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## **Storage and distribution possibilities of solar hydrogen**

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## Abstract

The production of hydrogen from solar energy presents itself as a promising solution for energy storage and mitigation of the intermittency of solar sources. However, production alone is not enough; it is crucial to ensure that the hydrogen generated can be stored, which will allow it to be used as an energy source during periods when solar energy is not sufficient to meet energy demand. This implies that the hydrogen must be able to be stored for extended periods of time or not, as well as being transported and distributed. This article provides a comprehensive review of current technologies for storage and distribution of solar-produced hydrogen.

Keywords: hydrogen storage, ammonia,

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### 1. Solar Hydrogen Production

Solar energy, as a renewable energy source, allows the production of hydrogen through various methods, which differ in the raw material used to obtain hydrogen, the process by which solar energy is used and the products obtained from this process, so the use of solar energy for this purpose does not always guarantee the production of hydrogen free of emissions or by-products. Photochemical, electrochemical or thermal processes such as solar thermal methane reforming allow the production of solar hydrogen, but the treatment of possible emissions such as carbon dioxide or other by-products such as solid carbon, as in the case of the solar methane cracking process, must be contemplated.

Because there are several hydrogen production processes, not only based on solar energy, a classification based on colors was adopted to identify its origin and recognize the treatment of its emissions, so the main ones are gray hydrogen, which is produced from natural gas under reforming processes without considering CCUS technologies, there is also blue hydrogen which, unlike gray hydrogen, does consider the use of CCUS technologies. Another known classification corresponds to green hydrogen, which is produced from the electrolysis process powered by renewable energy sources, as well as other colors associated with different production processes such as turquoise, pink, red, purple hydrogen, among others, whose classification depends on the hydrogen production process, the energy source, the raw material used to obtain hydrogen, and the emissions and/or by-products obtained.

Although there is a worldwide challenge to use energy sources that are not based on fossil fuels, and this is why the focus has been placed on renewable energy sources such as the sun, wind, waves, among others capable of providing energy. However, all of these have a great challenge which is their intermittence, that is, they are unable to provide constant energy during the same day or even hour by hour, due to their dependence on atmospheric conditions. To solve this problem is that hydrogen is proposed as a solution to energy storage.

## 2. Solar energy Storage

To address the problem of solar energy intermittency, several alternatives, methods and technologies have emerged to store the excess energy obtained from the sun. This is either to use it when the resource is not enough to feed the process that is being fed with this renewable energy source or to take advantage of its excess in other processes not connected to the same network and transfer it to other places where there are other processes that require this clean energy supply.

In response to this, concepts such as power-to-gas (Ptg) and power-to-liquid (Ptl) have emerged, which in turn are encompassed in a more generalized concept of power-to-x (Ptx). The power-to-x concept refers to the conversion of renewable energy into different chemical fuels, hydrogen being one of these, and where the power-to-gas concept describes the conversion of surplus or intermittent renewable electricity into hydrogen, to be used in various applications. This integration of concepts offers a solution for energy management and storage.

Among the various technologies that have emerged for the storage of solar energy are the Battery Energy Storage Systems (BESS), systems that allow storing the excess energy generated during the hours of maximum solar radiation for later use in periods of low solar radiation, however, one of its disadvantages is its high cost [1]. There are also Thermal Energy Storage systems, which are a well-known and mature method, where solar energy in the form of heat can be transformed into electricity, it is a system that uses hot fluids or materials with phase change to store energy and can also be integrated with concentrating solar power systems [2].

In addition to the above systems, there are also hybrid storage systems that combine technologies such as hydrogen and batteries to improve storage efficiency, as well as Photo-enhanced Rechargeable batteries that combine photovoltaic technology with high-power metallic batteries, simplifying device configuration and reducing costs [3]. These systems can be classified in

different ways and their selection depends on factors such as storage capacity, discharge time and application requirements [4]. Another such technology is hydrogen, which is increasingly being recognized as a promising technology for storing solar energy due to its clean and renewable nature.

This is how hydrogen emerges as an energy vector, which from its production from renewable resources such as solar energy, can be used as storage of the same, to be used as an emission-free fuel for later being used as an energy source for the same process that the network based on solar energy feeds or to be transported as an energy source for some external process. The hydrogen produced by solar energy can be stored in various forms, such as compressed gas, liquid hydrogen, metal hydride and others, however, these storage and distribution or transportation purposes are still under various limitations and investigations.

### 3. Hydrogen – energy carrier and a fuel for the future

Hydrogen, the most abundant element in the universe and the lightest, in its molecular form, dihydrogen ( $H_2$ ) has a great versatility of uses, among which today it stands out as a potential clean and profitable fuel for the economy of the future [5]. Due to its versatility of applications, both in the petrochemical, metallurgical and even in the food industry, it is in great demand, registering a demand of 70 million tons in 2019, which is projected to increase significantly, reaching a demand of 73-568 Mt by 2050 depending on different scenarios [6], [7].

Among some of its properties is that it has a high energy density of 141,86 MJ/kg at least 2 times more than methane with an energy density of 55,5 MJ/kg, making it a highly efficient fuel [5], [8]. In addition, in its chemical combustion it has the characteristics of having a high adiabatic flame temperature, wide flammability range, and high flame speed, as well as the advantage of only producing water in its combustion. However, one of its disadvantages is that as a fuel it can lead to NO<sub>x</sub> emissions in internal combustion engines under certain conditions, thus in gas turbines it generates higher NO<sub>x</sub> emissions than natural gas even with improved fuel-air mixing [9].

Although it is the most abundant element in the universe, on earth it only exists in compounds such as water and organic materials, due to its reactivity. In this way hydrogen is artificially manufactured, being produced mostly from fossil fuels. The most common method of production corresponds to steam methane reforming that produces significant CO<sub>2</sub> emissions, averaging 11,2

kg CO<sub>2</sub>e/kg H<sub>2</sub>, becoming responsible for about 843 metric tons of CO<sub>2</sub> emissions per annum, equal to the combined total emissions of the UK and Indonesia [10], [6].

While the above is not the only way to obtain hydrogen, there are also multiple ways to obtain hydrogen from hydrogen-containing materials, whether hydrocarbons or not, considering photonic, electrical, chemical, bioenergetic, calorific or a combination of these methods [6]. Thus, due to the great impact of hydrogen production, focus has been placed on production methods based on renewable energies. An example of this is green hydrogen produced from water using renewable energy sources that has a much lower environmental impact factor of 0,0001 compared to 0,036 for CO<sub>2</sub> generating energy sources [11]. However, alternative methods for cleaner hydrogen production are still being researched and developed, as even fossil fuel-based methods remain more economically viable [12].

Because hydrogen has advantageous characteristics and can be produced in cleaner ways, it has emerged as a promising alternative fuel and energy carrier for the future. Hydrogen's high energy density and zero carbon emissions during combustion make it an attractive option for the automotive industry, which could replace current fossil fuels. It can be used in internal combustion engines and fuel cells, offering versatility in transportation and electricity generation [13], [14].

It is also emerging as an energy carrier and storage for renewable energies, especially solar. Its properties and versatile production methods make it ideal for bridging gaps in energy supply and demand. Hydrogen can be stored in various forms, such as metal hydrides or liquid hydrogen, and transported over long distances, making it a flexible energy carrier [15]. Systems that can combine solar energy with hydrogen storage will thus be able to ensure a stable energy supply, even during periods of low solar irradiation, by storing excess energy produced during peak sunlight hours [16], [17].

Some of the challenges that hydrogen presents in its use as a fuel or energy carrier relate to its low volumetric density, safety and storage. It has a volumetric density of 8,6 MJ/L in its liquid state at 20K, and 2,8 MJ/L at 350 bar and 298,15 K quite low compared to other fuels such as gasoline or diesel which have a volumetric density of approximately 36 MJ/L, including others such as methanol, ethanol, butanol and carboxylic acids which have volumetric energy densities of 15,6-22,7 MJ/L, 20,9-26,8 MJ/L and 24,6 (levulinic acid) MJ/L respectively. [18], [19]. This indicates that to store the same amounts of energy from other fuels, a larger volume is required. Additionally,

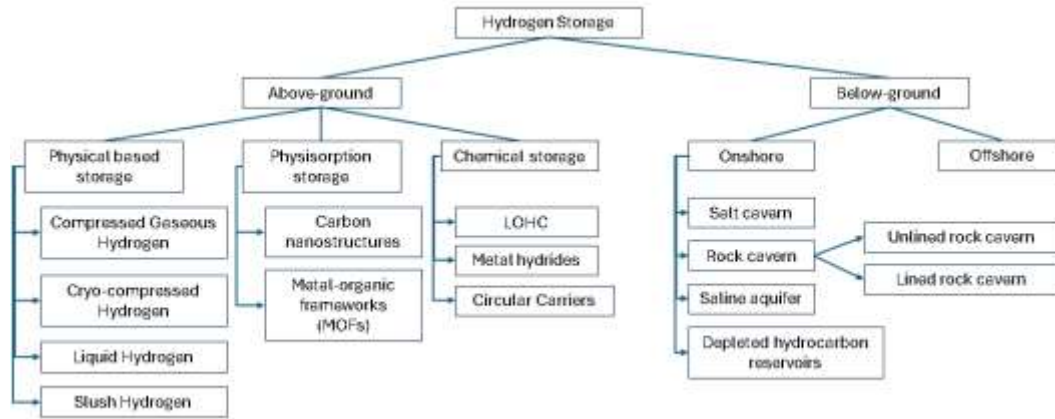
hydrogen has high flammability and can present risks such as flares in premix burners and leaks due to its small molecular size, its safe storage requires a better understanding of its properties, and the potential hazards associated with its use in various systems [20].

Other disadvantages related to its storage are the limitations of the different materials, due to their own compositions. Engineering challenges also include the design of storage systems to withstand high pressures and low temperatures. Another major obstacle is the economic viability of storage technologies, generally associated with the advanced materials and sophisticated systems employed [21].

#### 4. Types of Hydrogen Storage

Hydrogen has emerged as a promising energy carrier for sustainable development and enabling the transition to a low-carbon economy [22]. Potential applications include mobility, heat and industrial processes. However, efficient and safe storage remains a major challenge, especially for transportation [23]. Different technologies have emerged for this purpose including compressed gaseous hydrogen, liquid hydrogen, metal hydride storage, among others.

There are two main types of storage, above-ground and below-ground, where although the above-ground alternatives are mostly developed, they are limited by their storage and discharge capacities [24][25]. These in turn are divided into whether the storage is based on the physical properties of the hydrogen, its state, or whether it is contained in some other substance or material, this for above ground classification, while for below ground classification, it is classified according to the site and the type of site according to its geological characteristics. The classification of these methods is shown below according to the *figure (1)*:



*Figure 1: Hydrogen Storage Classification.*

Each of these storages allows different temporalities for the subsequent use of hydrogen, as some allow stationary storage, as others mobile storage that allows its distribution, which means that hydrogen can have a dynamic use, which allows the consumption of hydrogen in a short period after it has been produced, or some allow the consumption of hydrogen after a long period after it has been produced. Stationary storage is understood in various investigations to mean that the location of the tanks does not usually move, whereas mobile storage usually involves transporting the hydrogen by truck, rail or ship.

#### 4.1 Above-ground

Some of the properties of hydrogen storage materials are expected to be lightweight, low cost, safe, have excellent adsorption and desorption kinetics and recyclability [26].

##### 4.1.1 Physical Based Storage

This type of storage is based on the physical-chemical properties of hydrogen by modifying its state through the modification of parameters such as temperature and pressure. To consider its physical storage, it is first important to know some of its main properties in different states, such as its critical point which is at 33,18 K and 1,3 MPa where hydrogen has a smooth transition behavior between gas and liquid phases with no defined phase boundary, and the one above, regardless of the pressure applied, will not be liquid. The triple point where its gas, liquid, and solid phases coexist in equilibrium, is at a temperature of 13,95 K and a pressure of 0,00721 MPa [27], [28]. It is also important to know its normal boiling point, which is approximately 20,3 K at atmospheric pressure [29].

The types of storage based on the hydrogen state correspond to: compressed gaseous hydrogen, cryo-compressed hydrogen, liquid hydrogen and slush hydrogen .

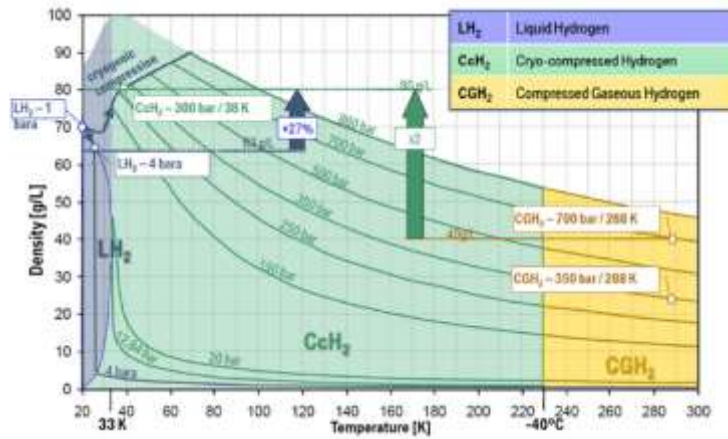


Figure 2: Physical based storage of hydrogen showing its density as a function of temperature and pressure [30].

For hydrogen storage, it is also important to know that molecular hydrogen at room temperature (25 °C) is composed of approximately 75% orthohydrogen (o-H<sub>2</sub>) and 25% parahydrogen (p-H<sub>2</sub>), collectively known as normal hydrogen (n-H<sub>2</sub>). As it approaches the boiling point, the hydrogen changes almost completely to the parahydrogen state, preferred for its lower boiling rate. The conversion from ortho to para is an exothermic reaction, which increases the total reversible work by 15%. Although the density difference between n-H<sub>2</sub> and p-H<sub>2</sub> is small (<0.3%), thermal properties such as enthalpy, conductivity and heat capacity exhibit notable differences, which can affect the design of storage and transport systems. This is amplified when considering the combination of conversion and vaporization near the hydrogen boiling point [31].

Ortho-para conversion (OPC) is essential to avoid energy losses during liquefaction and long-term storage. If n-H<sub>2</sub> liquefies without converting to p-H<sub>2</sub>, significant boiling can occur leading to massive energy losses and vaporization [31].

#### 4.1.1.1 Compressed Gaseous Hydrogen

This is one of the most widely used methods for storing hydrogen for use in vehicles. This technology allows the storage of hydrogen at high pressures, up to 70 MPa, being in development those tanks that can withstand more than 100 MPa. This type of storage can be used for both mobile and stationary applications, stationary as storage in caverns or mobile as storage in pressurized

tanks, generally cylinders but also be polymorphous or toroidal [30], [32]. There are 5 types of tanks for the storage of compressed hydrogen gas. Among these, tanks type III and IV, which operate at pressures above 30 MPa, are the most used, mainly for application in fuel cell vehicles (FCV), such as the type 4 tanks used in the current Toyota Mirai. Tanks types I and II are usually used for stationary applications due to their high weight and tanks type V are under development [33], [30].

Type I tanks are the simplest form of compressed gaseous hydrogen storage, made from all metal, allow hydrogen storage at 20-30MPa, with a low mass storage efficiency (1 wt%) [32]. This is commonly produced from steel and is thus the heaviest vessel [34]. Type III tanks are mainly composed of an aluminum shell wrapped with a composite material, usually carbon fiber, and unlike type IV tanks, they transmit heat more quickly, which can cause a more rapid rise in temperature and pressure, which is also a risk in fire situations. They are also heavier than type IV tanks [35]. In the case of type IV tanks, these consist of a polymeric liner fully wrapped with a composite material, usually carbon fiber. Compared to type III tanks, they have shown better performance in structural and explicit simulations, which makes them suitable for mobile applications, in addition to meeting the European weight efficiency target of 4,8 wt% of hydrogen stored in the system at an operating pressure of 70 MPa [32], [36].

In the process of filling vehicles with compressed hydrogen gas, the high-pressure tank is connected to the vehicle to balance the pressure so that the residual pressure in the vehicle's tank can be determined to calculate a heating curve and the final pressure required for full refueling. Finally it is refueled up to this target pressure [37].

Among the advantages of this storage is that it allows the storage of high purity hydrogen, it also allows fast loading and unloading of hydrogen, improving operational efficiency and it does not comprise complex equipment, simplifying its design and maintenance [38], [39].

While among the disadvantages and challenges presented by this storage are its relatively low volumetric density, which despite increasing the pressure in the tanks is still low compared to other storage methods. Another point to consider is that the cost of storing hydrogen in these tanks is significantly high, in addition to the cost of the materials used in the tanks. It is also important to consider that the high pressures pose safety risks due to the possibility of leaks and require a significant amount of energy to reach these high pressures, which can reduce the overall efficiency

of the hydrogen storage and utilization process [33], [38]. Another potential risk of high-pressure hydrogen storage is the risk of metals becoming more brittle when in contact with hydrogen [34].

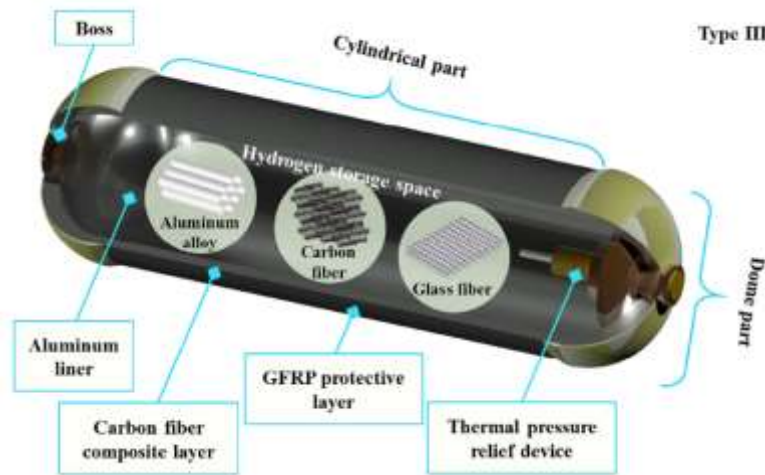


Figure 3: Inner structure of a Type III compressed hydrogen storage [34].

#### 4.1.1.2 Cryo-compressed Hydrogen

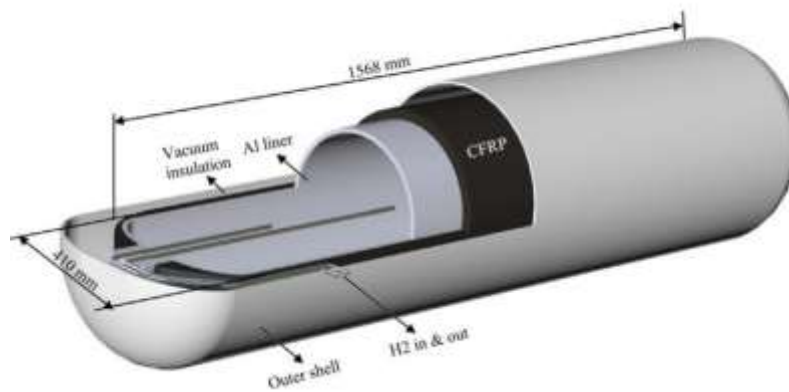
Cryo-compressed hydrogen (CcH<sub>2</sub>) storage is a method that combines the advantages of compressed gas and cryogenic liquid hydrogen storage. Cryo-compressed hydrogen is a supercritical cryogenic gas, unlike liquid hydrogen, in this method no liquefaction occurs, and the hydrogen is stored at low temperatures (20 K) and high pressure (>30 MPa). This type of storage has shown promise in terms of its storage capacity and level of security. It provides high storage density (80 g/L, which is about 10 g/L more than conventional cryogenic storage), fast and efficient replenishment, and a high level of security due to the existence of a vacuum chamber [40].

When designing cryo-compressed hydrogen storage tanks, it is important to consider their materials and properties, examples of which are carbon fiber reinforced plastics, as well as their structure, such as the configuration of the layers and their winding angles, which significantly influence the performance of the vessel. It is also important to consider the thickness because at cryogenic temperatures, the thickness of the carbon fiber layers must be increased by approximately 47,06% compared to room temperature to maintain performance [41].

The filling of these tanks is more economical than in the case of liquid hydrogen storage, because they can be filled with hydrogen in either liquid or gaseous state at ambient temperature, so in

terms of infrastructure, these tanks offer flexibility because of their compatibility with both states [32].

Among the disadvantages of this type of storage is the complexity of the design and construction of the storage containers, which must withstand high pressures and extremely low temperatures, where these same conditions can affect the performance and durability of the materials used. Also, according to its safety, there are possible vacuum failures in the system that can lead to a rapid release of hydrogen. Also among its challenges is its complexity of filling, as traditional methods can be inaccurate, so it is necessary to develop more accurate sensors, such as capacitive meters [42], [43].



*Figure 4: Structure of a cryo-compressed hydrogen storage vessel [41].*

#### 4.1.1.3 Liquid Hydrogen

Liquid hydrogen storage is a method that takes advantage of the high density of liquid hydrogen ( $70.8 \text{ kg/m}^3$ ) compared to gaseous hydrogen ( $0.0838 \text{ kg/m}^3$  at atmospheric pressure) [44]. Although this type of storage has been used by the aerospace industry as a propulsion fuel due to its high specific impulse, due to its demand it is also being evaluated for use in other more conventional means of transportation. However, in the case of liquid hydrogen, its application in this non-space industry is difficult due to its low boiling point, making it prone to become a biphasic gas-liquid flow in the storage tank, which is undesirable in the space industry due to its unstable flow characteristics [29].

This storage method requires cryogenic technology to maintain hydrogen at temperatures below its boiling point, vessels operate at low temperatures and at low pressures [44]. Due to its high energy

density, it is expected to be suitable for long-distance transport as well as for applications requiring compact storage [30]. Storing hydrogen at cryogenic temperatures also requires cryogenic technologies, for which advanced insulation techniques such as multilayer insulation (MLI) and vapor-cooled shields (VCS) are employed [45]. The MLI generally consists of a low emissivity reflector and a low thermal conductivity spacer arranged in alternating layers under high vacuum conditions of  $10^{-3}$  Pa to reduce the heat entry [45], [46]. Also for its design, its operability must be considered, since in case of mobile applications, the tank size must be minimized, as well as in its large-scale use the energy consumption is high for vacuum is high, so low-vacuum insulation is often used [45].

One of the main disadvantages of hydrogen liquefaction is its high energy consumption. Theoretically, the energy required to liquefy  $H_2$  at ambient pressure, using liquid helium as a cooling medium, is about  $3960 \text{ kJ/kg}$  consuming approximately 25-30% of the energy content of the stored hydrogen [47]. The energy required for liquefaction includes the energy consumed for pre-cooling from ambient to saturated gas (at  $-253^\circ\text{C}$ ), the energy of condensation from gas to liquid and the energy of conversion from ortho to para-  $H_2$  [44].

Large-scale hydrogen liquefaction is usually performed using refrigeration cycles, with the Claude cycle and the Brayton cycle being the most common methods, where the Claude cycle is usually more suitable due to its lower specific energy consumption and smaller equipment size requirements. Both refrigeration cycles involve compression and expansion processes with throttling used to change the pressure [48].

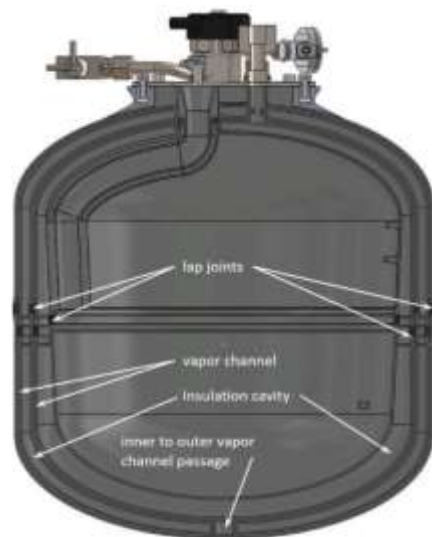
During hydrogen liquefaction, throttling and Joule-Thomson effects are important concepts. Throttling is often used to create non-ideality. In contrast, the Joule-Thomson effect is concerned with the maximum inversion temperature compared to ambient temperature. Cooling during throttling occurs if the reversal temperature is higher than the ambient temperature. In addition, the Joule-Thomson coefficient represents the extent and direction of the temperature change during the isenthalpic change of state [44].

Among the disadvantages of this storage method, in addition to the high energy consumption in the liquefaction process, are the associated costs, mostly associated with the use of specialized cryogenic tanks. Also compared to other methods liquid hydrogen has a lower overall energy

efficiency, for example ammonia storage is estimated to have a higher energy efficiency (34-37%) [49].

Another challenge of this type of storage is the boil-off phenomenon, where hydrogen evaporates due to the incoming heat, leading to potential fuel leaks and safety issues, evaporation of liquid hydrogen during storage is indicated at 1-5% per day due to boil-off losses [30]. To address this, Zero Boil Off technologies have emerged that use cryocoolers to keep hydrogen at cryogenic temperatures, as well as recent research focused on modeling non-adiabatic blowdown dynamics for CCH<sub>2</sub> tanks, considering heat transfer effects crucial for safety engineering [50].

As mentioned above, this type of storage can be used for mobile or stationary applications. An example of a stationary application is the spherical liquid hydrogen tank that was built in Japan, used at Hytouch Kobe to load and unload LH<sub>2</sub> transported to Japan from Australia [45]. In mobile applications, such as road transport, tank trucks with a capacity of 25 to 65 m<sup>3</sup> are used and can store between up to 4 tons of liquid hydrogen with a daily evaporation rate of 0.5%, while their transport by train can reach even 85-120 m<sup>3</sup>. In the case of transport by ship, Kawasaki Heavy Industries built the first liquid hydrogen transport vessel with a 1250 m<sup>3</sup> cylindrical storage tank with vacuum insulation and double walls, enabling the transport of liquid hydrogen between Japan and Australia [45].



*Figure 5: Liquid hydrogen tank [45]*

#### 4.1.1.4 Slush Hydrogen storage

It involves the storage of hydrogen in a mixture of solid and liquid states, which is achieved by first liquefying the hydrogen then cooling it to its triple point or beyond [30]. It is of interest to the aerospace industry as a potential propellant due to its light fuel characteristics [51].

Beyond aerospace applications, slush hydrogen shows promise as a coolant for cold neutron generation and superconducting equipment, as well as a medium for hydrogen transport and storage [52]. Different methods are used for its production: spray method, freeze-thaw method and the auger method. The spray method involves introducing liquid hydrogen into an evacuated container and expanding it through an expansion valve, causing solidification. The solid is then mixed with liquid hydrogen to form slush [53][52]. In the auger method, an auger rotates inside a helium-cooled tube, scraping off solid hydrogen formed on the surface to create small particles [54].

For the freeze-thaw method the temperature of the liquid hydrogen is reduced, through the elimination of latent heat by reducing its pressure. When the liquid reaches the triple point pressure, a frozen layer forms on the surface of the liquid, which then sinks and using a stirrer breaks into small particles of several mm in diameter [55].

When transporting hydrogen slush through pipelines, it is important to take into account the pressure drop due to straight pipelines, as well as flow restrictions such as valves, converging-diverging pipes and orifices. Higher pressure drop during the transport of hydrogen slush requires higher pumping power, which reduces the overall performance of the transport system [55].

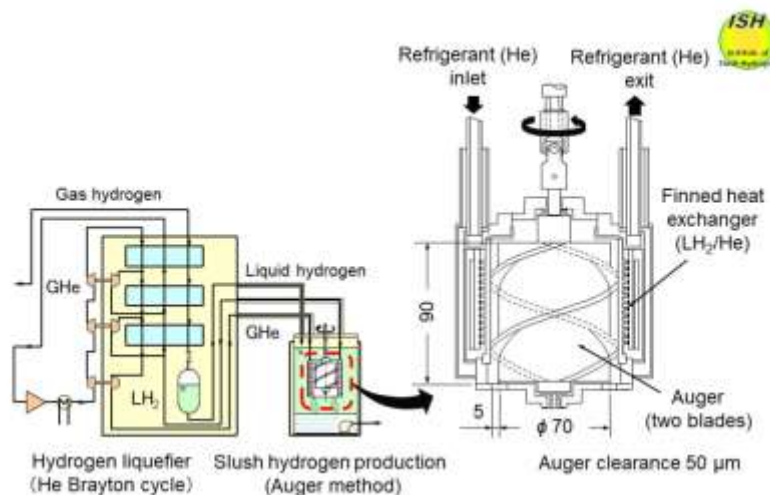


Figure 6: Scheme of slush hydrogen production by the auger method [56].

#### 4.1.2 Physisorption storage

In the hydrogenation process, hydrogen molecules are adsorbed through physical adsorption on materials with a large surface area such as activated carbon, zeolites and carbon nanotubes or metal-organic frameworks (MOFs). Very low temperatures are required for this type of hydrogen adsorption and high pressures because weak van der Waals interactions are primarily responsible for the attractive forces between the hydrogen and the matrix where it is incorporated forming weak bonds [57].

##### 4.1.2.1 Carbon nanostructures

Carbon-based materials have great potential for hydrogen storage because they are inexpensive, lightweight, have large surface areas, are chemically stable, and come in a wide variety of pore and bulk architectures [57]. Structures such as graphene and nanotubes allow the adsorption of hydrogen within and between nanotube spaces, increasing storage capacity.

Storage efficiency depends on the hydrogen-material binding energy, which varies between 5-15 kJ/mol for adsorption-based systems. This energy determines the temperatures at which hydrogen can be released, influencing the design of storage systems [58].

Some carbon nanostructures are single and multiwalled carbon nanotubes, carbon nanofibers and activated carbon that can adsorb large quantities of hydrogen. Carbon nanotubes are graphene sheets rolled into seamless tubes with diameters that are of the order of nanometers and carbon nanofibers basically consist of an intercalation of these graphitic planes at a fixed distance (0.355 nm) from each other to form various structures. Carbon nanotubes and nanofibers are usually grown on metal surfaces by the catalytic action of one or more transition metals [59].

The maximum storage capacity by chemisorption in a graphene layer is 8.3%, corresponding to a fully saturated graphene layer with one hydrogen atom per carbon atom (graphane) [58]. This can be shaped into tubular structures called carbon nanotubes.

Activated carbons are disordered nanostructure characterized by its pore size distribution, which may involve micropores, mesopores, or macropores and its specific surface area. These have been studied as storage materials for low-pressure physisorption storage of natural gas and hydrogen, requiring cryogenic conditions (77 K) for the storage of the latter [58].

Although some theoretical work suggests that layered graphitic structures could be successful, and several carbon nanostructures exhibit excellent hydrogen storage capacity, to date no reproducible experimental data have been obtained to demonstrate their application in automotive [58]. However, they may be viable for applications where volumetric constraints are less, such as public transport or stationary storage.

#### 4.1.2.2 Metal-organic frameworks (MOFs)

These are porous materials with a structure formed by metal ions and organic ligands through coordination interactions. In these metal ions are employed as nodes or central points, while the organic ligands function as nexuses. They have a large surface area in the range of 1.000-10.000  $m^2/g$  as well as a high porosity, which allows adsorption and storage of hydrogen [33].

MOFs possess several properties that make them promising hydrogen storage, such as their extraordinarily high surface areas, ultra-high porosities, tunable pore sizes, modifiable internal surfaces, rapid hydrogen adsorption/desorption kinetics, and high hydrogen storage capacity at low temperatures [60], [61]. At present, the highest hydrogen storage capacity of MOF at the low temperature of 77 K is 17.6 wt% [61]. While at room temperature conditions, the pores of 3D structured MOFs can strongly adsorb hydrogen gas molecules and condense them [62].

Metal-organic frameworks (MOFs) can be synthesized using a variety of energy sources, such as conventional electrical heating, microwave (MW) irradiation, ultrasound (US), even mechanical force and electric potential. This synthesis usually takes place at temperatures between room temperature and about 250 °C in the presence of a solvent, where the most common method is solvothermal synthesis which entails heating a mixture of organic ligands and metal salts in a solvent system at temperatures typically below 250 °C [60], [63].

Among the advances of these materials is that the preparation of hybrid materials incorporating MOFs is an effective strategy for hydrogen storage. The addition of metal nanoparticles in the MOF structure can significantly increase the storage capacity due to the hydrogen spillover effect. These hybrids, which combine MOFs with carbon materials, often have a higher specific surface area compared to the original MOFs, resulting in a substantial improvement in hydrogen uptake [61].

Despite the significant progress in MOFs research, many challenges still need to be overcome for MOFs to be used as practical hydrogen storage materials.

### 4.1.3 Materials Based on Chemical Storage

#### 4.1.3.1 Liquid-organic Hydrogen Carriers (LOHCs)

LOHCs, liquid organic hydrogen carriers, are organic compounds that store hydrogen by catalytic hydrogenation and release it by dehydrogenation, in these the hydrogen molecules are stored by forming covalent bonds [64]. The volumetric density of these compounds is 50 g/l, and their gravimetric density is greater than 5 wt% [64].

These compounds must meet certain criteria, such as having a low melting point and a high boiling point, to maintain their liquid state at ambient temperature, they must not decompose; have a high thermal stability, their dehydrogenation and hydrogenation must be selective and are expected to have a low viscosity making them more accessible for pumping into tanks and existing pipelines [64], [65]. It is important to know its thermodynamic properties, as well as to focus on kinetics, since the hydrogen absorption process is an exothermic process, while the dehydrogenation process is an endothermic process, which requires good management of heat transfers with the medium, aided by heating or cooling systems as required [64].

Another important aspect to consider is the toxicity of LOHC molecules, which is expected to be minimized to conform to environmental concerns and prevent its effects on human health [65]. Since these LOHC molecules are well known, it is easier to manage the risks of these molecules compared to the environmental risks of crude oil [64].

Hydrogenation process is carried out at optimum enthalpies between a range of 9,56–16,73 kcal/mol, at temperatures between 373–573 K and a pressure of 1–5 MPa in the presence of catalysts. While the dehydrogenation of LOHCs takes place at a temperature of 423–673 K and a pressure of 1–0.5 MPa, in the presence of catalysts too (Pt, Pd). The dehydrogenation process releases hydrogen without other gases such as CO<sub>2</sub>, CO and their by-products and throughout all stages of both processes the organic liquid carriers remain in a liquid state [64].

There are two types of catalyst systems to accelerate the hydrogenation and dehydrogenation process: Homogeneous catalysts, whose low-temperature performance is better, since it is more useful to modify the catalyst with various ligands to improve its capacity, but with poor recyclability, since it is difficult to recover the catalyst after the reaction; and heterogeneous catalysts, which have good thermal stability and recyclability, since it is easier to separate the

catalyst from the LOHC by filtration, and can be used for continuous flow processes to scale up hydrogenation and dehydrogenation in the industry [65].

The conventional storage system for LOHC is equipped with individual reactors for the hydrogenation and dehydrogenation processes, due to the different temperatures and pressures at which they are carried out [64]. This type of storage can be used for long-term storage under ambient conditions as well as for long-distance hydrogen transmission and marine supply chain applications [30]. These compounds can be transported by vehicles and delivered to refueling stations in tanks to be taken to reactors. The reactor is heated for dehydrogenation, obtaining a mixture of gas and liquid, which passes through a separator, where the gaseous hydrogen leaving the separator is stored in a buffer tank to acquire the desired pressure to operate the fuel cells [64].

Among its advantages is that it is a low-cost, secure and easy-to-manage type of storage. It does not have boil-off problems, nor does it depend on high pressures or extreme temperatures, and they also have a strong compatibility with the current infrastructure of gasoline [30], [64]. In addition, the hydrogen obtained from certain LOHCs is pure and does not require any further purification steps [64].

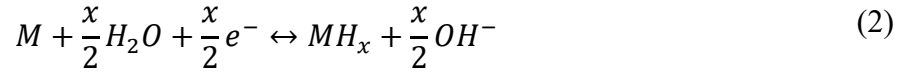
Potential and common LOHC candidates include N-Alkylcarbazole, N-Propyl Carbazole, methylcyclohexane, dibenzyltoluene (DBT), N-ethylcarbazole, phenazine and pyridine derivative [66].

#### 4.1.3.2 Metal Hydrides

This type of storage originates from a chemical reaction, where hydrogen molecules bind to a metal under moderate temperatures and pressures, usually between 3 to 30 atm, lower pressures than compressed hydrogen gas tanks, making these systems safer. Although this type of storage originates from a chemical reaction, it is considered a solid type of storage, with high volumetric energy densities and good storage efficiency, since they have a large capacity to hold a significant amount of hydrogen in their structures [5].

When the metal encounters hydrogen gas, it is absorbed on the surface of the metal first, and by adding sufficient energy to the system, the hydrogen molecules dissociate into atoms, which diffuse into the bulk and occupy the interstitial sites of the metal crystal lattice and form a solid solution that grows until the metal is saturated with hydrogen [5]. There are two possible ways of hydration

of a metal: direct dissociative chemisorption and electrochemical water splitting. These reactions are represented by *equations (1) and (2)* where M is the metal [67]:



The key aspects for evaluating a material suitable for hydrogen storage in hydrides are mainly linked to its thermodynamic adsorption properties. These properties are determined by measuring, under equilibrium conditions, how the pressure varies as a function of hydrogen composition at a specific temperature. In addition to the thermodynamic parameters, the kinetics of the process are crucial. The absorption of hydrogen releases heat, being an exothermic process, while its desorption (release) consumes energy, making it an endothermic process. Therefore, efficient management of heat exchange with the environment is essential, including heating systems to facilitate desorption and cooling systems to enhance absorption, thus preventing the kinetics of the process from being negatively affected [32].

Among its challenges is the great weight of these tanks, which does not make them a problem for the stationary storage of hydrogen, but for its incorporation in mobile applications, so new lightweight materials are being researched [5].

Metal hydrides can be categorized according to their number of species, chemical composition, bonding involved and according to these, they can also be classified according to their application. In the case of classification by number of species these groups metal hydrides according to the number of different metals present, Binary Hydrides, those composed of a single metal element and hydrogen, Ternary Hydrides, which consider two different metallic elements, Quaternary Hydrides, which include three different metallic elements. In the case of classification according to their chemical composition there are AB<sub>5</sub> class, AB<sub>2</sub> class and Multinary hydrides. Another classification is based on the bonds of the metal hydride, finding in this classification Ionic Hydrides, covalent hydrides and metallic hydrides or also classified as elemental hydrides, intermetallic hydrides and complex hydrides. [68][69].

Complex hydrides are those where hydrogen evolves on contact with water. Sodium, lithium and beryllium are the only elements lighter than magnesium that can also form compounds in the solid state with hydrogen, reaching a hydrogen content of 18%(wt) in the case of  $\text{LiBH}_4$  [67]. The disadvantages of these hydrides are their unfavorable thermodynamics, poor kinetics, and reversibility issues.  $\text{LiBH}_4$  decomposes to  $\text{LiH} + \text{B} + 3/2\text{H}_2$ , releasing 13.9 wt% hydrogen theoretically, but rehydrogenation requires high temperatures 600°C and pressures of 155 bar [70].

In the case of intermetallic compounds, these are obtained by combining an element that forms a stable hydride with an element that forms an unstable hydride [67]. They can be classified into  $\text{AB}_5$  (e.g.  $\text{LaNi}_5$ ),  $\text{AB}_2$  (e.g.  $\text{ZrFe}_2$ ) and  $\text{AB}$  (e.g.  $\text{FeTi}$ ) types. Their advantages include their safety, convenience and low cost, being a better storage solution than liquid hydrogen. Intermetallic hydrides also exhibit self-cooling effects, which increases safety in case of leakage. [71].

#### A) Magnesium based Hydride

Magnesium hydride ( $\text{MgH}_2$ ) is one of the most promising hydrides for hydrogen storage. It is classified as an elemental hydride, whose advantages include a high hydrogen storage capacity of 7,6%(wt), low-cost availability, heat-resistance, vibration absorbing, reversibility and recyclability, in addition to having the highest energy density of all hydrides considered for hydrogen storage, 9  $\text{MJ/kg Mg}$  [69], [67].

The disadvantages of magnesium hydride are its high discharge temperature, slow desorption kinetics, due to its high stability, leading to relatively high desorption enthalpy, 300°C at 1 bar  $\text{H}_2$ , as well as high reactivity to air and oxygen. Thus, several research have focused on reducing its desorption temperature and accelerating the re/dehydrogenation reactions, some attempts are modifying the microstructure of the hydride by ball milling and innovating in the use of catalysts [67].

Although it has other unfavorable characteristics such as a violent reaction with water, and is considered more sensitive to ignition and explosive than other hydrides, it is one of the most active and easy to obtain hydrogen from, and because it is in a solid state, it is expected that unlike other storage substances, it can be isolated and handled more easily.

#### 4.1.3.3 Circular carriers

Circular hydrogen carriers are compounds capable of storing and transporting hydrogen by chemically bonding it to other molecules, which then decompose to release the stored hydrogen. These carriers are particularly advantageous because they can be integrated into existing fuel infrastructures and allow higher hydrogen storage density compared to other methods.

##### A) Methanol (MeOH)

Methanol is a chemical compound with a high versatility of uses, used in the fuel industry, in the petrochemical industry, and others, being highly demanded worldwide, reaching global methanol production of over 111 million metric tons in 2022, even slightly more than hydrogen [72]. Among its advantages is that it can take advantage of the already available infrastructure of traditional fossil fuels such as gasoline, diesel, and kerosene for various applications, as well as being relatively stable in its liquid state and easy to store under normal environmental conditions [73].

Methanol is a potential hydrogen storage medium. Among its properties is that it is liquid at room temperature, can be converted to hydrogen at lower temperatures than other fuels, it has a high hydrogen content of 12,5 wt%, and due to its chemical nature allows a high H/C ratio 4:1 [74], [75]. This compound has advantages for both H<sub>2</sub> storage and CO<sub>2</sub> hydrogenation [76].

Commercial methanol is mostly produced from synthesis gas (syngas) from the catalytic reaction of its components, hydrogen, carbon monoxide and carbon dioxide. This is done through processes such as steam reforming of natural gas or carbon gasification, where syngas is mostly obtained from fossil fuels, but nowadays alternatives such as biomass are being developed [74]. Methanol produced from biomass is called bio-methanol, while methanol based on electricity from renewable resources is called e-methanol [77].

Among the disadvantages of methanol are the environmental problems it can cause as CO<sub>2</sub> release. The standard method of CO<sub>2</sub> separation and capture, which is based on absorption by an amine solution, requires a high energy consumption 1,1 kWh/kg<sub>CO<sub>2</sub></sub> [76].

Hydrogen is obtained from methanol through the processes of MSR (methanol steam reforming), MD (methanol decomposition), POM (partial oxidation), ATRM (autothermal reforming), all carried out at temperatures above 300 K.

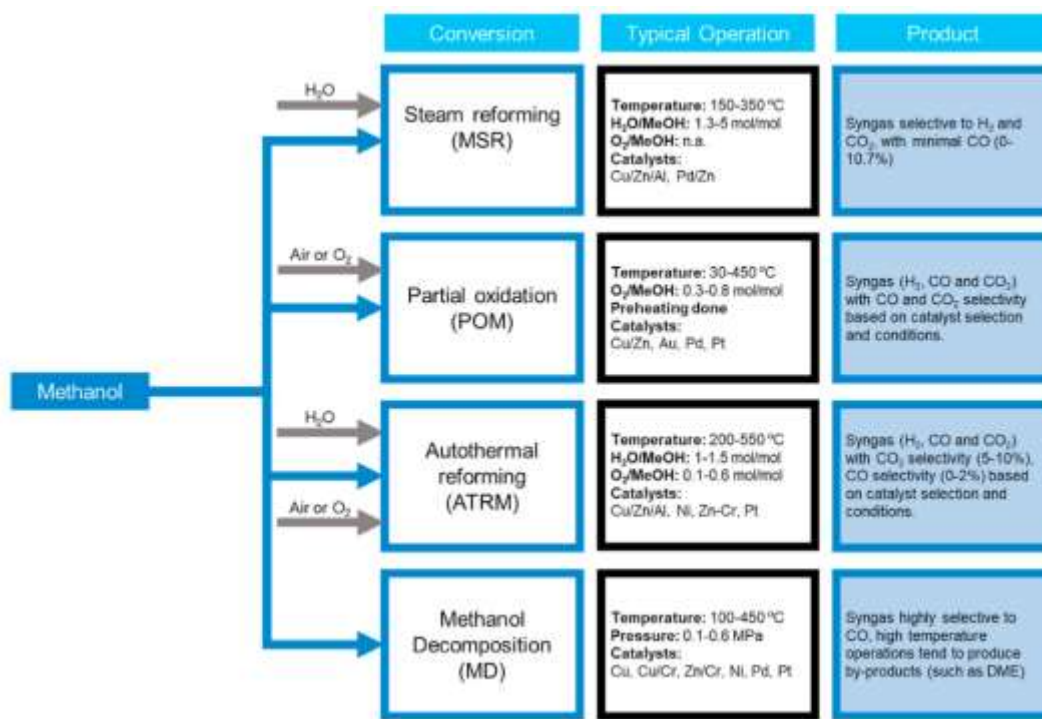


Figure 7: Different processes for the production of hydrogen from methanol[74].

Methanol steam reforming (MSR) is recognized as an endothermic process that offers high conversion and selective hydrogen production, along with low carbon monoxide (CO) emissions and relatively simple temperature control. However, it has limitations, such as slow start-up and the need for external heat to initiate and maintain the reaction [74].

On the other hand, partial methanol oxidation (POM) allows rapid heating of the reactor by regulating the oxygen flow, which increases fuel combustion. However, temperature control is more complicated, increasing the risk of CO formation. Although POM facilitates fast start-up and operational flexibility, the efficiency and hydrogen selectivity it achieves are inferior to those of MSR and still require significant improvements [74].

Autothermal reforming of methanol (ATRM) combines air and water in the reactor, simplifying the system design. This technique operates in a theoretically thermo-neutral manner, without consuming or producing external energy, giving it higher efficiency and hydrogen selectivity compared to POM. In addition, ATRM has a better dynamic response than MSR and can be adapted to the use of various types of fuels. Finally, methanol decomposition (MD), although kinetically slower than MSR and POM, generates CO. While this is a disadvantage for proton exchange

membrane fuel cell (PEMFC) applications, MD is advantageous for *in situ* reforming in internal combustion engines, where CO is used as fuel [74].

#### B) Ammonia (NH<sub>3</sub>)

Ammonia is one of the most produced chemicals in the world with a worldwide production of 176 million metric tons in 2014, this high demand is due to its great versatility of uses, where a large part of it is intended for use as fertilizer, it is also used for the manufacture of pharmaceuticals, plastics, textiles and explosives [78][79]. In addition to all its uses, it is also considered one of the most promising hydrogen energy carriers, due to its properties that allow storing in the same tank up to twice the amount of energy. The gravimetric hydrogen capacity of ammonia is 17,6-17,8 wt % while the volumetric density is  $121 \text{ kg}_{\text{H}_2}/\text{m}^3$  in its liquid ammonia form, which is higher than that of liquid hydrogen [80]. Ammonia tanks have a hydrogen volumetric density of 8,2-9,8 kgH<sub>2</sub>/100L while liquid hydrogen tanks is lower 2,3-5,0 kgH<sub>2</sub>/100L at the same conditions of 0.1 MPa, 20K, however, the hydrogen gravimetric densities and heats of combustion become similar considering hydrogen tanks of 20-30 tons [81].

For storage, unlike hydrogen, it can be liquefied at a reasonable temperature at atmospheric pressure, -33,34°C and because of its established economics, it already has cost-effective storage systems [33]. It is also estimated that the efficiency of ammonia and hydrogen use in a fuel cell is ~19-22%, like that of liquid hydrogen [80]. Ammonia is stored in tanks in its liquid or gaseous state, for this there are 3 main different types of storage tanks; non-refrigerated pressurized tanks, which operate at room temperature and at a pressure of 18,25 bar. There are also the refrigerated storage spheres that operate at temperatures of -1 to 2 °C and pressures of 3,8 to 5,15 bar, and the fully-refrigerated storage tank that operates at temperatures of -33 °C and pressures of 1.1 bar. Each has a capacity of 270, 450-2.750 and up to 45.000 t respectively [82].

Ammonia can be stored in hard rock caverns in various types of formations, provided they are strong enough to be excavated without heavy support. However, due to its high affinity for water and the highly exothermic nature of its dissolution (2,000 kJ/kg), it is crucial to isolate ammonia from water. In hard rock caverns, this involves the use of steel liners. Lined caverns (LRC) are feasible with moderate R&D stresses and allow storage at pressures of tens of bars, as well as at lower temperatures, between 0°C and -40°C [83].

The transport of ammonia can be via sea transport or through the pipeline network, where if this compound is transported as such and not in its conversion to hydrogen, the current infrastructure can be used for its trade, although it will need to be expanded along with the increase in world trade of ammonia [84].

Today about 85% of the ammonia produced worldwide is made through the Haber-Bosh process, a process in which hydrogen reacts with nitrogen at high temperatures (400-500 °C) and high pressures (150-300 °C) using a catalyst, which is usually magnetite ( $Fe_3O_4$ ). It is a highly energy-intensive process, consuming substantial fossil fuels and contributing to 1.6% of global CO<sub>2</sub> emissions [85][86]. Although its energy consumption has decreased by 74% compared to the last century, it is still considered a global warming factor [87].



Its main production is from fossil fuels , for which efforts are also being made to make its production cleaner, and thus, like hydrogen, ammonia can also be classified on the basis of colors, corresponding to gray ammonia, that produced from natural gas, blue ammonia considering processes with CCUS and green ammonia that produced by hydrogen obtained from electrolysis and with the use of renewable energies. Where green ammonia presents the lowest production energy efficiency 56,1% (LHV) compared to gray ammonia with 67,9% (LHV), but both are higher than the energy efficiency of liquid hydrogen production [81].

For cleaner ammonia production, there is a green version of the Haber-Bosch process that uses green hydrogen, produced from the electrolysis of water and nitrogen from an air separation unit (ASU) as raw materials [88]. However thermochemical and electrochemical methods have been proposed too, as well as combined systems consisting of solid oxide electrolyzer, nitrogen production with pressure-swing adsorption and Haber-Bosch process or other integrated systems involving methane steam reforming and Haber-Bosch process. They mainly focused on system integration and heat recovery to improve the total energy efficiency [89].

As for the decomposition or cracking of ammonia to obtain hydrogen, this is an endothermic process that occurs at high temperatures and requires catalysts [33]. Due to the high temperatures required for this process, several efforts have been made to improve the catalysts and thus reduce the conversion temperature (< 500 °C), noble metal catalysts have been developed, based on iron

and nickel, carbides and nitrides of transition metals [90]. Some of the technologies that have been developed include: thermocatalytic decomposition, photocatalytic decomposition, plasma-catalytic decomposition, and electrocatalytic decomposition [91].



In the case of *thermocatalytic decomposition*, the catalytic dissociation of ammonia develops from the adsorption of ammonia molecules on the active sites of the catalyst, leading to a sequence of reactions involving dehydrogenation and recombinative desorption [91]. Recent research has focused on the development of efficient and cost-effective catalysts for the conversion of NH<sub>3</sub> to H<sub>2</sub>, a variety of materials have been explored, including including electrides, hydrides, and perovskite oxides, as alternatives to conventional fused-Fe and promoted-Ru catalysts [92]. Despite the presence of a catalyst, this is a slow process, requiring external energy input to heat the catalyst to at least 400 °C [91].

For *photocatalytic decomposition* ammonia is decomposed using sunlight through photocatalysis under alkaline conditions. This can be carried out using recyclable catalysts at room temperature, however there are only a limited number of photocatalysts that are effective in this process [91].

In the *electrocatalytic decomposition* when ammonia is electrolyzed, hydrogen molecules are produced at the cathode along with the release of amide ions, which are oxidized at the anode to form nitrogen molecules. Liquid ammonia has a theoretical electrolysis voltage of 0.077 V lower than that of water electrolysis of 1.23 V, however, the current efficiency is only 85% at a high cell voltage of 2 V due to the inevitable reverse reaction [91]. This is a promising method because of the generation of hydrogen at moderate temperature and because of its simplicity and cost-effectiveness. However, its disadvantage lies in its slow kinetics and poor selectivity. Also to increase efficiency several types of electrocatalysts have been studied, but still their performance does not satisfy their industrial applicability [91].

For *plasma-catalytic decomposition*, the conversion of ammonia is carried out using non-equilibrium plasma generated in electrical discharge, which can be combined with a catalyst to accelerate the chemical reactions, because the ignition of the plasma raises the reactor temperature, which causes a higher activation of the catalyst [93], [94]. The synergistic effect of plasma-

catalysis favors NH<sub>3</sub> decomposition by increasing the average electron energy and facilitating NH<sub>3</sub> dissociation [95]. Importantly, plasma catalysis can overcome surface nitrogen poisoning, a major limitation in conventional catalytic NH<sub>3</sub> decomposition [96].

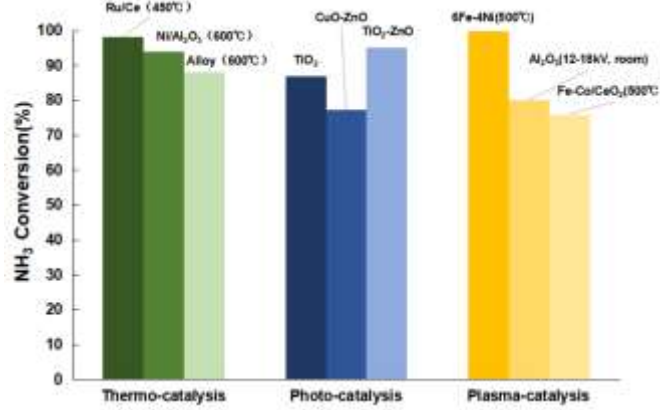


Figure 8: Comparative graph of the different technologies for ammonia decomposition [91].

Like hydrogen, ammonia has also emerged as a fuel of the future, not in its hydrogen storage form, but under a direct combustion of this compound. It also has the characteristic of reducing emissions, since its combustion does not produce soot or hydrocarbons [97]. However, its combustion properties present some challenges such as its corrosiveness, its low laminar burning velocity (LBV), its high autoignition temperature and its narrow flammability range, which is an advantage over hydrogen in case of accidental leaks [98].



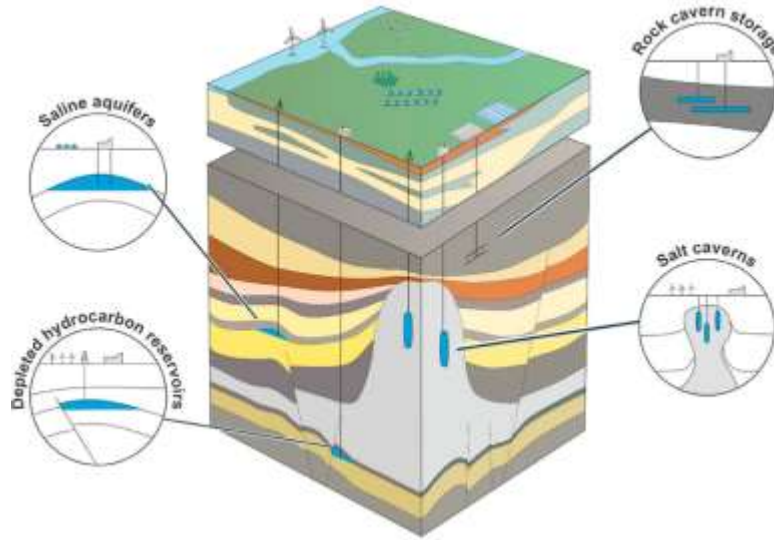
There are several innovations that consider ammonia as a fuel as well as an energy carrier. These initiatives include engines for ships as well as its use for gas turbine and coal-fired power plants, demonstrating its potential in large-scale energy applications [99], [100].

In terms of safety, ammonia has low flammability compared to hydrogen and other LOHCs such as methylcyclohexane or toluene, but its greatest danger is associated with its toxicity [101]. It reacts with the water in human tissue, being an exothermic reaction, causing thermal lesions in these, as well as causing necrosis and saponification of fats. In the event of ammonia leaks, water is used to remove this compound and prevent its diffusion [101].

## 4.2 Below-ground

Also known as underground hydrogen storage (UHS) is a technique for storing hydrogen below ground, in salt caverns, reservoirs or depleted gas field with the objective of being an alternative for the storage of large volumes at ambient conditions, however, as previously indicated, this requires high pressures or cryogenic storage [33].

Among the challenges of hydrogen geological storage are its lower viscosity and greater mobility than other fuels such as natural gas, which could be related to the likelihood of leaks or uncontrolled mobility in the environment. Another challenge has to do with the fact that hydrogen acts as an electron donor for various microbial processes, so its presence in the presence of hydrogenotrophic microbes could mean losses due to hydrogen consumption. Also, possible geochemical reactions can damage hydrogen storage, altering its composition and that of the minerals, which can directly affect the integrity of the deposit and the efficiency of its recovery [24].



*Figure 9: Types of underground hydrogen storage (UHS)[102].*

### 4.2.1 On Shore

#### 4.2.1.1 Salt Caverns

In this type of storage, compressed gaseous hydrogen can be stored at a pressure of 50-100 bar resulting in a relatively low volumetric density of hydrogen storage of 10 g/l [30]. This type of storage offers physicochemical and mechanical properties and a chemically stable environment for hydrogen storage, due to the salinity that limits hydrogen consumption by microbes [103], [33]. In

addition, its favorable properties include lack of water, low porosity and permeability, and good conditions for heat conduction [103].

The volume of these deposits tends to be between 100,000-300,000  $m^3$  even up to 700.000  $m^3$  and with respect to their thickness, some stratified deposits are characterized by a large horizontal length and a relatively small thickness of about 200 to 300 m, while some diapiric deposits are up to 6 km thick [103].

The construction of this type of storage begins with the drilling of a well from the surface into the salt formation at a required depth, then an annular pipe is installed and arranged in the middle of the cavity, where fresh water is pumped through it to dissolve the salt, and then this brine is removed by another pipe, giving way to the cavern [33]. When it has been formed, a mechanical integrity test is performed to check the conditions and ensure gas tightness [33]. The deburring process, which uses gas pressure to displace the remaining brine, completes the cavern preparation [33]. The two-well horizontal cavern construction method is recommended for thin-bedded salt rocks, as it offers higher efficiency and larger cavern volumes [104]. Factors influencing construction are water injection direction, pipe elevation and distance between wells [104].

The advantages of this type of storage include negligible hydrogen loss, large storage capacity, the advantage of injecting and withdrawing hydrogen quickly, and low capital cost compared to building dedicated storage vessels with advanced technologies [105]. However, among its disadvantages is its unquestionable dependence on its artificial or natural geological formation, which involves an uneven distribution and availability of such formations around the world, where only some may be suitable for use, either due to physical limitations in storage capacity or due to possible environmental impacts [30].

#### 4.2.1.2 Rock Caverns

Rock caverns (RC) are another method of subway oil and gas storage that may be suitable for hydrogen storage. They are usually constructed in igneous or metamorphic rock formations and are widely used to store liquid hydrocarbons. Currently, three different types of rock caverns are distinguished according to the techniques used for their sealing [105].

### A) Unlined Rock Caverns

Unlined Rock Caverns, CRUs, are rock chambers artificially created by conventional mining techniques, such as borehole drilling or blasting. Shallow CRUs have been used to store liquid hydrocarbons, such as refined petroleum, crude oil and liquefied hydrocarbons, such as butane, propane and liquefied natural gas (LNG), as well as for the storage of compressed gases (compressed air and natural gas) [105].

The caverns have been developed at a depth of 955-961 m in a granite host rock with an in situ stress of 34 MPa in the horizontal direction. The maximum pressure at which an installation has operated successfully has been 12.5 MPa and the largest cavern currently has a volume of  $1.1 \times 10^6 \text{ m}^3$  [105]. However, storage of compressed hydrogen gas in existing CRUs built for liquid hydrocarbon storage would be challenging due to their large horizontal cross-sectional areas and shallow construction depth, which would induce uplift failures [105].

URCs are usually stabilized by cushion gas, which maintains the operating pressure of the storage, while the working gas, hydrogen, is being extracted, cushion gas also helps to prevent excessive water ingress at low working gas pressures inside the cavern. Several cushion gases, including  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{N}_2$ , have been investigated for the UHS, in addition to  $\text{H}_2$  itself [105].

The rocks that host the caverns are usually hard crystalline rocks, composed mainly of silicate minerals, whose reactions with hydrogen are negligible even under the extreme conditions, not affecting hydrogen storage in CRU[105].

### B) Lined Rock Caverns

A lined rock cavern (LRC) is a subway chamber excavated in hard rock formations sealed with a special lining system to create a safe storage space. In these the surrounding rock mass withstands pressure and the lining system provides a barrier to prevent gas leaks and maintain the structural integrity of the cavern [106].

Hydrogen can be stored underground by injecting it directly into a lined rock cavern, in its gaseous state, or under cryogenic conditions, to be stored in its liquid state. Storage in either state requires a liner due to extremely high pressures or extremely low temperatures [83]. In the case of hydrogen transport by pipeline, hydrogen must be stored as a gas, but for transport in tankers, hydrogen must be stored as a cryogenic liquid, at  $-253^\circ\text{C}$  [83].

The depth of the LRC will depend on the quality of the rock, even with the presence of a liner to ensure hydrogen tightness, it will be necessary to control the operating pressure to avoid large deformation of the rock mass and of the liner itself. A rigid rock at a relatively large depth, for example 100 or 200 m, will allow pressures up to 100 or 200 bar [83]. It is also necessary to consider the thermodynamic behavior of hydrogen and the properties of the material, to consider the corrosion and embrittlement of the steel jacket, and possible permeation of hydrogen through the jacket [83].

LRCs demonstrate a high degree of flexibility in terms of location, as they can be adapted to a wide range of geological requirements. This flexibility allows the installation of these hydrogen storage infrastructures in strategic proximities, such as near industrial clusters, power plants, major airports, renewable energy centers and import/export stations [106].

Hydrogen can also be stored underground by converting it into a liquid carrier, such as ammonia, which can then be stored in a Lined Rock Cavern. In terms of costs, the costs of a pressurized hydrogen or ammonia LRC are expected to be 50% to 100% higher than an unlined rock cavern, while the costs of a cryogenic hydrogen LRC will be 100% higher than an unlined rock cavern [83]. The main challenge is to maintain long-term integrity, which still requires solving several basic problems [104].

#### 4.2.1.3 Saline Aquifers

Aquifers are sedimentary formations saturated with saline water that are typically found at depths of hundreds to thousands of meters underground [107]. These basins are distributed over most of the world's continents and over marine and terrestrial locations around the Atlantic, Arctic and Indian Oceans. In general, aquifers located in tectonically active areas are not suitable for gas storage, as they offer less security for storage [107].

Saline aquifers present a significant opportunity for cost-effective long-term hydrogen storage due to their geographic accessibility, as they are distributed throughout the world, have large storage capacities (hundreds of millions of standard cubic meters) and are more environmentally friendly due to their low impact on the environment. Aquifers are sometimes the only accessible geological formation for hydrogen storage that is at an acceptable distance from renewable energy generation sources [107].

However, not all are suitable for commercial operations, since for hydrogen storage they must have ample porosity and high permeability with an existing formation pressure. The potential aquifer must have an impermeable layer to ensure confinement of the injected gas [107].

Generally, large quantities of gas can be stored in aquifers, although they are somewhat rigid to function and require a high proportion of cushion gas so to use these geological structures as hydrogen storage, it is necessary to evaluate the problems of biological and chemical processes [104].

Despite the advantages demonstrated by aquifers, there is no known experience of pure hydrogen storage in aquifers. Current knowledge about them is mainly based on experiences with storage of other gases such as natural gas and CO<sub>2</sub> in saline aquifers [107].

#### 4.2.1.4 Depleted hydrocarbon reservoirs

The use of depleted oil and gas reservoirs for gas storage is a well-known and widespread technique worldwide. This practice takes advantage of existing wells and infrastructure and, in some cases, requires the installation of new wells for gas injection or extraction. To be effective, they must have sufficient porosity, permeability and a cover rock to prevent leakage. Its main advantages include reducing investment and operating costs by minimizing the need for cushion gas and utilizing an already well-studied and known geological environment [102]. Oil and gas fields are typically depleted in a few decades, although the exact time frame depends on factors such as the size of the field, its characteristics and the rate at which it is depleted [108].

Transforming a depleted oil reservoir into a hydrogen storage site (H<sub>2</sub>) presents significant technical challenges. One of the critical aspects is avoiding chemical reactions between hydrogen and residual oil, as these can reduce the purity of the stored gas. In addition, hydrogen could dissolve in residual hydrocarbons, which can lead to significant H<sub>2</sub> losses and affect storage efficiency [102].

This type of storage has advantages for hydrogen storage, due to its already proven impermeability and above all for its known geological conditions, which can lead to a better understanding of the behavior of hydrogen with the geological materials of the reservoir [33]. While among its disadvantages is that various factors such as human activity, biological transformation, and gas mixing with remaining gas in the reservoir can affect gas quality and storage cycles [33].

One of the research proposals for this type of storage is also the production of hydrogen in situ through processes such as dark fermentation and at the same time leaving the carbon dioxide stored in the reservoir [108].

#### 4.2.2 Off Shore

Offshore geological storage of hydrogen (OGSH) allows the storage of hydrogen in subsea reservoirs. This method takes advantage of depleted oil and gas reservoirs or subsurface geological formations located under the sea. Where the advantages are similar to the advantages of the same reserves located on shore, these include the use of existing infrastructure, which reduces development and decommissioning costs, and the ability to handle large volumes of hydrogen in a geologically suitable environment [25].

Underwater hydrogen storage is based on principles like those used for underwater compressed air storage. This method takes advantage of the hydrostatic pressure of the deep sea, where the internal pressure equilibrates with the external pressure, minimizing the need for robust containment structures and allowing the system to operate at isobaric conditions, which increases energy density without requiring cushion gas [109].

One of the outstanding advantages is the design of lightweight structures that can be anchored without the need for direct attachment to the seabed, thus reducing environmental impact. Hydrostatic pressure increases by approximately 1 bar for every 10 meters of depth, making this method viable for long-term storage. Although the size of underwater tanks may be limited, they are useful as intermediate storage prior to hydrogen compression in offshore wind energy installations [109].

Offshore storage also reduces potential risks of environmental impact on land and avoids competition for space with other land uses. However, it involves challenges related to the integrity of geological formations, possible hydrogen diffusion leaks, and the need to properly manage pressure to avoid mechanical problems in the structures [25].

#### 4.3 Pipeline storage and distribution

The pipeline network can also be used for hydrogen storage, where the main advantage of pipeline storage is that the storage (and transport) of energy through a gas grid experiences much lower

losses ( $<0.1\%$ ) than in an electricity grid (8%). However, some of the problems with this type of storage relate to system safety, durability of materials and hydrogen leakage [110].

In terms of safety, this is essentially related to the risk of ignition and explosion of the methane-hydrogen mixture, as the addition of low concentrations of hydrogen (volumes of 20% or less) to existing natural gas pipeline systems results in an increased risk of ignition [110]. Also with respect to pipe durability, some metallic pipes may degrade when exposed to hydrogen for long periods, especially with hydrogen at high concentrations and high pressures [110].

Another challenge with this type of storage is the leakage of hydrogen through the pipe walls. Hydrogen has a permeability rate that is four to five times that of methane in polymer pipelines commonly used in natural gas distribution systems and also has a leak rate a factor of 3 higher than that of natural gas [110].

As for hydrogen distribution by pipeline, according to an IEA report, for distances up to 1,500 km, piped hydrogen is the most cost-effective option if all stages of the supply chain (conversion, transmission, distribution, storage and reconversion) are included, but for distances greater than 1,500 km, transport by ammonia carriers or liquid organic hydrogen is more economical [109].

For the transmission of hydrogen through pipelines it is important to take into account the same challenges mentioned above, so although for cost reasons it is recommended to use existing piping systems, it is necessary to clean this network so that the hydrogen does not come into contact and there is no likelihood of reactions with other chemicals.

Pipes used for transportation and distribution are usually made of low-strength carbon steels, suitable for ambient temperatures. On the other hand, austenitic stainless steels are frequently used in local distribution systems, such as gas manifolds. Although carbon steels are more economical, those intended for hydrogen handling require special treatments to ensure homogeneous microstructures and fine grains. In addition, in both onshore (buried) and offshore (seabed) infrastructures, the use of internal, external and cathodic protection is essential to protect pipelines from environmental conditions [109].

## 5. Conclusions

The different hydrogen storage technologies present a mixed picture in terms of maturity and applicability. Technologies such as compressed and liquid hydrogen storage are already viable and used in commercial and industrial applications. However, they still face significant challenges, such as optimizing energy efficiency and reducing costs for mass adoption. For example, hydrogen liquefaction, while effective in terms of energy density, requires expensive processes and careful management due to evaporation losses.

Among the hydrogen storage options, circular carriers such as ammonia and methanol stand out for their potential and advantages in terms of storage and transport. These carriers allow hydrogen to be stored more stably and safely and can release it through decomposition processes when needed. One of the main advantages of these technologies is that both compounds are already well established in the industry, with global distribution and marketing networks that could be adapted for the hydrogen economy. This significantly reduces initial infrastructure costs and eases the transition to a hydrogen-based storage and distribution system.

On the other hand, more advanced and sophisticated technologies, such as storage in metal hydride and carbon materials, show great potential, but need further research to overcome current limitations. These options, while promising for their ability to provide denser and safer storage, still need to demonstrate their feasibility at larger scales and overcome technical and economic barriers before they can be implemented beyond the laboratory.

Research in these areas is crucial to developing sustainable solutions that will enable hydrogen to become a mainstay of large-scale renewable energy storage and distribution. Its high energy density and ability to generate no carbon emissions in its combustion, in addition to its integration with renewable energies, make it a great alternative clean fuel contributing to the decarbonization of various energy sectors, even those that present greater difficulties, such as heavy or energy-intensive industry and heavy transport. Thus, its potential as an energy vector and sustainable fuel positions it as a fundamental piece for a clean and resilient energy future.

## 6. References

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