mass of gas is therefore $W = p_1V_1 - p_2V_2$

Applying the first law of thermodynamics to this transition where no heat is gained or lost by the gas (Q=0): $\Delta U = Q + W \rightarrow U_2 - U_1 = p_1V_1 - p_2V_2 \rightarrow U_2 + p_2V_2 = U_1 + p_1V_1$.

U+pV is a thermodynamic state function, called Enthalpy (H). → → $H_2 = H_1$ (Constant Enthalpy). The Joule-Thomson experiment therefore involves a constant-enthalpy, or isenthalpic, expansion.

Note that cooling observed when a gas does external work under (reversible) adiabatic conditions, is a constant-entropy, or isentropic, expansion. In Joule and Thomson's first experiments with their apparatus, they varied the upstream pressure and temperature, while the downstream pressure was always atmospheric since the end of the pipe was open to the air. It was later realised that more useful results are obtained if the upstream pressure and temperature are held constant, and the downstream pressure is held at several decreasing values at each of which the downstream temperature is measured.

5.3.1. The Joule-Thomson (J-T) Coefficient

In Joule-Thomson (J-T) experiment, If the upstream pressure and temperature are held constant, and the downstream pressure is held at several decreasing values at each of which the downstream temperature is measured. Then data is recorded on a temperature-pressure plot. Each point on the plot represents a state for which the enthalpy is equal to the initial (upstream) enthalpy. By joining up the points, a constant-enthalpy line, or isenthalpic curve, is obtained. The slope at any point on an isenthalpic curve is known as the Joule-Thomson coefficient, μ_{JT}.

The maximum point of the curve, at which the coefficient is zero, is called the inversion point for the isenthalpic curve in question. By joining up the inversion points on each isenthalpic curve, an **inversion curve** is obtained. In the region within the inversion curve where μ_{JT} is positive, cooling will occur. In the region outside the inversion curve where μ_{JT} is negative, heating will occur. The upper intersection of the inversion curve with the line of no pressure denotes the maximum inversion temperature for the given gas. Above this temperature the Joule-Thomson effect cannot produce cooling at any pressure.
This Joule-Thomson coefficient, μ_{JT} has the definition:

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$$

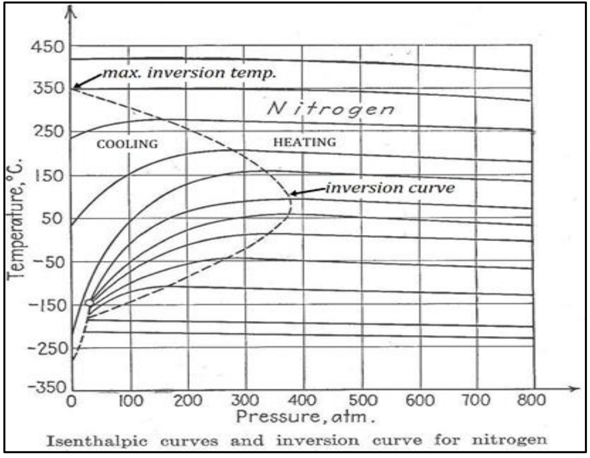

Image Link - https://carnotcycle.files.wordpress.com/2014/04/jtgraph021.jpg

Figure 19. Isenthalpic curves and inversion curves for nitrogen

This Joule-Thomson coefficient has the definition: $\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H$. Since the initial pressure is always greater than the final pressure in the Joule-Thomson experiment, ∂p is always negative. So, a positive slope ($\mu_{JT} > 0$) on the isenthalpic curve means that ∂T is also negative i.e., cooling will occur. Conversely a negative slope ($\mu_{JT} < 0$) on the isenthalpic curve means that ∂T is positive i.e., heating will occur.

The upper intersection of the inversion curve with the line of no pressure denotes the maximum inversion temperature for the given gas. Above this temperature the Joule-Thomson effect cannot produce cooling at any pressure. For Hydrogen, the maximum inversion temperature is 195.37 K. i.e., Hydrogen will cool upon expansion only if it is already cold. To exist as a liquid, Hydrogen must be cooled below its critical temperature of 33 K. To be in a fully liquid state at atmospheric pressure, Hydrogen needs to be cooled to 20.28 K.

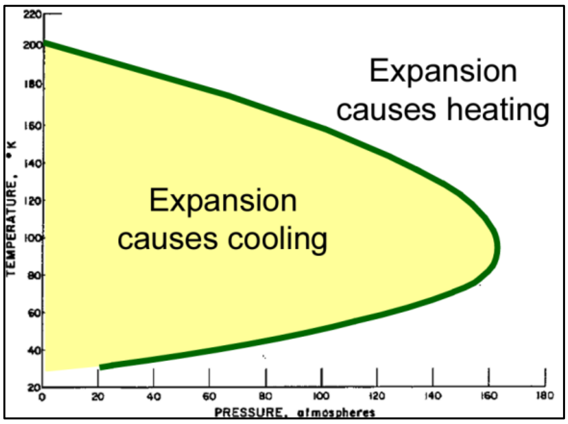

Figure 20. The J-T inversion curve for hydrogen

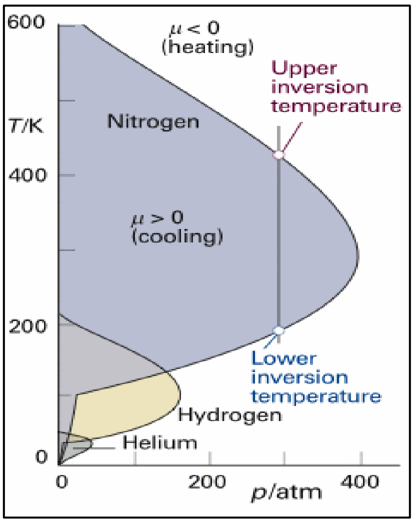

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Figure 21. Inversion temperatures

Table 9. Maximum inversion temperature of some gases

Gas	Maximum inversion temperature (K)
Nitrogen	620.93
Air	603.15
Hydrogen	195.37
Helium	23.15

It is difficult to think physically about what the Joule–Thomson coefficient, μ_{JT}, represents. Also, modern determinations of μ_{JT} do not use the original method used by Joule and Thomson, but instead measure a different, closely related quantity. Thus, it is useful to derive relationships between μ_{JT} and other, more conveniently measurable properties.

The first step in obtaining these results is to note that the Joule–Thomson coefficient involves the three variables T, p, and H. A useful result is immediately obtained by applying the chain rule; in terms of these three variables that rule may be written as $\left(\frac{\partial T}{\partial p}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial p}{\partial H}\right)_T = -1.$

Each of the three partial derivatives in this expression has a specific meaning:

$\left(\frac{\partial T}{\partial p}\right)_H = \mu_{JT}$ is the Joule–Thomson coefficient.

$\left(\frac{\partial H}{\partial T}\right)_P = C_p$ is the specific heat capacity at constant pressure.

$\left(\frac{\partial H}{\partial p}\right)_T = \mu_T$ is the isothermal Joule–Thomson coefficient which is more easily measured than μ_{JT}.

$\mu_{JT} = -\frac{\mu_T}{C_p}$ from Maxwell relation $\mu_T = -TV\alpha + V$ where α is the cubic coefficient of thermal expansion.

$$\mu_{JT} = \left(\frac{\partial T}{\partial p}\right)_H = \frac{V}{C_p}(\alpha T - 1)$$

This provides an expression for the Joule–Thomson coefficient in terms of the commonly available properties heat capacity, molar volume, and thermal expansion coefficient.

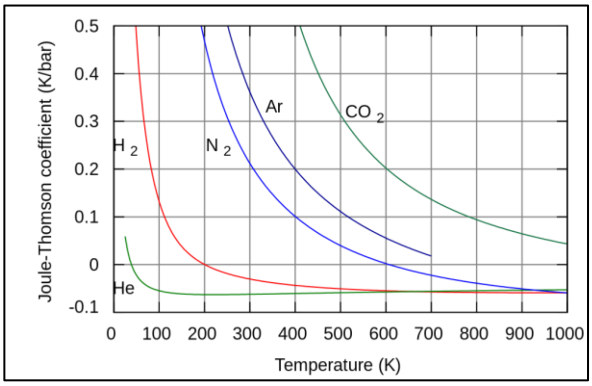

Image Link - https://upload.wikimedia.org/wikipedia/commons/thumb/8/8f/Joule-Thomson_curves_2.svg/400px-Joule-Thomson_curves_2.svg.png

Figure 22. Joule-Thomson curves

5.4. Hydrogen Cooling for Liquefaction

For Hydrogen, the maximum inversion temperature is 195.37 K. i.e., Hydrogen will cool upon expansion only if it is already cold. Therefore, hydrogen needs to be pre-cooled below the maximum J-T inversion temperature (204.15 K, -69°C) being at a pressure that corresponds to a point on the inversion curve. Expanding from this pressure to ambient pressure results in the maximum decrease in hydrogen temperature, which however may not be sufficient to liquefy hydrogen.

However, the gas that has been cooled by throttling is used to cool incoming gas, thus lowering even more the gas temperature. After successive cooling cycles, the temperature of the gas is lowered to such a temperature that, after throttling, some liquid is formed. Precooling is typically done using cold or liquid nitrogen. In a next step, hydrogen is cooled even further in one or more stages using neon, helium, or hydrogen itself as a working fluid, depending on the liquefaction process.

Ultimately, the gas is expanded using a JT valve (in small plants) or a cryogenic turbine (in larger plants) to reach the liquefaction temperature. The most commonly used liquefaction processes are the Linde cycle and the Claude cycle. However, it is instructive first to review the case of the ideal liquefaction process, a theoretical process that consumes the least energy for liquefaction when compared with real cycles and thus is used as a measure to compare the efficiency of liquefaction processes.

5.5. The Ideal Liquefaction Process

The process comprises an isothermal compression followed by reversible isentropic expansion to cool the gas and transform it into liquid.

The ideal liquefaction process: gaseous hydrogen (GH2) is initially compressed and then expanded in a J-T valve resulting in the drop in its temperature, below its boiling point, forming liquid hydrogen (LH2). The work needed in this theoretical process is called the ideal work of liquefaction and has been calculated as 11.620 MJ/kg by W.A. Amos and 11.88 MJ/kg by M.T. Syed.

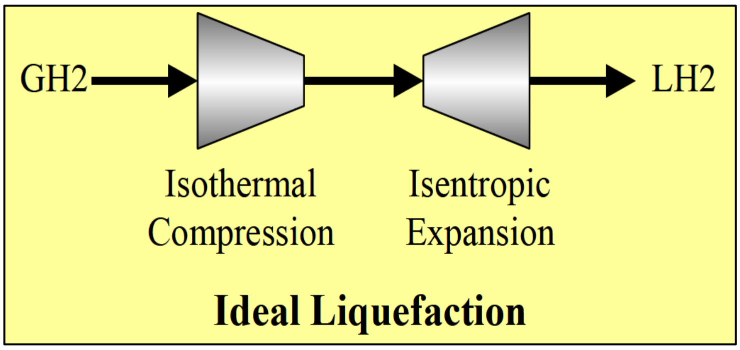

Figure 23. Ideal Liquefaction

The ideal work of liquefaction considers the energy required to reduce the temperature of the gas to its boiling point, the energy of the phase transformation from gas to liquid and the energy for the transformation from ortho- to parahydrogen during cooling. In comparison, the ideal work of nitrogen liquefaction is about 15 times less than the ideal work of liquefaction of hydrogen. The work of ideal liquefaction depends on the initial pressure and temperature of the gas, and the initial and the ultimate concentration of parahydrogen.

5.5.1. The Linde Liquefaction Process

Many gases are liquefied using the Joule–Thomson effect. This approach is embodied in the Linde liquefaction process, and a schematic of the equipment is shown in Fig. 24 (a), while the thermodynamic processes are depicted in Fig 24(b). The Linde process is similar to a refrigerator operating on a vapour compression cycle (i.e., the typical refrigeration cycle), except that it includes a heat exchanger to transfer energy equal to QA and QB from the high temperature working fluid to that which has already been cooled through throttling processes.

The gas is supplied to a compressor at state 1 and make-up gas is supplied at state 11, which is the same as state 1. This is then compressed to a high, supercritical pressure (which might be hundreds of atmospheres) by a multi-stage reciprocating compressor with inter-stage cooling. The gas finally reaches state 2, and it is then passed through a heat exchanger which cools it to state 3. At this point it is throttled for the first time and is cooled by the Joule–Thomson effect to state 4 and passed into a receiver. Some of the gas entering the receiver is passed back to the compressor via the heat exchanger, and the remainder is passed through a second throttle until it achieves state 6.

At this stage it is in the liquid–vapour region of the state diagram, and liquid gas can be removed at state 9. The yield of liquid gas is y, defined by the quality of state point 6 on the T–s diagram.

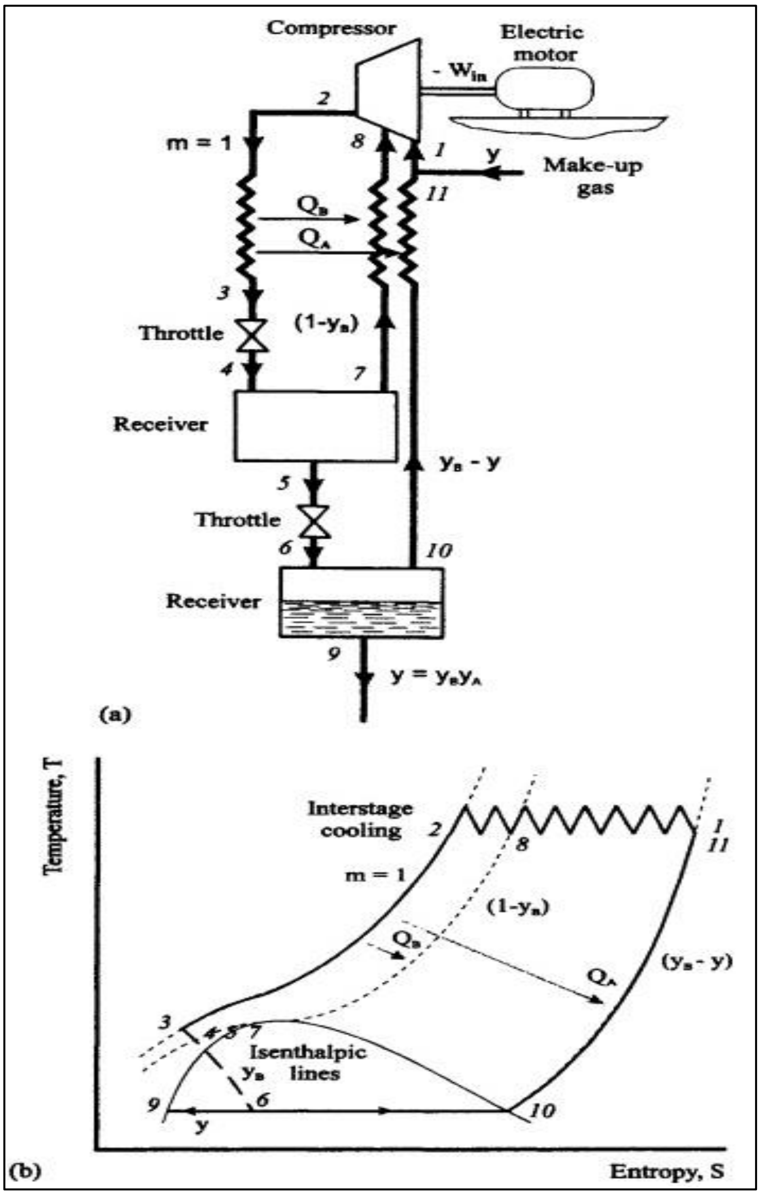

Image Link - https://www.sciencedirect.com/topics/engineering/joule-thomson-effect

Figure 24. Linde liquefaction process - Joule-Thomson effect

5.5.2. The Claude Liquefaction Process

Modern high volume liquefaction plants rely on the Claude cycle, a hybrid of the Linde cycle and the Brayton cycle where heat exchangers and mechanical expanders are used to cool the compressed and pre-cooled hydrogen below its inversion temperature. The introduction of an expansion engine in the Claude process can produce a lower temperature before isenthalpic expansion (as adopted by the Linde process). In addition, as the expansion engine becomes the main refrigeration source, cooling using liquid nitrogen is not essential. The compressed gaseous hydrogen is cooled through several series of heat exchangers, where an expansion engine is installed between the heat exchangers. A part of the compressed gas is fed to the expansion engine and used to cool the remaining gas.

Theoretically, isothermal compression and isenthalpic expansion are employed. The expansion engine cannot practically be used for condensation, as the liquefied substance potentially damages this expansion engine. Using this expansion engine, a part of the high-pressure hydrogen is expanded to generate a lower temperature of hydrogen. Then, it was mixed with cold hydrogen at a low temperature, which was then heat exchanged with the high-pressure hydrogen in the heat exchanger (HE2).

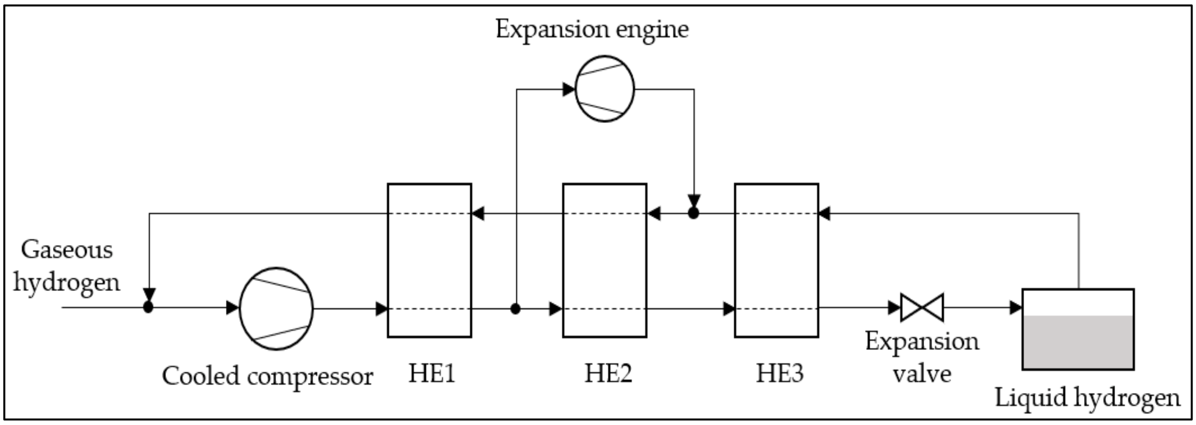

Figure 25. Expansion Engine

Discussion Tasks →

- Search for other liquefaction processes. Discuss their pros and cons.
- Search for enhancements on Linde and Claude liquefaction processes. Discuss their pros and cons.
- Explore the liquefaction plants in Europe and specify their liquefaction processes.

CONTINUOUS ASSESSMENT 3:

-------- End of Block 5 --------

-------- BLOCK 6 --------

6.1. Hydrogen Storage Technologies

For successful application of hydrogen as an energy carrier, hydrogen needs to be stored safely for variable periods of time as efficiently as fossil fuels, while simple handling and low costs should also be ensured. Storage is a challenging issue that cuts across production, delivery and end-use applications of hydrogen as energy carrier. It constitutes a key enabling technology for the realisation of a hydrogen-powered economy.

Under normal temperature and pressure conditions, 1kg of hydrogen will occupy a volume of 12.15m3 and an energy content of 33.5kWh, whereas for the same energy content, the volume that gasoline occupies is 0.0038m3. Thus, for hydrogen to become a competitive energy carrier, its volume density must be increased.

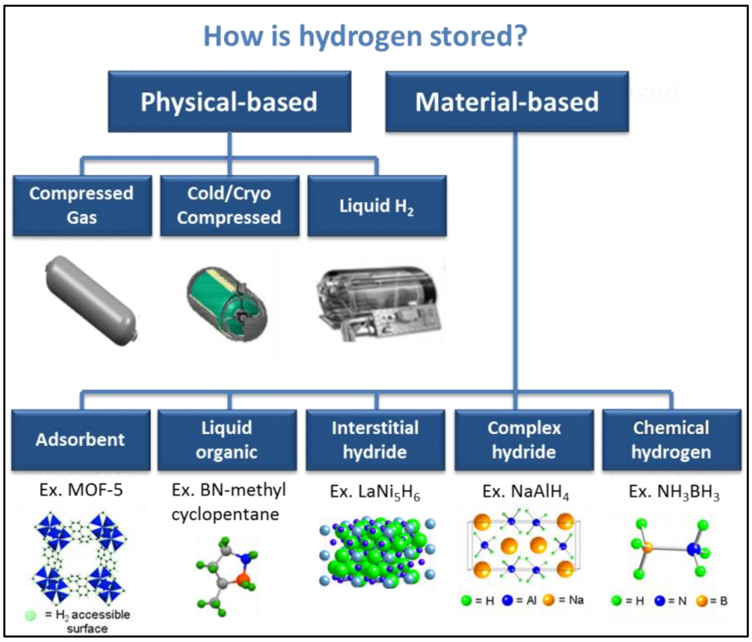

Image Link - https://www.energy.gov/sites/default/files/styles/full_article_width/public/fcto_storage_tree_chart2.png?itok=bbg2lBYZ

Figure 26. Hydrogen storage technologies

Therefore, Hydrogen can be stored in one of the three main different ways:

- Compressed gas form under high pressures.
- Liquid form under cryogenic temperatures.
- Hydrogen storage in other media, on the surface of or within solid and liquid materials.

6.2. Hydrogen Storage in Gaseous Form

Compressed hydrogen storage in gaseous form is the most established hydrogen storage technology; it involves the physical storage of compressed hydrogen gas in high-pressure vessels (tanks). This is currently one of the simplest, most common and efficient storage technologies in use. The high-pressure vessels are thick-walled tanks (mainly of cylindrical or quasi-conformable shape) made of high strength materials to ensure durability.

The high-pressure hydrogen storage vessels can be classified into four standard types:

- Type I: all metal cylinders.
- Type II: load-bearing metal liner hoop wrapped with resin-impregnated continuous filament.
- Type III: non-load-bearing metal liner axial and hoop wrapped with resin-impregnated continuous filament.
- Type IV: non-load-bearing non-metal liner axial and hoop wrapped with resin-impregnated continuous filament.

In 2010, Composites Technology Development Inc. (United States) developed an all-composite liner-less vessel, referred to as Type V. Although it is significantly lighter than Type IV vessels, the Type V vessels do not operate at pressures high enough for storing adequate amounts of hydrogen for nonlaboratory use.

6.2.1. Hydrogen Storage Vessels: Type I

Type I hydrogen gas vessels (tanks) are an all-metal vessel (usually steel) and hence the heaviest, typically employed in industry for stationary use. These Type I hydrogen gas vessels store only 1% to 2% hydrogen storage compared to the cylinder mass at 200–300 bar. So, the mass of hydrogen stored to the mass of cylinder ratio is very low.

Type I hydrogen gas vessels are the least expensive to manufacture and can be built to huge sizes. These Type I hydrogen gas vessels are unsuitable for vehicle applications due to their low hydrogen storage density, heavyweights, and also because of hydrogen embrittlement challenges. The figure 27 given below shows the typical components that will be found on most hydrogen vessels.

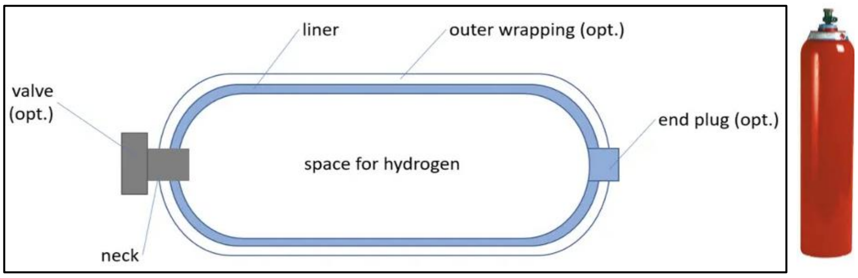

Figure 27. Typical components found on most hydrogen vessels.

6.2.2. Hydrogen Storage Vessels: Type II

Type II hydrogen gas vessels (tanks) are load-bearing metal liner hoop wrapped with resin-impregnated continuous filament. These gas vessels (tanks) are weighing less than Type I vessels. Type II hydrogen gas vessels store only 1% to 2% hydrogen storage compared to the cylinder mass at 200–300 bar. So, the mass of hydrogen stored to the mass of cylinder ratio is very low.

Figure 28. Type II hydrogen gas vessels

Types II as Type I hydrogen gas vessels are unsuitable for vehicle applications due to their low hydrogen storage density, heavyweights, and also because of hydrogen embrittlement challenges.

6.2.3. Hydrogen Storage Vessels: Type III

Type III hydrogen gas vessels (tanks) comprise a fully wrapped composite cylinder with a metal liner that serves as the hydrogen permeation barrier. The metal liner is made of aluminium (Al), which solves the problem of embrittlement, and it contributes >5% to the mechanical resistance. The composite overwrap (usually carbon fibre embedded in resin) acts fully as the load-bearing component.

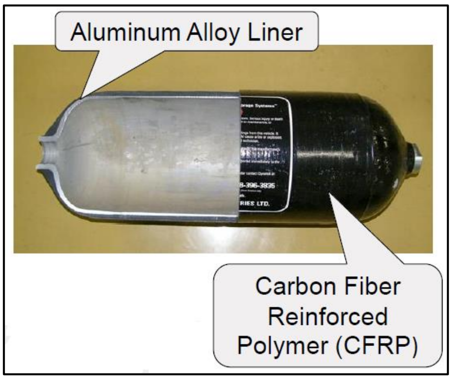

Figure 29. Type III hydrogen gas vessels

Type III hydrogen gas vessels (tanks) offer a 25–75% mass gain over Types I and II vessels, making them more suitable for vehicle applications; however, they are more costly. These vessels have also been shown to be reliable at pressures up to 450 bar but there are still challenges associated with pressure cycling tests at 700 bar.

6.2.4. Hydrogen Storage Vessels: Type IV

Type IV hydrogen gas vessels (tanks) comprise a fully wrapped composite cylinder with a plastic liner (typically high-density polyethylene), which acts solely as the hydrogen permeation barrier. The composite overwrap serves as the load-bearing structure and is typically made up of carbon fibre or carbon/glass fibre composite in an epoxy matrix.

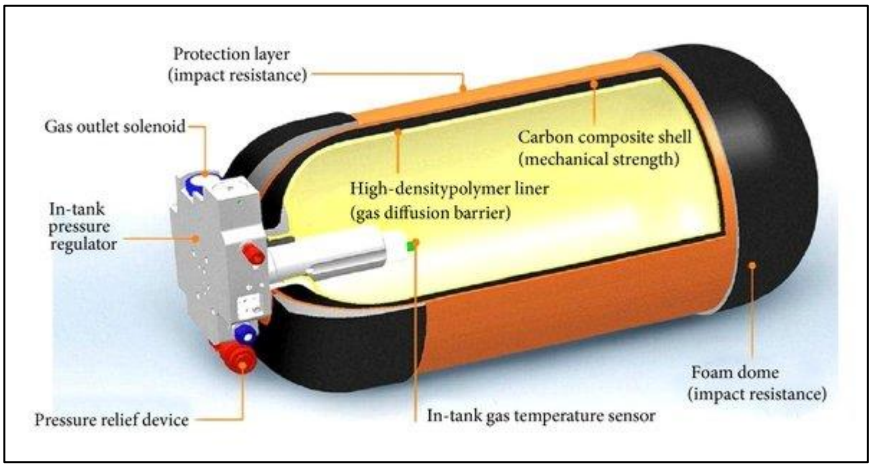

Figure 30. Type IV hydrogen gas vessels

Type IV vessels are the lightest of the pressure vessels, making them most suitable for vehicle applications, and they can endure high pressures up to 1,000 bar. However, they are too costly, due to the considerable cost contribution of the carbon fibres. Cost projections show that the carbon fibre cost constitutes about 75% of the storage vessel cost, taking the high production volumes into consideration. Types III and IV vessels are currently widely used in the hydrogen vehicle industry.

6.3. Hydrogen Compression: Pressure-Density

Understanding of hydrogen compression requires understanding the detailed analysis of the pressure-density diagram for hydrogen, as presented in the Figure below. At lower pressures (up to 15 bar) the pressure is almost proportional to the density (straight line). For high pressures, the hydrogen density does not increase linearly with the pressure. A hydrogen density of almost 20 kg/m3 is reached at 300 bar (30 MPa) for the temperature of 30 °C. At a pressure of 800 bar (80 MPa) the density can be increased to around 41 kg/m3.

High-pressure storage of hydrogen allows volume reduction of 5 kg to 0.125 m^3 at 700 bar. Compressed hydrogen in hydrogen tanks at 350 bar (5,000 psi) and 700 bar (10,000 psi) are currently being used for hydrogen tank systems in vehicles developed by various manufacturers such as Honda and Nissan. Utilising the ideal and combined gas laws can be used to develop the pressure-density diagram for hydrogen assuming hydrogen as an ideal gas.

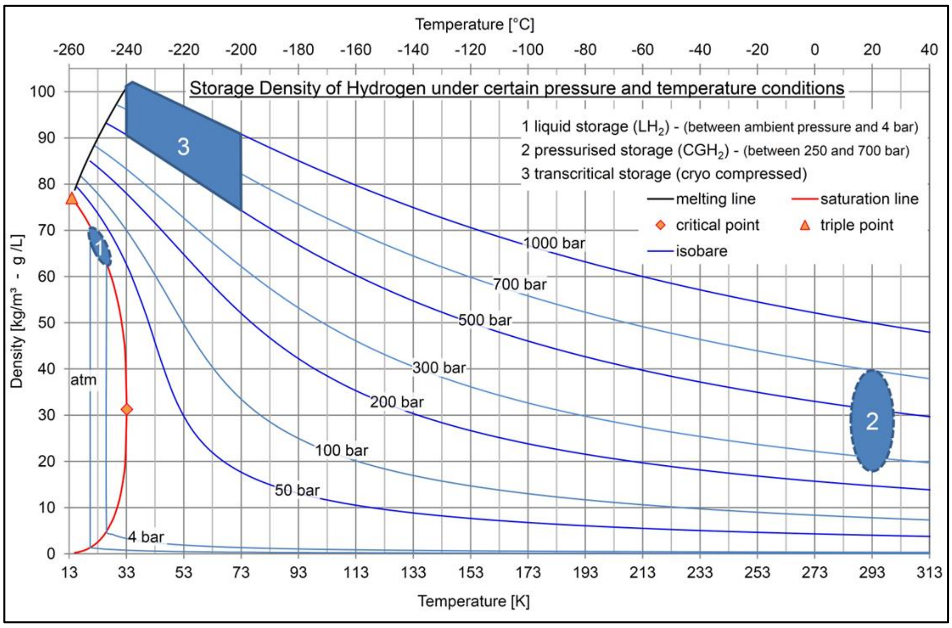

Image Link - https://upload.wikimedia.org/wikipedia/commons/thumb/9/90/Storage_Density_of_Hydrogen.jpg/1024px-Storage_Density_of_Hydrogen.jpg

Figure 31. Storage density of hydrogen

6.4. Perfect Gas Laws

6.4.1. Perfect Gas Laws: Charles's Law

"The volume of a given mass of an ideal gas is directly proportional to its temperature on the absolute temperature scale (in Kelvin) if pressure and the amount of gas remain constant; that is, the volume of the gas increases or decreases by the same factor as its temperature."

Mathematically, Charles's law can be stated as:

$$V \propto T \quad or \quad \frac{V}{T} = Constant \quad \rightarrow \quad V_1 T_2 = V_2 T_1$$

Charles's law explains how a gas expands as the temperature increases; conversely, a decrease in temperature will lead to a decrease in volume. The equation shows that, as absolute temperature increases, the volume of the gas also increases in proportion.

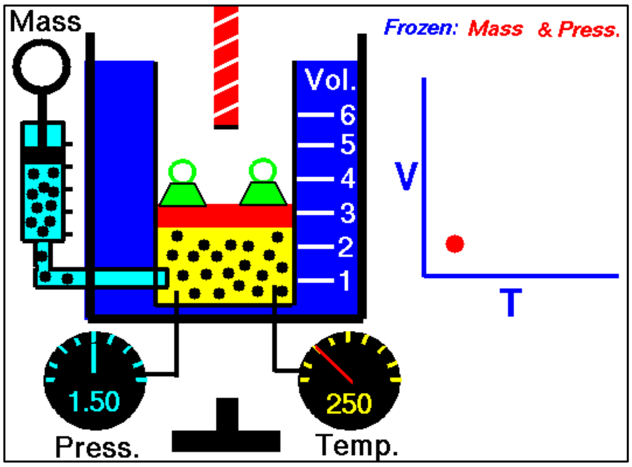

Image Link - https://www.grc.nasa.gov/www/k-12/airplane/Animation/gaslab/Images/gastil.gif

Figure 32. Charles's law experiment outcomes

6.4.2. Perfect Gas Laws: Boyle's Law

"The absolute pressure exerted by a given mass of an ideal gas is inversely proportional to the volume it occupies if the temperature and amount of gas remain unchanged within a closed system."

Mathematically, Boyle's law can be stated as:

$$\mathrm{p} \propto \frac{1}{\mathrm{V}} \quad \text{or} \quad \mathrm{pV} = \text{Constant} \quad \rightarrow \quad \mathrm{p_1V_1} = \mathrm{p_2V_2}$$

Boyle's law is used to predict the result of introducing a change, in volume and pressure only, to the initial state of a fixed quantity of gas at constant temperature. The equation shows that, as volume increases, the pressure of the gas decreases in proportion. Similarly, as volume decreases, the pressure of the gas increases.

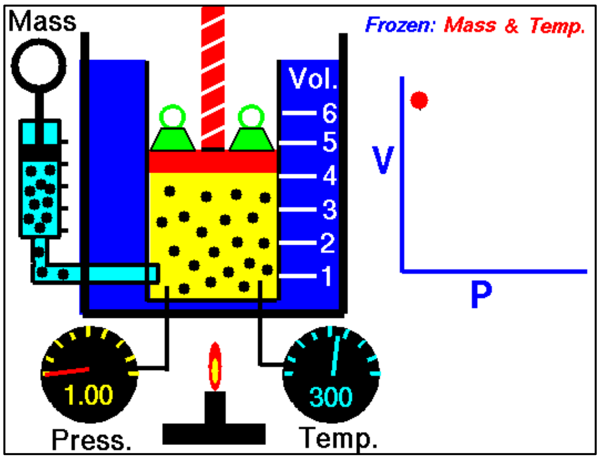

Image Link - https://www.grc.nasa.gov/www/k-12/airplane/Animation/gaslab/Images/gastil.gif

Figure 33. Boyle's law experiment outcomes

6.4.3. Perfect Gas Laws: Gay-Lussac's Law

"The pressure of a gas of fixed mass and fixed volume is directly proportional to the gas's absolute temperature."

Mathematically, Gay-Lussac's law can be stated as:

$$p \propto T \quad or \quad \frac{p}{T} = Constant \quad \rightarrow \quad p_1 T_2 = p_2 T_1$$

This law holds true because temperature is a measure of the average kinetic energy of a substance; as the kinetic energy of a gas increases, its particles collide with the container walls more rapidly, thereby exerting increased pressure.

6.4.4. Perfect Gas Laws: Avogadro's Law

"Equal volumes of all gases, at the same temperature and pressure, have the same number of molecules."

Mathematically, Avogadro's law can be stated as:

$$V \propto n \quad or \quad \frac{V}{n} = Constant \quad \rightarrow \quad V_1 n_2 = V_2 n_1$$

Where n is the amount of substance of the gas (measured in moles) which is (the number of molecules divided by Avogadro's Number). This law explains how, under the same condition of temperature and pressure, equal volumes of all gases contain the same number of molecules. The equation shows that, as the number of moles of gas increases, the volume of the gas also increases in proportion. Similarly, if the number of moles of gas is decreased, then the volume also decreases. Thus, the number of molecules or atoms in a specific volume of ideal gas is independent of their size or the molar mass of the gas.

6.4.5. The Combined and Ideal Gas Laws

"The ratio between the pressure-volume product and the temperature of a system remains constant."

The combined gas law is a gas law which combines Charles's law, Boyle's law, and Gay-Lussac's law. Mathematically, the combined gas law can be stated as:

$$pV = KT \; \rightarrow \; \frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2}$$

Where K is a constant

With the addition of Avogadro's law, the combined gas law develops into the ideal gas law:

$$pV = n\tilde{R}T = mRT \; \rightarrow \; pv = RT \quad or \quad P = \rho RT$$

Where n is the amount of substance of the gas (measured in moles) and R is the specific gas constant (R for H_2 is 4124.2 J/kg K).

Discussion Tasks →

- Search for latest research directed towards the development of new methodologies for reliability design and safety qualification of these high-pressure storage systems. Discuss these.
- Explore the next generation of compressed hydrogen storage systems: tanks with complex shapes, optimal use of materials and of high safety level.

CONTINUOUS ASSESSMENT 4:

-------- End of Block 6 --------

-------- BLOCK 7 --------

7.1. Hydrogen Storage in Liquid Form

The physical storage of hydrogen can be in the form of a cryogenic liquid at atmospheric pressure. Hydrogen in liquid form has a considerably higher energy density than in its gaseous form, making it an attractive storage medium.

Storage of hydrogen as a liquid increases its volumetric density where the theoretical volumetric density of liquid hydrogen (LH2) is 70 g/L at the boiling point of hydrogen (−253°C) and atmospheric pressure, whereas it is 24 g/L and 40 g/L for compressed hydrogen at 350 and 700 bar, respectively, at room temperature.

This hydrogen storage technology is rather effective but has disadvantages:
- The key disadvantage is the higher energy required by the liquefaction process.
- The strict control needed on the container temperature stability to avoid any risk of overpressure.
- It also requires cryogenic vessels and suffers from hydrogen losses through evaporation from the containers.

7.2. Liquid Hydrogen Storage Vessels

The cryogenic temperature required necessitates that LH2 vessels be thermally insulated. Hence, cryogenic hydrogen vessels are usually vacuum insulated; they are double-walled vessels, with a vacuum providing thermal insulation between the inner and outer walls. To minimize if not eliminate thermal losses, effects of thermal radiation, thermal convection and thermal conduction must be considered when designing the vessels.

The cryogenic temperature required necessitates that LH2 vessels be thermally insulated. Hence, cryogenic hydrogen vessels are usually vacuum insulated; they are double-walled vessels, with a vacuum providing thermal insulation between the inner and outer walls. The complex design of a liquid hydrogen vessel system is schematically illustrated in below Figure.

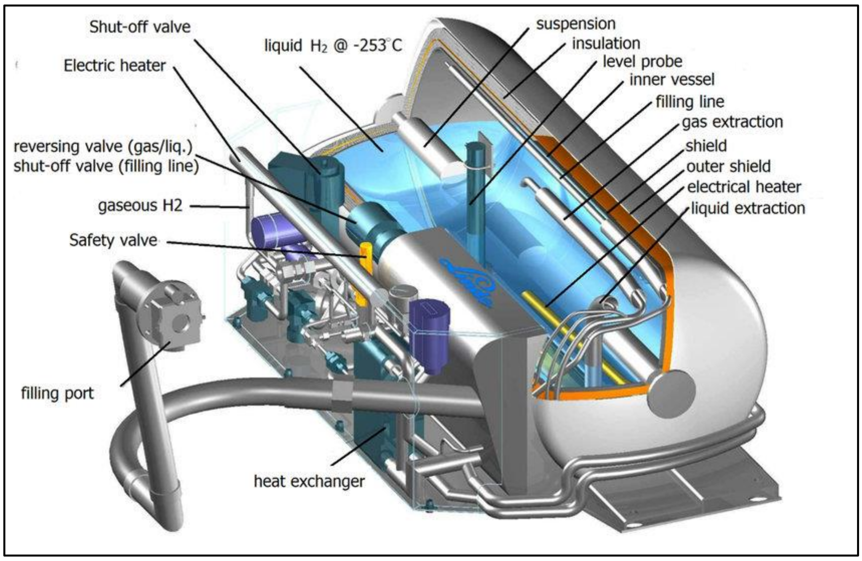

Figure 34. Schematic of a cryogenic hydrogen tank (source: Linde ®)

7.3. Liquid Hydrogen Storage Losses

Regardless of the efficiency of the LH2 storage vessel, boil-off losses are unavoidable due to heat flow from the environment to the LH2 and thermal conduction through other components. The boil-off rate is not only a function of thermal insulation, but also of the size and shape of the vessel; it can be up to 0.4% per day. Boil-off losses may cause safety concerns if the vessel is in a confined space, for instance, if a vehicle that has a cryogenic hydrogen tank is left parked in a closed garage for several days.

Other issues associated with liquid hydrogen are the fuelling equipment and transferring lines, which must be properly insulated to avoid losses. Due to the liquefaction penalty, cost, and inevitable boil-off associated with cryogenic hydrogen storage, its potential application has been limited to where high energy density is necessary and the hydrogen is used within a short period, where the cost has a minimal concern.

7.4. Cryo-compressed Hydrogen Storage

Cryo-compressed hydrogen storage is a combination of the attributes of compressed hydrogen storage and cryogenic hydrogen storage. Cryo-compressed storage serves to curtail the disadvantage of compressed hydrogen storage of large volumes and high pressures required, and the disadvantage of cryogenic hydrogen storage of the inevitable boil-off losses.

The insulated vessel used to store cryo-compressed hydrogen is capable of withstanding cryogenic temperatures and high pressures. The capability of the insulated vessel to hold high pressures permits a higher rise in pressure within the tank than in the case of cryogenic storage, and extends the dormancy period, resulting in increased storage density and decreased boil-off losses. Furthermore, the lower pressures employed in cryo-compressed hydrogen storage (typically <300 bar) relative to compressed hydrogen storage (700 bar) may reduce the requirement for more costly carbon fibre composites.

An example of a Generation 2 cryogenic vessel for cryo-compressed storage is shown in the below Figure.

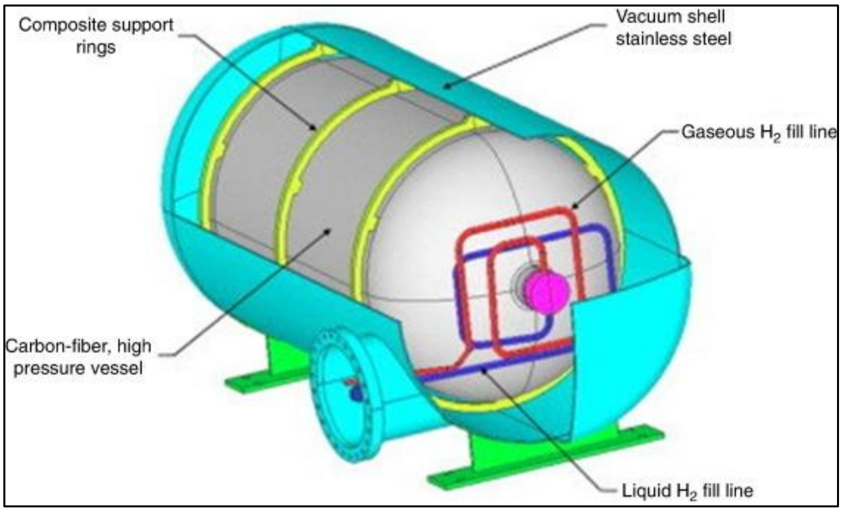

Figure 35. Generation 2 cryogenic-capable pressure vessel design

The vessel consists of an inner vessel made up of an Al liner wrapped with carbon fibre composite (Type III) and enclosed in a vacuum space containing sheets of highly reflective metalized plastic to limit heat transfer from the environment to the vessel, and an exterior stainless-steel jacket.

Discussion Tasks →

- Search for latest research directed towards the development of new methodologies for reliability design and safety qualification of these cryogenic storage systems. Discuss these.
- Explore the issues associated with LH2 and explain why the "cryogenic coupling" is the weakest link in the whole process of LH2 fuelling equipment and transferring lines.

CONTINUOUS ASSESSMENT 5:

-------- End of Block 7 --------

-------- BLOCK 8 --------

8.1. Hydrogen Adsorption Storage

Many different materials have been investigated for their potential use in the storage of hydrogen through adsorption. These include porous materials, ranging from classical materials such as zeolites and activated carbon (AC) to carbon nanotubes, fullerenes. zeolite-templated carbons and, more recently, relatively newer classes of materials such as metal–organic frameworks (MOFs), covalent organic frameworks (COFs), and polymers of intrinsic microporosity (PIMs).

In the adsorption storage of hydrogen, hydrogen molecules are bound to the surface of the pores of the materials through physical interaction (physisorption), which involves weak van der Waals forces. There are several advantages of physisorption-based storage over chemisorption-based storage: fast hydrogen adsorption/desorption kinetics, complete reversibility, and high stability over many cycles. The very low interaction energy involved in physisorption (typically 4–10 kJ mol−1) makes the process fully reversible and leads to less heat generation than in the case of chemisorption. Generally, in porous materials, hydrogen storage capacities strongly depend on the surface area and pore volume of the materials accessible to the hydrogen molecules. Due to the weak interactions between hydrogen molecules and the surface of these materials, high hydrogen storage capacities can only be achieved at cryogenic temperatures (usually 77 K) and high pressures. At ambient temperature and pressure conditions, hydrogen adsorption capacities become very low (usually <1 wt%).

Amongst the different classes of porous materials that have been studied, the following have been extensively investigated: MOFs, carbon-based materials, and porous organic polymers (POPs). These are now discussed in more detail.

8.1.1. Metal–organic Frameworks

MOFs constitute an extensive class of crystalline porous materials, also known as coordination polymers. They consist of metal nodes (ions or clusters) coordinated to organic molecules, resulting in a network of pores and channels. MOFs have extremely large surface areas (up to 10,000 m2 g−1) and ultrahigh permanent porosity; furthermore, their framework topology, pore size, and internal surface area can be readily tuned to target specific applications.

In this regard, various features have been explored: the effect of open metal centers, the surface area, and pore volume, pore size, functionalization of ligands, doping with metal ions, incorporation of nanoparticles (NPs), and formation of composites. Removal of coordinated solvent molecules helps to generate open metal sites in MOFs, which can enhance the binding of hydrogen molecules to the MOFs. Enhancement of the isosteric heat of adsorption, which reflects the strength of hydrogen interaction with a MOF, can also be achieved by tuning the pore size of the MOF. When pores are large, the interaction energy of hydrogen molecules with the pore surface is low; however, it can be enhanced in small pores were overlapping of the potential fields from opposite walls is favored. Functionalization of ligands can modify the electronic environment for hydrogen interaction and influence the hydrogen adsorption of MOFs. At low pressure, hydrogen adsorption correlates with the pore size and, consequently, the heat of adsorption, but at moderate pressure, it depends on the surface area, while at high pressure it relates to the pore volume.

To systematically investigate the effect of surface area and pore volume on hydrogen uptake, one of the common approaches employed is to vary the length of the ligands of MOFs with the same topology.

Post synthetic modification of MOFs by doping with alkali metals has been reported to be a good approach to enhance the hydrogen storage capacity of MOFs. Formation of composites of MOFs with other materials, particularly carbon materials, has been shown to enhance the hydrogen uptake. Many studies have been carried out in which metal NPs, such as Pd and Pt NPs, were incorporated in MOFs, with claims of significantly enhanced hydrogen storage capacity at room temperature. These reports have attributed the enhancement to a phenomenon known as the spillover effect, which involves the dissociation of hydrogen molecules on the metal NPs and subsequent migration of the atoms to the surface of the MOF. However, enhancement of hydrogen storage by spillover has been a subject of debate and these considerably high enhancement claims could not be successfully reproduced independently.

Although gravimetric hydrogen storage capacities are frequently reported in the literature, equally important is the volumetric hydrogen storage capacity, especially in relation to onboard hydrogen storage applications. Any further increase in surface area to enhance the gravimetric uptake resulted in a decreased volumetric uptake.

Another relationship between volumetric absolute hydrogen uptake and volumetric surface area gave a linear plot. To improve the volumetric hydrogen storage capacity of MOFs, the compaction of MOF powders has been proposed. Recently, a rare case was reported in which UiO-66, pelletized at high pressure (∼7000 bar), yielded an unprecedented total volumetric capacity of up to 74 g L−1 (compared with 29 g L−1 for the powder) at 77 K and 100 bar and, critically, with no compromise on the total gravimetric uptake obtained for the MOF powder. Such properties are beneficial for practical hydrogen storage.

8.1.2. Carbon-based Materials

Many different carbon-based materials have been studied as potential hydrogen storage materials. Examples include carbon nanotubes/nanofibers, fullerenes, graphene, AC, carbon aerogels, and templated carbons. In general, carbon-based materials have garnered considerable attention for hydrogen storage due to their high surface area, chemical stability, thermal stability, relatively low cost, and lightweight. The early optimistic results for hydrogen storage in carbon nanotubes/nanofibers were met with controversies, however. It was later established that errors in measurements and poor sample quality/presence of impurities hugely influenced the reported results.

One of the most highly investigated types of carbon materials for hydrogen storage is AC. It can be derived from a wide variety of carbon-based precursors, such as biomass, lignite coke, coal, carbon rich polymers, and waste feedstocks. Such versatility in precursor materials affords the relatively low-cost production of these carbons and implies that ACs with a range of textural properties can be produced. At moderate pressures (∼10–100 bar) and 77 K, hydrogen uptakes for ACs reported in the literature have generally been within the range 2–7 wt%, with high hydrogen uptakes usually ascribed to favorable textural properties, e.g., high surface area, large micropore volume, and narrow pore size distribution.

Templated carbons are prepared by employing other porous materials (such as silicas, zeolites, clays, and MOFs) as templates. The templating approach can generate carbon materials with ordered porous structures and readily allows for the predetermined control of porous structures of the carbon products. Therefore, ordered microporous, mesoporous, or hierarchical porous carbons can be created based on the type of template, source of carbon, and synthesis conditions utilized. Amongst the numerous templated carbons reported, zeolite-templated carbons (ZTCs) have shown the most promise as hydrogen storage materials because they generally possess high surface areas and pore volumes, with considerable microporosity. To enhance the hydrogen storage capacity of ZTCs, activation with various agents (e.g., KOH) have been reported. Other strategies such as heteroatom doping (e.g., with nitrogen) have revealed that N-doping can be advantageous only at lower coverage (low hydrogen uptake); at higher coverage (high hydrogen uptake) it is disadvantageous.

Another potential carbonaceous hydrogen storage material is graphene-based materials. Graphene consists of a single layer of atoms in a two-dimensional hexagonal lattice. However, a single graphene sheet is not appropriate for hydrogen storage; therefore, multiple graphene sheets are employed. In addition, functionalization to enhance hydrogen storage performance is required. Efforts have been made to dope graphene with elements such as boron and nitrogen, alkali, alkaline earth, and transition metals; however, challenges pertaining to clustering tendency of decorated atoms and low hydrogen adsorption capacity were noted.

In graphene, molecular hydrogen is stored between the layers of the graphene sheets. Thus, studies have been conducted in efforts to increase the interlayer spacing of graphene by incorporating nanomaterials, such as carbon nanotubes, as separators. Porous graphene, also known as holey graphene, was investigated both computationally and experimentally. It was later predicted that, by creating tiny regular holes in graphene, the surface area was improved to 5100 m2 g–1, and a high hydrogen uptake of up to 6.5 wt% at 77 K was attained with the holey graphene. However, from experiments, the holey graphene synthesized had a surface area of only 2900 m2 g–1 and hydrogen uptake of 5.5 wt% at 77 K.

Graphene oxide has also been proposed for use in hydrogen storage. Graphene oxide possesses a variety of oxygen-containing functional groups, such as carboxyl, hydroxyl, and epoxy groups, amongst others, that can be exploited for the improvement of hydrogen storage.

8.1.3. Porous Organic Polymers

POPs can be synthesized from a range of organic reactions. POPs do not include heavy elements, which implies they have very low densities. They are also stable at ambient atmosphere and easy to handle, making them attractive for hydrogen storage applications. There are several categories of POPs.

COFs, a class of POPs, are crystalline materials similar to MOFs but they do not contain the metal nodes; instead, the frameworks are linked together by strong organic covalent bonds. Their low weight, high stability, and large surface area make them promising for hydrogen storage. A high hydrogen uptake of 7.24 wt% at 77 K and 35 bar has been achieved with COFs. Modifications to improve the hydrogen storage properties have been conducted and numerous theoretical studies have been reported.

Another category of POPs, hyper-cross-linked polymers (HCPs), are copolymers synthesized from cross-linked polymeric precursors. The textural properties of the rigid networks can be tailored by the choice of monomers, resulting in narrow pore structure, high micropore volumes, and large surface areas, which make HCPs promising materials for hydrogen storage. Recently, HCPs were synthesized from chlorinated polypropylene (CPP) grafted with polyethylenimine (PEI) by a hydrothermal amination reaction [26]. Very high hydrogen storage capacities of 11.26 wt% at 77 K and 50 bar, and 2.47 wt% at 300 K and 50 bar were reported, but the shape of the curves did not follow the normal shape observed for porous materials at 77 K. The isosteric heat of adsorption was calculated to be 38.79 kJ mol–1 for one of the samples. Such a high enthalpy value is likely associated with chemisorption, although it was claimed that the adsorption process of CPP-g-PEI was reversible physical adsorption.

Conjugated microporous polymers (CMPs) are amorphous polymers consisting of three-dimensional network structures built from aromatic compounds with conjugation linkages. They possess high micropore volumes and large surface areas, which make them potentially suitable for hydrogen storage. Several studies have been carried out to tune the textural properties of CMPs in order to improve their hydrogen storage capacities. For example, varying the structure of the monomers to vary the pore size and surface area has been reported. Similarly, to MOFs and carbon-based materials, doping with metals (such as Pd, Li, and Ca) and other heteroatoms (such as N) have also been applied to CMPs in an attempt to improve their hydrogen storage capabilities—some improvements have been reported.

Polymers of intrinsic microporosity consist entirely of fused ring subunits designed to be simultaneously rigid and contorted to pack space inefficiently. This results in a continuous network of interconnected free volume with an accessible internal surface area up to 2000 m2 g–1, which, together with their solution processability, chemical homogeneity, stability, and lightweight, render them attractive for hydrogen storage. Specific properties of PIMs can be tailored, depending on the choice of the monomers. Attempts have been made to functionalize PIMs in efforts to enhance their hydrogen adsorption, e.g., by substitution of a subunit within the PIM network with a functional group.

-------- End of Block 8 --------

-------- BLOCK 9 --------

9.1. Chemical Hydrogen Storage

Chemical hydrogen storage involves the binding of atomic hydrogen chemically within the structure of a material. Chemisorption can result in relatively high hydrogen storage capacities, but the hydrogen uptake and release kinetics may be slow; the release of hydrogen usually requires high temperatures, with such materials displaying irreversible hydrogen uptake due to high the activation energy involved. Therefore, a great deal of attention has been placed on enhancing the thermodynamics, kinetics, and cyclability of hydrogen uptake/release for chemical hydrogen storage materials.

9.1.1. Metal Hydrides

Hydrogen interacts with various metals and alloys at various temperatures and pressures to form metal hydrides. One of the key features that make metal hydrides attractive for hydrogen storage is their high volumetric storage capacities, thus providing a safer and more compact storage than possible with conventional methods of compressed and LH2 storage. Metal hydrides can be classified into three groups: intermetallic hydrides, binary hydrides, and complex metal hydrides.

Intermetallic hydrides are considered low-temperature hydrides and the hydrogen storage capacities of AB5, AB2, A2B, and AB type intermetallic alloys where there is no substitution with other metals are limited to <2 wt% due to the limitations arising from the crystal structure and unit cell volume. In these alloys, A denotes an element with high affinity for hydrogen (usually an alkaline earth or rare-earth metal) and B refers to an element that does not form a stable hydride under normal conditions (usually a transition metal). For example, LaNi5, an AB5 type alloy, can reach a hydrogen storage capacity of 1.4 wt%, and FeTi, an AB type alloy, can achieve 1.9 wt% hydrogen uptake. Partial substitution with other metals can tune the equilibrium pressure and control the stability, which would enhance their practicality for hydrogen storage. The intermetallic hydrides that store hydrogen in interstitial sites in the metal lattice exhibit relatively fast hydrogen absorption/desorption kinetics.

Nanostructure formation has also been widely exploited to enhance the properties of intermetallic hydrides. Due to the low gravimetric hydrogen storage capacities of interstitial hydrides, other types of hydrides have been extensively studied. Amongst these is the binary hydride, MgH2, which is the most studied binary hydride.

Magnesium hydride is attractive for hydrogen storage because of its high theoretical gravimetric (7.6 wt%) and volumetric (110 g L–1) hydrogen storage capacities, lightweight, and the high abundance and low cost of Mg metal. However, its hydrogen uptake/release kinetics are slow and high temperatures (typically >300°C at 1 bar) are required for hydrogen desorption, which reduces their suitability and efficiency for practical hydrogen storage.

Another binary hydride, AlH3, benefits from low cost and high abundance of Al metal, and also has a high gravimetric hydrogen storage capacity of 10.1 wt% H. However, it is difficult to directly synthesize AlH3 from its constituent elements due to the extreme pressures (>1000 bar) and high temperatures required.

Complex hydrides (such as LiAlH4, NaAlH4, Ca(AlH4)2, LiBH4, Mg(BH4)2, and Zn(BH4)2) have attracted much attention due to their high theoretical gravimetric hydrogen contents. However, the major impediment in utilizing these materials for hydrogen storage is their high stabilities, requiring high decomposition temperatures, and their lack of reversibility. To overcome the problems associated with these binary and complex hydrides, various strategies have been widely investigated. These include alloying with other elements, catalyst addition, nanostructuring, nanoconfinement, and formation of composites in order to enhance the kinetics and thermodynamics of hydrogen release/uptake. For instance, Ti-doped LiAlH4 has been reported to desorb up to 7 wt% hydrogen, commencing at temperatures as low as 80°C, and the material could be recharged almost to its initial desorption amount under extraordinarily mild conditions, entailing the use of dimethyl ether as a solvent. Nanostructuring reduces the particle size of metal hydrides, which can lead to the improved surface area, increases the number of nucleation sites for hydrogen reactions, and reduces the diffusion distance for hydrogen. These properties would likely result in faster kinetics and/or reduce the enthalpy or activation energy required for hydrogen desorption.

Nanoconfinement of hydrides in porous materials enables the stabilization of NPs, preventing them from recombining and forming aggregates—the interaction of the hydride particles with the pore surface of the host material is also promoted. Through a combination of nanoconfinement and nanocatalysis, improved hydrogen storage reversibility and decreased dehydrogenation temperature for nanoconfined LIBH4 relative to bulk LiBH4 have been reported.

Clearly, significant improvements have been made in terms of enhancing the kinetics and/or thermodynamic properties of metal hydrides through single approaches or a combination of strategies.

9.1.2. Liquid Organic Hydrogen Carriers

Hydrogen storage in the form of liquid organic hydrogen carriers (LOHCs) has recently attracted much interest. This is simply because LOHCs offer a more convenient way of handing hydrogen. LOHCs can be defined as organic molecules that can store and release hydrogen through a reversible catalytic hydrogenation reaction.

As shown in Fig. 9.1, a hydrogen lean molecule (H0-LOHC) is hydrogenated at a certain pressure (e.g., 30 bar) and temperature (e.g., 150°C) in the presence of a catalyst, to produce a hydrogen-rich molecule (Hn-LOHC). The Hn-LOHC molecule is then dehydrogenated at a certain temperature (e.g., 300°C) and 1 bar pressure, in the presence of a catalyst, to produce the H0-LOHC molecule and hydrogen gas. A surplus energy produced by renewables sources (e.g., solar or wind) can be used to produce green hydrogen by the electrolysis of water. This hydrogen can be stored by hydrogenating the LOHC—in this manner, the logistics of handling gaseous hydrogen is simplified. In addition, gray hydrogen (from fossil fuels) and blue hydrogen (incorporating carbon capture technology into gray hydrogen production) can also be stored using the LOHC method, provided that gaseous impurities are not poisonous to the hydrogenation catalyst. The hydrogenated LOHC can be stored under normal conditions (ambient temperature and pressure) for long periods without self-discharge—this could possibly allow seasonal energy storage.

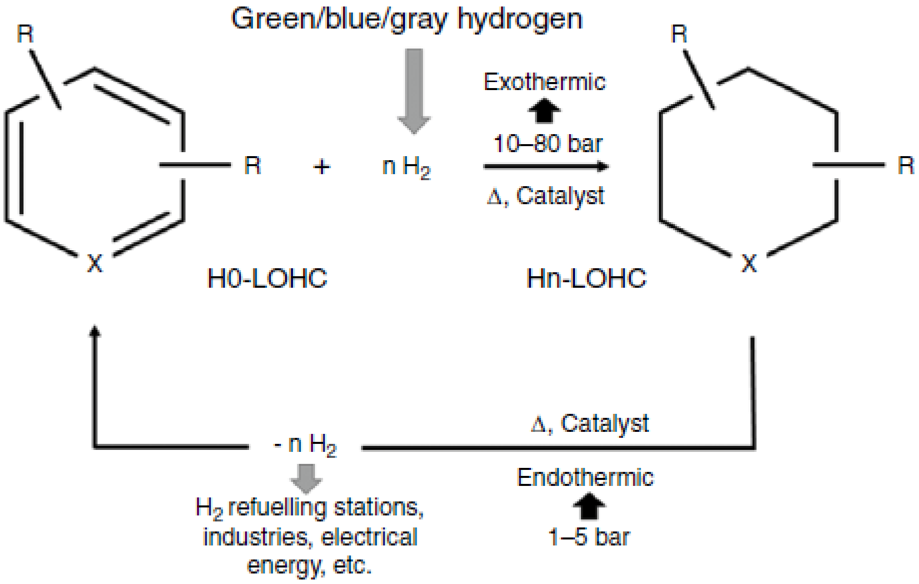

Figure 9.1 The concept of hydrogen storage using LOHCs (R: alkyl (e.g., ethyl, methyl) or aryl (e.g., phenyl), X: heteroatoms (e.g., N), n: number of molecules).

Therefore, LOHCs can play an important role in the storage, transport, and trading of energies from different sources. Furthermore, LOHC hydrogen can couple the sites where hydrogen is produced with the sites where it is consumed. For example, hydrogen can be used as a feedstock for many industrial processes (chemicals, steel processing, food, glass, etc.) and as an energy source for mobile and stationary power applications.

Hydrogenation and dehydrogenation reaction conditions strongly depend on the properties of the LOHC molecule and the catalyst used. For example, some molecules will require temperatures of ~300°C to be dehydrogenated, whereas others can be dehydrogenated at <200°C. In this situation, the higher reaction enthalpy of the LOHC molecule the higher the dehydrogenation temperature. This is described for LOHC molecule in more detail later. The use of LOHCs for the storage of hydrogen is not new. However, the latest developments in this field reveal very unique properties of LOHCs, which span a wide range of applications.

9.1.3. Ammonia

Ammonia is one of the most promising chemical alternatives for the storage of hydrogen (besides compressed gas and LH2 itself). The process of ammonia synthesis (the Haber–Bosch process) has been applied since the early 1900s. Later that century, it led to a significant increase in global crop production, with ammonia acting as agricultural fertilizer. In 2019, the global annual ammonia production rate was estimated at ∼170 million metric tons. Although ammonia is a carbon-free molecule, the hydrogen necessary for its synthesis comes with significant carbon emissions due to the reforming of natural gas and the gasification of coal—processes still applied today for hydrogen production. The ammonia synthesis process can, however, be decarbonized, with the implementation of electrolytic hydrogen production, using renewable energy sources.

Ammonia supports a hydrogen density of 108.5 kg m–3, and liquefies at a pressure of 8.6 bara and temperature of 20°C. The two most energy-intensive steps to produce ammonia are, first, the cryogenic distillation of air to produce pure nitrogen and, second, the compression stages for hydrogen and nitrogen, since the Haber–Bosch process operates at reaction pressures in the order of 200 bar. Modified iron catalysts are typically applied during the synthesis step [59]. Recent efforts have been directed at developing catalysts for low-pressure ammonia synthesis. From a thermodynamic perspective, high-pressure operation favors ammonia production, which means that the number of recycling steps for unreacted gas will need to be increased significantly during low-pressure operation. Ammonia is used as raw material in the production of ammonium nitrate and ammonium sulfate fertilizers (and as precursor to explosives), nitric acid, urea, hydrazine, and cleaning agents.

The renewable production of ammonia benefits from several encouraging factors. Unlike all carbon- based hydrogen carriers, syngas or carbon dioxide (CO2) is not required for ammonia synthesis. This benefits scenarios of ammonia production in locations such as Morocco, which has an abundance or solar energy, but with few CO2 producing industries [60]. Hank et al. [60] has demonstrated, under certain model assumptions, for the year 2030, that ammonia is the most economic chemical (comparing LH2, NH3, CH3OH, LCH4, and LOHC) for energy export from Morocco to Germany, with a levelized cost of ammonia delivered to Germany of 124 € MWhLHV–1. Renewable hydrogen can be generated using any sustainable power source, and the nitrogen production step can benefit from more compact technologies such as pressure swing adsorption. It has been reported that, in Northern Europe, ammonia will be a cost-competitive storage and transportation medium for wind energy in a scenario-based entirely on renewable energy by 2050, with ammonia production costs expected to be in the range 431–528 € ton–1 (83–102 € MWhLHV–1). In both these examples mentioned, the cost of renewable energy and the capital investment for electrolysis are the major cost contributors.

Ammonia for power generation finds application through internal combustion engines, FCs and gas turbines. The demonstration of ammonia combustion engines may be a future clean alternative for utility-scale diesel generator sets. Conventional FCs that are supplied with ammonia-derived hydrogen have been extensively investigated. Alkaline FCs are looking particularly encouraging, as the equilibrium- limited ammonia reforming process does produce parts per million (ppm) values of residual ammonia in the hydrogen-rich stream, which can be tolerated by alkaline FC technology. This is less so in the case of PEM FCs (<1 ppm NH3 required), due to the acidic nature of the FC membrane, which shows a high affinity for the alkaline ammonium ion (NH4 +).

Direct ammonia FC technology (alkaline and solid oxide) is less mature. The combustion of ammonia using gas turbine technology could fill significant gaps in the large-scale power generation sector (>100 MW plants) as a sustainable alternative to natural gas. Both Mitsubishi Hitachi Power Systems and Siemens have reported developments in this regard [64]. Retrofitting of combustion chambers is necessary due to the slower burning characteristics of ammonia. Additional NOx emissions are obtained from the ammonia combustion process, but subsequent neutralization with ammonia may solve this issue, producing ammonium nitrate. The combustion of ammonia and natural gas mixtures has also been demonstrated. The combination of these future end-use prospects, coupled with the ease of renewable ammonia production using electrolytic hydrogen, and expanding existing ammonia storage and distribution infrastructure, has led to the belief that ammonia may well be the primary chemical alternative to green hydrogen in decades to come.

9.1.4. Formic Acid

Formic acid (FA), the simplest carboxylic acid, has great potential as a hydrogen carrier due to its high hydrogen density (53.5 kg m–3) and the acid's occurrence in the liquid state at atmospheric conditions. FA is widely used in the leather and textile industries. Its global production capacity is ∼800,000 metric tons per annum. FA has both reactive carbonyl and hydroxyl groups, therefore, it is a key building block in the production of various other fuels and specialty chemicals. FA is produced on large scale by the hydrolysis of methyl formate, which, in turn, originates from the carbonylation reaction of methanol and carbon monoxide (CO) at elevated pressures. Of particular interest is the acid's direct synthesis from the hydrogenation of dissolved CO2 in the presence of a homogeneous catalyst (e.g., RuCl2(PTA)4). Dimethyl sulfoxide appears to be a good solvent; substantially increased yields of FA are obtained with it, compared with water as solvent. This process route realizes the possibility of utilizing renewable hydrogen and waste CO2 from a concentrated point source for hydrogen storage application using FA. However, the separation and recycling of homogeneous catalysts and solvents adds to the complexity of the synthesis step. The thermodynamics associated with FA synthesis in a gas-phase reaction are unfavorable. Furthermore, due to FA's high ionization constant, its corrosion properties are problematic when using common stainless steels such as SS304 and SS316 at high acid concentrations or elevated temperature. The application of zirconium alloys has proven to be the most economical alternative to tolerate FA's acidic properties.

The release of hydrogen (and CO2) from FA is referred to as its decomposition reaction. A secondary reaction (an unwanted reaction, at least for low-temperature FC applications) may occur, yielding CO and water. The CO poisoning of Pt-containing PEM FC anodes is cause for great concern when the source of hydrogen originates from the reforming of carbon-containing fuels. To an extent, Pt–Ru bimetallic FC catalysts, which are more tolerant toward CO, have been developed. CO-containing hydrogen streams have led to the application of water–gas shift and low-temperature methanation technology in reforming systems to reduce CO concentrations to within acceptable levels (ppm). Recently, the demonstration of new catalysts such as Au/m-ZrO2 has shown high selectivity toward the production of hydrogen (81.8 L gAu −1 h−1) and CO2 from FA in the aqueous phase at temperatures as low as 80°C. CO levels of <9 ppm and catalyst reusability were demonstrated.

With the application of high-temperature solid oxide FCs, CO together with hydrogen can be used as the fuel source. These high-temperature FCs are still under development, but appear to offer a promising technology. The world's first FA-based power unit has been developed by the Swiss Federal Institute of Technology and the GRT Group (Switzerland). The unit is based on the decomposition of FA, and uses a PEM FC to generate up to 1 kW electric power, with a system efficiency of 40–45%. Direct FA FCs are encouraging, considering the fuel's high energy density, the global production volume, and ease of transportation.

However, the electrooxidation of FA is not so simple; the CO intermediates formed, using commercial Pt anodes, show significant poisoning effect. Pd is prone to dissolution in strong acid, and bimetallic catalysts have not shown substantial increases in activity and durability. Nevertheless, continuous developments in the field of electrocatalysts for direct FA FCs will ensure the fuel's future potential as a hydrogen energy vector in years to come.

9.1.5. Methanol

In addition to FA, methanol is another C1 molecule that can act as a hydrogen storage method via its synthesis. Methanol is a liquid at 20°C and 1 atm, which simplifies its storage and transportation in nonpressurized vessels, and it supports a hydrogen density of 100 kg m–3. As in the case of FA, the production of renewable methanol may occur by combining emitted CO2 from an existing process with renewable hydrogen. Methanol synthesis typically occurs at reaction temperatures of 200–300°C and pressure of ∼50 bar. Reactant utilization is incomplete due to equilibrium limitation, therefore gas recycling is necessary.

Although commercial methanol catalysts convert CO/CO2 syngas mixtures, the use of pure CO2 as reactant places additional strain on the catalyst and affects its longevity due to the amount of water by-product formation. Current research in the field of clean fuel alternatives has seen numerous studies on catalyst modification and synthesis for the direct CO2 to methanol process, in efforts to enhance the kinetic turnover rates and increase catalyst durability. One of the disadvantages of CO2- to-methanol is the increased stoichiometric molar ratio of hydrogen required—3:1 (H2:CO2) due to water by-product formation compared with the CO pathway, 2:1 (H2:CO). In part, this has led to the investigation of alternative syngas sources such as biomass gasification, steel mill off-gas, and the pyrolysis/gasification of municipal waste.

In Italy, the oil and gas company Ente Nazionale Idrocarburi (ENI S.p.A.) has developed an automotive fuel that contains 15% methanol and 5% bioethanol, called "A20." The fuel is compatible with petrol vehicles manufactured from 2001 onwards. Globally, there exists numerous fuel standards limiting the oxygen content in automotive fuels. Vehicles fueled by pure methanol are a great prospect. China, the world's largest producer of methanol, has implemented >10,000 methanol-fueled vehicles (cars, buses, and trucks) up to 2019. Methanol-fueled vehicles support lower emissions and engine efficiency increases are up to

50%, as a result of an increased pressure ratio and lower stoichiometric air/methanol ratios. Methanol, with a low cetane number (not suited for compression ignition engines), may well be used toward the production of dimethyl ether and oxymethylene ether as diesel fuel alternatives. The trade and transport of methanol by ship may result in its use as a global maritime fuel. In fact, the first commercial vessel to use methanol was the MS Stena Germanica, a Swedish-operated passenger ferry, in 2015. The combustion of methanol results in significant reductions in SOx, NOx, COx, and particulate emissions, compared with heavy fuel oils and distillates for ship propulsion.

Since 2011, the operation of the George Olah renewable methanol plant by Carbon Recycling International in Iceland has attracted significant attention for the renewable production of methanol. The plant produces ~4000 tons of methanol annually Geothermal power for electrolysis (6 MW) and emitted CO2 (5500 tons annually) from the Svartsengi geothermal power plant are used as input to the production facility. Recently, Carbon Recycling International ‘s focus for the production of renewable methanol has expanded toward mainland Europe, under the FReSMe and MefCO2 project consortia. The production of green methanol has been reinforced by companies such as BioMCN (Netherlands), which produces methanol from biogas.

The hydrogen that is stored in methanol can be regenerated via methanol steam reforming, a process that has been demonstrated extensively, and, for fuel processors, on the multi-kW scale.

The process takes place at mild temperatures (250–400°C). When using conventional Cu/ZnO catalysts, CO concentrations >2% may be obtained in the product due to the effects of the reverse water–gas shift reaction. Of course, CO is undesired in low-temperature FCs for power generation purposes. On the contrary, much higher selectivity toward CO2 and H2 products has been shown using PGM-based catalysts such as Pd-In/Al2O3. Nonetheless, selective methanation, preferential oxidation, or other separation techniques need to be applied upstream of the lowtemperature HFC.

Direct methanol FCs have been demonstrated for portable and low power (<10 kW) applications using PEM technology (90–130°C) and Pt–Ru bimetallic anode catalysts. Currently, anode catalyst loadings are in the order of 4 mg cm–2, to ensure high turnover rates of methanol. In conventional HFCs, the anode oxidation reaction is not the kinetically limiting factor. Consequently, methanol FCs have substantially lower efficiencies (~10%) due to both anode and cathode reactions being sluggish. Future prospects include catalyst improvements to reduce anode catalyst loading and more durable cathode catalysts (which are affected by methanol cross-over at high feed concentrations) to increase methanol FC efficiency.

Overall, it appears that renewable methanol production is a viable hydrogen storage and carbon sequestration process. Its combustion in spark-ignition engines supports more efficient and less polluting engine operation, while its production will be favored by future economics (cost of electrolysis technology) and political factors (increasing carbon taxation).

-------- End of Block 9 --------

-------- BLOCK 10 --------

10.1. Comparison of different hydrogen storage technologies

The criteria for hydrogen storage for onboard light-duty vehicles are the most stringent, and hydrogen storage options have been widely investigated for such applications. Fig. 10.1 compares the volumetric and gravimetric hydrogen storage capacities of various storage options, as well as their cost estimates, together with the US DOE 2020 and 2025, and ultimate hydrogen storage targets for onboard applications. Besides these three system criteria shown, there are many other technical systems targets—in terms of durability, charge/discharge rates, fuel quality, and environmental health and safety—that must be met simultaneously for a viable hydrogen storage system.
Compressed and/or LH2 storage are the most advanced technologies, with storage capacities approaching the stipulated system targets. as shown in Fig. 10.1. However, current cost estimates for compressed storage, which is the technology employed today in light-duty vehicles, are yet to meet cost targets. At present, only the chemical carriers of LOHC, methanol and liquid ammonia meets the capacity requirements for a hydrogen storage system.

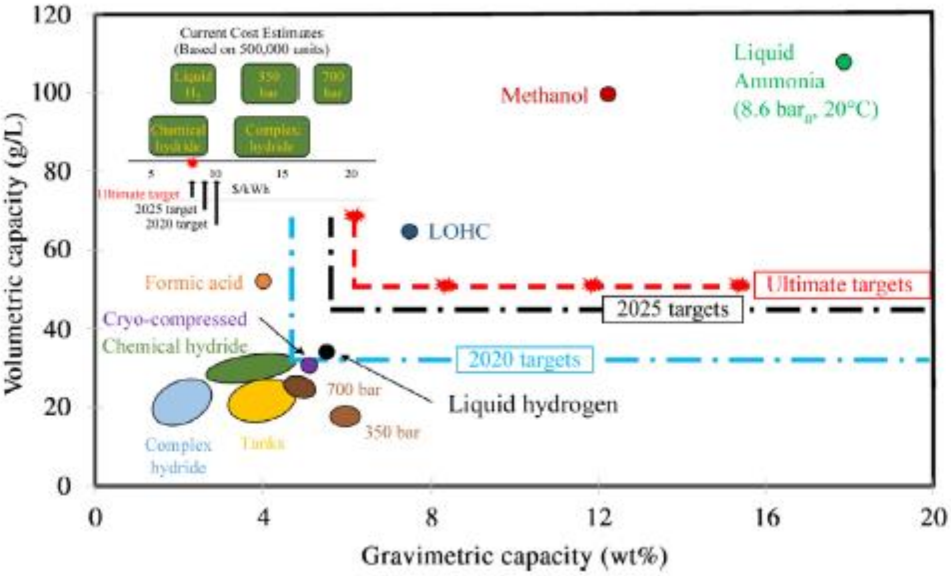

Figure 10.1 Current status of hydrogen storage systems—volumetric and gravimetric hydrogen density of existing developed hydrogen storage systems with respect to US DOE targets.

-------- End of Block 10 --------

References

Henrietta W. Langmi, Nicolaas Engelbrecht, Phillimon M. Modisha, Dmitri Bessarabov. (2021). Electrochemical Power Sources: Fundamentals, Systems, and Applications: Hydrogen Production by Water Electrolysis. Elsevier.

TZIMAS, E., FILIOU, C., PETEVES, S., & VEYRET, J. (2003). HYDROGEN STORAGE: STATE-OF-THE-ART AND FUTURE PERSPECTIVE. Luxembourg: Office for Official Publications of the European: Communities.

Industrial Metallurgists, L. (2016, SEPTEMBER 15). Hydrogen Embrittlement of Steel. Retrieved from imetilc.com: https://www.imetllc.com/hydrogen-embrittlement- steel/#text=Hydrogen%20embrittlement%20is%20a%20metal's, yield%20strength%20of% 20the%20metal.

Pfeifer, M. (2022, January 24). An Introduction to Hydrogen Embrittlement. Retrieved from https://www.corrosionpedia.com/: https://www.corrosionpedia.com/an-introduction-to- hydrogen-embrittlement/2/2568

Wikipedia. (2022, March 06). Hydrogen embrittlement. Retrieved from en.wikipedia.org: https://en.wikipedia.org/wiki/Hydrogen embrittlement#cite_note-31

Sdanghi, G., Maranzana, G., Celzard, A., & Fierro, V. (2019). Review of the current technologies and performances of hydrogen compression for stationary and automotive applications. Renewable and Sustainable Energy Reviews, 102, 150-170.

Fleming, P. (2021, March 8). The Joule-Thomson Effect. Retrieved from https://chem.libretexts.org: https://chem.libretexts.org/@go/page/84312

Industrial Metallurgists, L. (2016, SEPTEMBER 15). Hydrogen Embrittlement of Steel. Retrieved from Mander, P. (2013, January 1). Joule, Thomson, and the birth of big science. Retrieved from CarnotCycle, the classical blog on thermodynamics: https://carnotcycle.wordpress.com/tag/inversion-curve/
Wikipedia, t. f. (2022, February 11). Joule-Thomson effect. Retrieved from Wikipedia, the free encyclopaedia: https://en.wikipedia.org/wiki/Joule %E2%80%93 Thomson effect.

Winterbone, D. (1997). Advanced Thermodynamics for Engineers. London: John Wiley & Sons, Inc.

Figures and tables are referenced in caption when applicable.