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Technological comparison of different hydrogen storage methods

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Once someone told me that "Full effort is full victory" – M. Ghandi. So, this is for you, mom and dad, because all your effort through life enable me to be here now. Thank you for teaching me and guiding me, for being company even in the distance during all these years and for being my best example of courage, compromise and scarify. Thank you to my siblings, for being part of this effort.

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ABSTRACT

Although our energy system is changing towards a green-energy system (and economy), there are still some problems that need to be solved in order to make clean energies a feasible replacement of conventional ones.

Due to the promising potential of storing hydrogen to overcome the challenge of adopting clean energies, the aim of this research is a technical analysis and a presentation of the differences between diverse hydrogen storage methods.

In this thesis we will analyze the storage of hydrogen as a molecule (geological storage, compressed, cryogenic and cryo-compressed) and in material-based storage (in metal hydrides and in Liquid Organic Carriers) from a theoretical point of view. After this investigation, we will implement an analysis of some of the most important characteristics of the mentioned systems with Excel, in order to define -or at least to approach- the most convenient storage method for a certain amount of hydrogen.

PREFACE

Sebbene il nostro sistema energetico stia cambiando verso un sistema di energia verde (ed economia), ci sono ancora alcuni problemi che dovrebbero essere risolti al fine di rendere le energie pulite una possibile sostituzione di quelle convenzionali.

Dato il potenziale promettente di immagazzinare l'idrogeno per superare la sfida dell'adozione di energie pulite, l'obiettivo di questa ricerca è un'analisi tecnico e una presentazione delle differenze tra i diversi metodi di stoccaggio dell'idrogeno.

In questo articolo analizzeremo lo stoccaggio dell'idrogeno come molecola (stoccaggio geologico, compresso, criogenico e crio-compresso) e bassato in materiale (negli idruri metallici e nei vettori organici liquidi) da un punto di vista teorico. Dopo questa indagine, implementeremo un'analisi di alcune delle caratteristiche più importanti dei sistemi citati con Excel, al fine di definire, o almeno ingrandire, il metodo di stoccaggio più conveniente per una certa quantità di idrogeno.

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ACRONYMS

CH2: Compressed hydrogen

LH2: Liquid hydrogen

CcH2: Cryo-Compressed hydrogen

MH: Metal hydride

LOHC: Liquid Organic Hydrogen Carrier

LHV: Low heat value

HHV: High heat value

VD: Volumetric density

GD: Gravimetric density

1. INTRODUCTION

With the technology improvements during last years, human race is on track of needing more electricity each day. Electricity became an essential part in our lives. Nevertheless, if we continue producing the desired quantities of electricity without focusing in the environmental changes, is going to be untenable and, in addition, someday our sources are going to be finished.

Nowadays, accordingly of the gained damages on earth and, with the main objective of reduce possible future damages, there's a lot of investment and investigation in clean energies such as solar, biomass, hydraulic, Eolic or geothermal, which are endless and "*green*" -because of their compromise with earth-. The huge problem in the usage and integration of these energies on our energy system is their versatility/intermittent character, so it imposes the necessity of an energetic vector in order to attach the produced energy with the required energy: here is where the Hydrogen takes place.

For years, energy has been stored in batteries such as Lead-acid battery, Nickel-metal hybrid battery, Lithium-ion battery or Alkaline battery, but in the last years we have realized that the specific energy of the hydrogen is higher than the specific energies of all of the mentioned batteries, as shown in the figure below [81]. This is the main reason why the interest in hydrogen storage has increased a lot. Nevertheless, in a "near" future both technologies (and some hybrids) are going to compete for the dominance on the roads, having each of them different strengths and weaknesses.
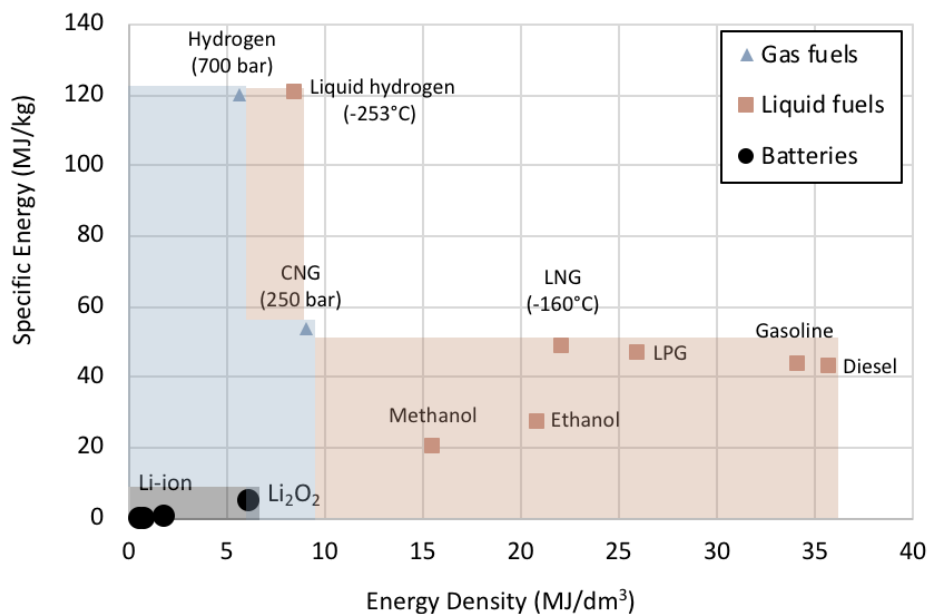

Fig. 1: Hydrogen -vs- batteries

The Hydrogen, known as the "energetic vector for the future", was first described by T. Von Hohenheim ("Paracelso", 1493-1541), who obtained this element mixing metals with strong acids. After that, in 1671, Robert Boyle re-discovered and re-described that the reaction produced between iron and acids filings generates gaseous hydrogen. Later, in 1766, Henry Cavendish coincidentally recognized the gaseous hydrogen as a discreet substance while doing experiments with acids and mercury. Although he wrongly assumed that the hydrogen was released by the mercury instead of the acid, he was able to accurately describe fundamental properties of the hydrogen. Also, he realized that its combustion generates water. Traditionally, he is the discoverer of this element. Few years later, in 1783, Antoine Lavoiser named this element as "Hydrogen" (From the Greek words which meant ''water-former'' water and generator) when he and Laplace proved that the Cavendish discovering which stated that that this gas generates water.

Regarding the importance of the really low boiling point of the hydrogen, one of its firsts applications was the utilization in the aerostatic balloons and, later, in other aircrafts. The gaseous hydrogen was obtained from the reaction of sulfuric acid and metallic iron. The high and fast inflammability of this gas was evidenced in the tragedy of the *Hindenburg zeppelin in 1937*, which was burnt while landing, producing 36 deaths. Because of its danger, was replaced for the gaseous helium, an inert gas.

On Earth, hydrogen is rarely found in the pure form, but usually in a wide variety of inorganic and organic chemical compounds, the most common being water (H_2O). Also, hydrogen can be find in big amounts above earth but is not easy to reach it because, due to its lightness and volatility, is on the highest layers of the atmosphere (in that low pressure, the hydrogen can exist in individual atoms because of their little chance to link). Although the real problem is not the difficulty to catch it (because its production is relatively easy and diverse) but is concentrated mainly in two things: the first one is its small volumetric density: due to this, it occupies large volumes for storage a little amount of gas and, also, its migration should be studied and controlled. To make this fact more visible: gaseous hydrogen is 8 times less dense than methane, while in liquid is 6 times less dense than liquid and 55 times less dense than gasoline [36]. The second main problem is related with what is mentioned before: in general, people are really concern about the security of this gas. Historically, the fear is based in its ignition capacity, linked with the colourless and odorless characteristics, which make it more dangerous because of the "impossibility" to recognize it. In reality, due to its small density, the speed at which it goes upwards when is released can reach the 72km/h, hence it's really difficult to reach the exact conditions to ignite.

Is expected in the future to talk about the called "hydrogen economy", which has some powerful reasons of being, such as: energy efficiency (due to the capacity of direct conversion from hydrogen to electricity), energy independence and environmental facts

[35]. Is conceivable that hydrogen will be employed not only in the industrial sector but in chemical usage, as a versatile energy carrier in the transport and in the energy utility sector including generation and heating. The European Union has sets its goal for renewable energy in gross final energy consumption to be 20% in 2020 which sets the share electricity production at about 30-40% [4]. However, there are handicaps in all of these applications. The suggestion of Hydrogen-fueled vehicles as a feasible alternative to fossil-fuel dependence has the main constraints of weight and volume. In the stationary applications such as power supply, the cost of the hydrogen and the pressure cycle life are the main issues [4]. In addition, for all the previous applications, is require the buildup of an adequate delivery infrastructure.

Along this project, we are going to expose and compare the most usual storage systems.

2. HYDROGEN

Hydrogen, which symbol is the letter "H" and its atomic number is 1, is the lightest of all elements and its atom is the simplest of all elements. As we commented before, the name came from Greek words that mean: the element that brings forth water. Is the most abundant element of the universe but just less than 1% is present in molecular form [59], accounting for 91% of our solar system by weight. Under normal conditions of temperature and pressure (20C, 1atm) is colourless, odorless, tasteless, non-poisonous, and flammable gas. consists of three isotopes.

As commented before, Hydrogen is an abundant element in our universe but is difficult to catch. During the years, Scientifics have developed some processes to produce hydrogen and to use it as fuel. Some of the methods to produce hydrogen are: electrolysis (water), reforming (natural gas, coal, gasoline), gasification (biomass, coal), thermochemical cycles (water) and biological production (biomass) [38]. In the other hand, some of the methods to its utilization are: direct electricity conversion from the chemical energy of hydrogen and direct combustion in reciprocating engines and gas turbine, as shown below [38]:
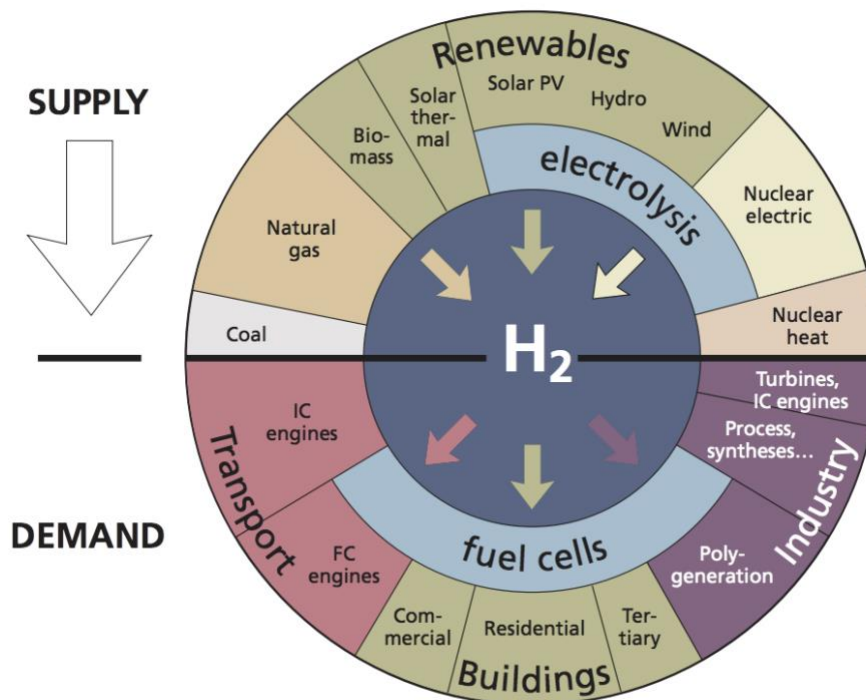
Fig. 2: Hydrogen supply and demand

The hydrogen molecule is formed of two atoms of Hydrogen and appears in two different forms: ortho-hydrogen and para-hydrogen, when the molecules have parallel spins or anti-parallel spins, respectively. Under normal conditions, ortho-hydrogen molecules are the 75% and the rest are para-hydrogen molecules, but it depends on the temperature, as we are going to explain in further chapters [4,33].

The ordinary one, H, is called *protium.* The next isotope, discovered in 1932, is present in the natural hydrogen to the extent of 0.015%, is stable and is called *"Deuterium" (D),* with an atomic weigh of 2 (one proton, one electron and one neutron). The other isotope, discovered in 1934, is unstable and is called *"Tritium" (T),* with an atomic weigh of 3 (one proton, one electron, two protons). Due to the excess of neutrons, it is unstable, and its half-life is approximately a year. Its nucleon changes or is disintegrated producing radiations [4].

At normal conditions, hydrogen is in gaseous state. It has the second lowest boiling point and melting point of all substances, after helium. Hydrogen is a liquid below its boiling point of -253 C (20 K) and a solid below its melting point of -259 C (14 K) and atmospheric pressure, taking the superconducting behavior as a simple metal. A phase diagram of hydrogen is shown in the next figure [34]. The boiling point of a fuel is a critical parameter since it defines the temperature to which it must be cooled in order to store and use it as a liquid.
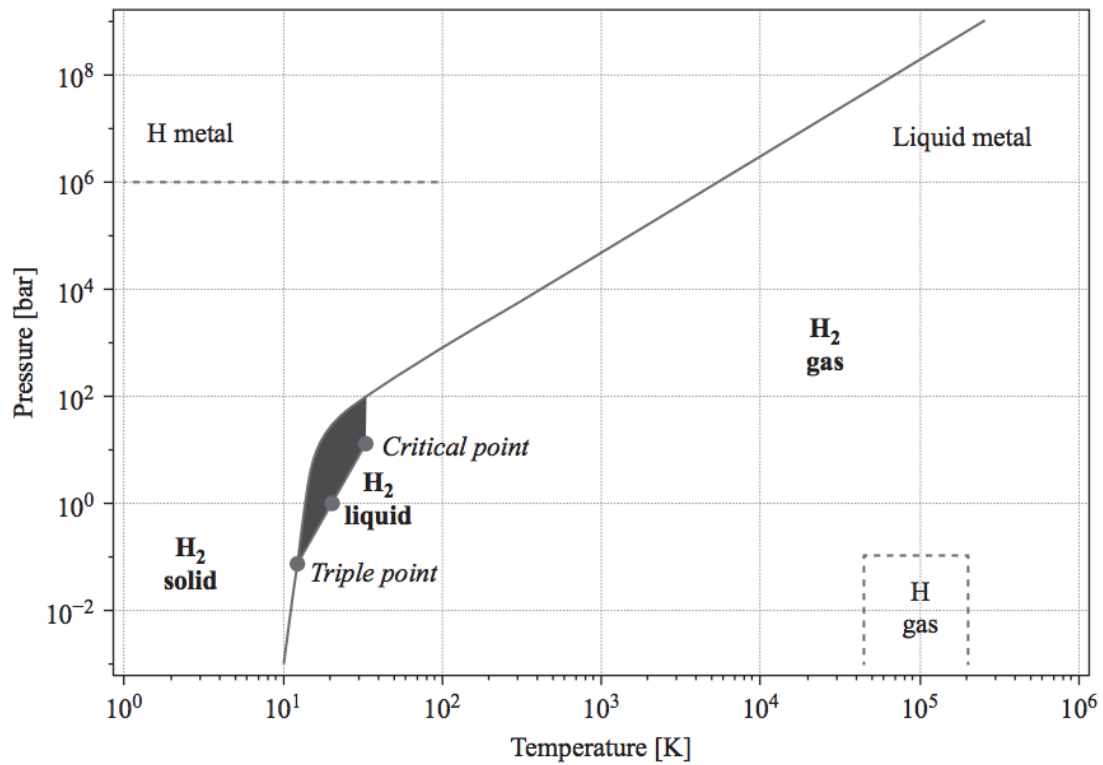
Fig. 3: Phase diagram of hydrogen

If we focus in the energy content of the hydrogen, we should know that when it reacts with oxygen, water is formed, and energy is released. This amount of energy is which we call *energy density* when is normalized with the quantity of hydrogen reacting, and we can express it in basis of mass or density. Comparing these energy densities of hydrogen with another typical fuels, the mass energy density of hydrogen is the highest, but its volumetric energy density is the lowest, as seen in the next figure [33]. Depending of the state of water released in the reaction, we can distinguish two different values of energy density: Low heat value (LHV) for vapor water (or net calorific value), and high heat value (HHV) for liquid water (or gross calorific value). Usually, the HHV is higher than LHV by about 10% [33].
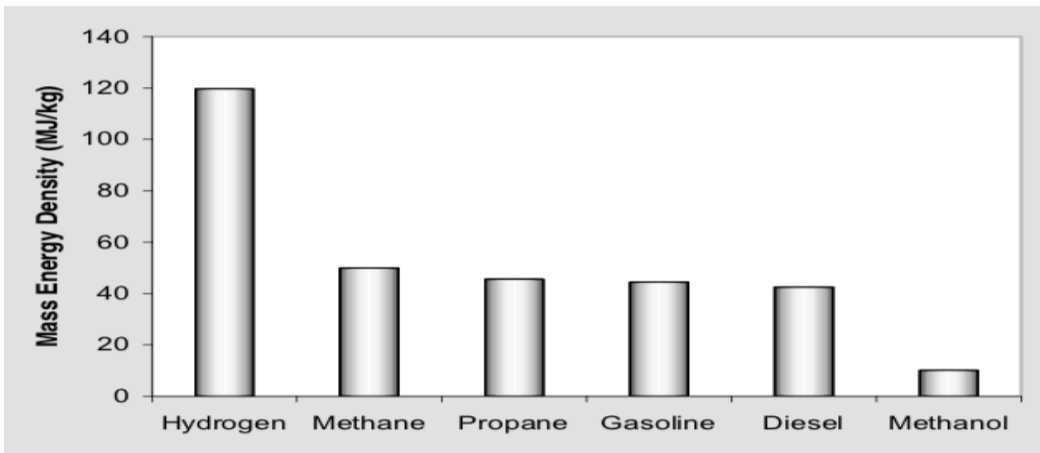
Fig. 5: Mass energy density comparison
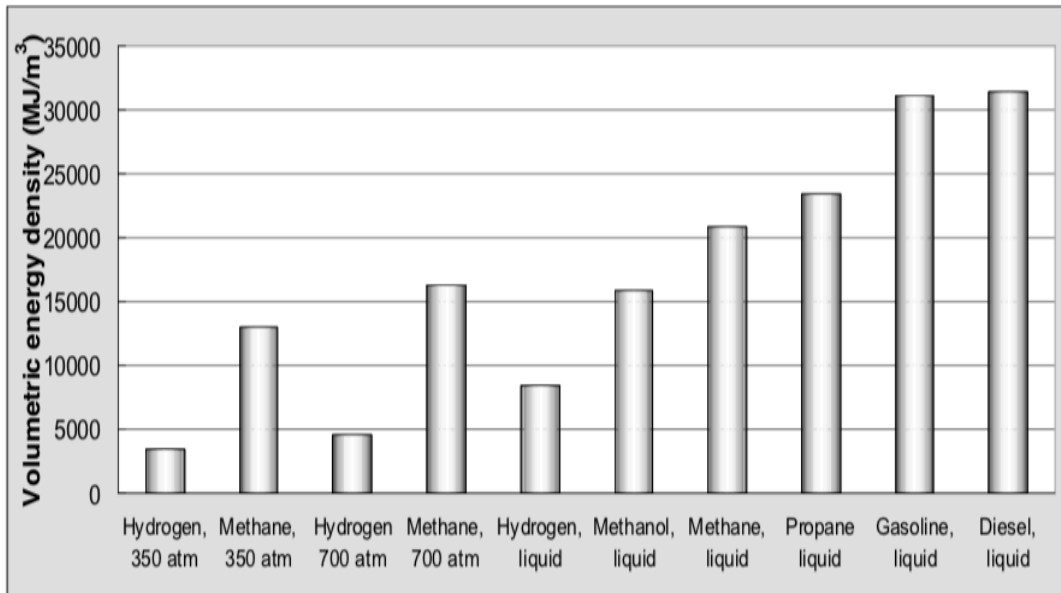
Fig. 4: Volumetric energy density comparison

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¿What about inflammability? Hydrogen is a flammable gas which can feed a fire or an explosion under specific conditions, like mixed with oxygen in a certain composition. The flammability range is the concentration range in air in which the gas is capable of supporting a self-propagating flame when ignited. Under ambient conditions, hydrogen is flammable in a wide range of concentrations (4-75%) and explosive in a range (15-59%) [39]. The upper flammability range of hydrogen (the highest concentration of hydrogen in air) is 75-85% (depending on temperature), which has important consequences for hydrogen storage: is evident that hydrogen is not flammable when stored (due to the lack of oxygen). Hydrogen becomes flammable only in the neighboring areas of a leak, where the mixing of hydrogen and air is within its flammability range, but, due to the diffusion velocity of the hydrogen, the chances for a fire and explosion may be encountered when leakage is in an enclosed environment [33].

Another important property of hydrogen is the auto-ignition temperature (minimum temperature required to star the self-sustained combustion in absence of an ignition source) and the ignition energy (minimum energy required to initiate combustion). In hydrogen, the auto-ignition temperature is 585°C, higher than the auto-ignition temperatures of methane (540°C) and gasoline (230-480°C). In the absence of such a high temperature, the hydrogen can just be combusted when there is a source of ignition. In the other hand, its ignition energy (0.03 mJ) is lower than those of the conventional fuel, therefore, Hydrogen can ignite more easily than the others [39].

Lastly, should be known that the hydrogen may degrade the mechanical behavior of metallic materials used in the hydrogen infrastructure and lead them to failure. This phenomenon is called hydrogen embrittlement and, being one of the major issues in the applications of this gas, is needed to be considered [33]. Hydrogen embrittlement is a physicochemical metallurgic process in which the hydrogen reacts with the metal and is manifested in different forms depending of the type of interaction. Its effects are more pronounced in steels, for example: reduce of ductility, ease of crack initiation/propagation, change in the yield behavior, etc.… All the consequences have adverse effects from the mechanical point of view.

In the following chapter we are going to analyze some of the different technologies that are actually in use for hydrogen storage. Hydrogen can be stored in the free form of the molecule, also called physical storage (geological storage, compressed and liquid) or being absorbed by other materials, also called solid storage (metal hydrides) and liquid storage (Liquid Organic Hydrogen Carrier systems). In those which the hydrogen is storage as a molecule, temperature and pressure are change in order to store the gas maximizing volumetric and gravimetric capacity.

3. THEORETICAL ANALYSIS OF HYDROGEN STORAGE SYSTEMS

3.1. Geological Storage

One of the limitations of hydrogen-fueled vehicles is the lack of infrastructures. The challenge is to have economically feasible ways to produce, transport, store and deliver the energetic vector. This is why some Scientifics are focusing in underground geological storage. Geological storage can provide a sizable economic strength and continuity of delivery in case of interruption in the supply chain. Also, another advantage is that the geological storage is the only one which can provide large storage capacity (more than 5GWh) for longer-term grid stability [61].

Furthermore, it seems to be something not really original because we can obtain the knowledge of this storage from the currently storage of natural gas or town gas but, the truth is that hydrogen storage within the same type of facilities will add challenges to the underground storage industry. Hydrogen is a small and light molecule that could reacts easily with other elements and also with steel (at high temperatures and pressures), which is the process called "embrittlement of steel due to hydrogen", consequently, the existing storage facilities need to be adapted to avoid it

The type of rock formation that we are considering will have wide effects on the physical and economic viability to use the site. We are going to have a look through four types of geological storage: Saline aquifers, depleted gas/oil fields, salt caverns and mined rock caverns abandoned [4].

3.1.1. *Pore space of sedimentary rocks*

The main different systems of geological storage in porous rocks are *saline aquifers* and *depleted gas/oil fields*. Usually, aquifers are more expensive to develop due to lack of infrastructures and uncertain geology [4].

Hydrogen storage in porous rocks requires a porous and permeable reservoir rock that provides the actual storage volume, an impermeable layer rock covering the reservoir (which should have a very low gas permeability and high capillary entry pressures for hydrogen, in order to avoid the stored hydrogen from migration upwards) and a three-dimensional structure, called "trap" [4] that confines the stored hydrogen in a predefined area, in other words, is which controls the lateral migration of the hydrogen. Ideal gas traps are structural highs as anticlines, with impermeable caprock and sufficient surrounding hydrostatic and threshold[1] pressures.

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[1] The ability of a caprock to contain gas is expressed in terms of its threshold displacement pressure, which is defined as the minimum pressure needed to initiate the displacement of a wetting phase by a nonwetting phase from a porous medium 100 percent saturated with the wetting phase.

The amount of porosity is related with the type of sedimentary rock and on his history (for example, taking into account its chemical and physical transformations). Typical reservoir rocks are sandstones and other classic sediments or carbonates, which provide volume of porosity. The sandstones have an amount of porosity that can be reduced due to compaction and cementation. Carbonates also show different porosity due to dissolution processes [4].

While the main geologic necessities and characteristics are similar for porous rock storage, the pressure conditions are really different. In *saline aquifers*, the space between the rocks is filled with brine and can be assumed to represent approximately the hydrostatic conditions, so, in order to inject hydrogen, the brine has to be replaced to create available space for the gas. This lateral displacement generates an increase of pressure in reservoir above hydrostatic. *In depleted gas/oil reservoirs*, the pore space is partly available (so there's no need to free spaces) and the reservoir is usually below hydrostatic pressure. That's why before the injection of the gas, the reservoir has to re-raise the pressure to a level at which economic injection/extraction is achievable [4].

Depending on the type of geological trap, storages may be classified as open, confined or semi-confined. Each of them has different pressures. For saline aquifers, for example, the confined reservoirs have more pressure due to injection that the open ones. Consequently, its capacity is smaller because the pre-defined fracture/threshold pressure limit is reached with less amount of injected gas [4].

The pressure in the reservoir also depends on its size, its permeability for the displaced formation brine and the injected hydrogen and also on the rocks' compressibility and formation fluids. Larger reservoirs and/or higher permeability results in lower pressure and greater horizontal spread of injected hydrogen.

However, if we compare the flow velocities in porous reservoirs and caverns storage, are lower in the first one. And, also, porous reservoirs are more inflexible with respect to injection/extraction rates when comparing with hydrogen storage in caverns. Due to these things (inflexibility and low flow rates), porous reservoirs are regularly used for seasonal gas storage within the frame of natural gas storage[4].

3.1.2. Caverns

These cavities may be salt caverns, mined rock caverns or abandoned mines (all of them artificially created). Among which salt caverns are, definitely, the most typical for natural gas storage -consequently we can assume that also for hydrogen storage- [4].

Salt caverns are usually cylindrically-shaped and are constructed from the surface by controlled injection of water down a well drilled into the salt rock. Can be created within salt domes or within bedded salt deposits. The latter have shallower depths than domes but are structurally less stable due to heterogeneity of rock types present.
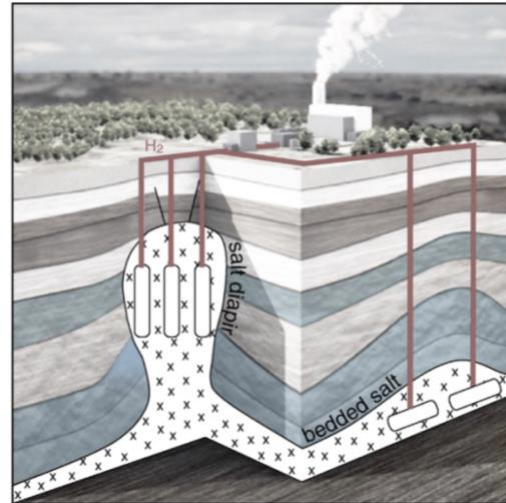
Fig. 6: Salt caverns

Depending on the conditions and the technical possibility, can be constructed at depths of down to 2000m, typical heights are of 500-1000m and diameters of 50-100m. Depending on the depth, the pressure can be up to 20MPa (or even above that, depending on the placement [2,4]. It is the maximum cementation and casing strength). This high pressure permits the storage of very large quantities of gas, for instance, a typical large gas cavern can keep more than 60 times the volume of a spherical gas tank.

Depending on the pressure requirements, salt caverns need -or not- a cushion gas. If the cavern works under variable pressures, approximately 1/3 of its volume will contain cushion gas [4]. The accurate amount of cushion gas needed is based on the minimum pressure[2] required to prevent salt creep. Besides, if the cavern works with constant pressure, the cushion gas is no needed. While withdrawing these type of caverns, saturated brine is injected in order to maintain the constant pressure. However, due to excavation process, a quantity of this brine will always remain at the bottom of the cavern and will increase the humidity, reason why depending on the predicted use of hydrogen, drying after extraction could be necessary.

Because of the favorable specific properties of the salt, caverns are tight with respect to gas and have long-term stability. Due to this tightness, is not necessary an additional gap rock. Moreover, is interesting to highlight that the salt is inert to reactions with the injected hydrogen.

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[2] We have to take into account that the maximum pressure is usually determined by fracturing tests and applying a safety factor. However, minimum pressure is so difficult to formulate: it depends not only on the depth location but also on the strength and rheological properties of the rock salt, shape and volume of the cavern.

Contrary to salt caverns, *mined rock* and *abandoned mines* just play a secondary role for hydrogen storage. Although *mined rock caverns* (constructed for storing gas or liquid) have a very low porosity and permeability, they may break during construction, offering fracturing permeability and, due to this, not intrinsically tightness. The tightness is strengthened with engineering techniques. By the other hand we have the *abandoned mines* not constructed for storing gas or liquid but to extract different natural resources. Due to this, the type, quality and suitability is very diverse. Its tightness and integrity are normally questionable [4].

Geological storage of gas is a verified and developed technology since a few decades. This kind of hydrogen storage has lower specific construction costs compared to surface gas tanks, have unlimited operating lifetime and a small surface footprint. One of the weaknesses of this storage is that the most relevant geological and technological aspects of the hydrogen storage are known because of its similitude with the storage of natural and town gas but, is known that the organic and inorganic chemical processes during hydrogen storage are different from those that happens during natural gas storage, so not everything is precise. In addition, hydrogen has a lower density and lower viscosity, which affects in the performance of the reservoir because influence in the subsurface behavior and, also, has a lower volumetric heating value than natural gas, which affects the energy storage capacity.

An optimized implementation of hydrogen generation from renewable energies and storage in salt caverns would have a really positive impact on power system. The flexibility of this kind of storage enables to produce hydrogen from variable renewable electricity without increasing CO_2 emissions, can reduce the limitation of wind power plants and hence help to integrate renewable energies into the power system. Nevertheless, good geological conditions are limited to a few sites [4].

If we analyze the infrastructural part, is more complex the geological storage compared with a normal on-ground facility, mainly because of the connected pipeline system, but also because the safety measures involve more components, the process has to be monitored, controlled and optimized. Moreover, the properties of hydrogen impose extra challenges mentioned above, since embrittlement and fissures can lead to serious incidents more easily compared to hydrocarbons.

The engineering processes like gas connection/transport (pipelines and tubing), the gas compression/expansion, the monitoring and the storage properties aren't easy to achieve. In the following paragraphs we are going to go a little deeper on those topics.

-Pipelines and Tubing: we could think that is a trivial point but, first of all, in order to transport all the volumes needed, the standard diameters of pipes are in the range of 56-81cm. Also, they have to achieve laminar flow even at the maximum point of volume going through it. In the other hand, typical pressure level is 1.5-8.0 MPa (lower pressure

levels would require less material because the tube has less mechanical stress) [62]. Height differences due to the background also influence the local pressure in the tubes so, the pipelines are routed preferentially at constant height (although that means that the installation is longer). Another common issue is the electrochemical corrosion of the pipelines since tubing is made of steel for economic reasons [63]. Knowing that this corrosion is due to big voltage drops, we can try to avoid it while decreasing eddy currents (that are which present heating or voltage drop along the tube). In order to decrease them, is prohibited routing the pipeline parallel to train tracks or electrical power lines, they need an angle of 90 grades [4]. Sometimes special polymers are used to electrically insulate the tube from surroundings, but it increases the costs, so it's only applied in specific parts of the line. Similarly, different pH values and chemical compositions of the soil along the pipeline, which mean electrical potential differences, can produce high currents. Thus, pipelines are covered with standard cathodic protections.

Hydrogen specific characteristics limit the material choice for the tubing materials compared to the natural gas. Instead of using the same material to transport hydrogen that to transport natural gas (that is a common reason of failure due to the embrittlement), we can used austenitic steels (18% chromium and 8% nickel) or chromium-molybdenum blended stainless steels [64]. Alternatively, tubing can also be embedded in concrete tubes (especially applied when the pipeline crosses swampy ground).

-Compressors: they have to provide high mass flow with a high efficiency. The normal pressure for the grid is 1,5 to 8,0 MPa [4]. The lower the pressure differences to bridge, the more efficient are these machines. Depending on this pressure different, diverse kinds of compressors can be used. The most common is the encapsulated centrifugal compressor [4], that is when high mass flow on the range of $5x10^5$ kgH$_2$/day is needed [65]. The problem is that the compressors market is small, especially for the large volume flux applications that we need at geological storage. The available can only bridge small pressure differences.

-Metering: the most common are based on measuring the real volumetric flux. However, this concept is limited to small mass flows. There are a lot of different metering methods but only a few of them are really accurate at high mass flows [66,67]. An alternative design is the orifice meter, which measures the flux by pressure difference (no movable parts are involved). Another option is ultrasound. The latter is used not only as inspection tool but also for permanent monitoring because allows the measurement from the outside of the pipeline.

-Controlling and Safety Components: are one of the most important parts of the system. The valves are used to control the gas flow not only limiting the flux, but also generating or shutting down units by emergency. As in the compressors, there are

movable parts involved. The material is mostly Duplex stainless steel (to handle mechanical and chemical stresses, which came mainly from the gas stream itself) [68].

Also, there is a flame arrestor which prevents the backdraft of a flame in a tube system in the case of an accident. Usually it element consists of finem meshes of metal or ceramic which prevent the inflowing gas from ignition or, in the case of a serious accident, the gas is burned in a controlled manner[4].

Even if the geological storage is really useful to save huge amounts of hydrogen due to its elevated pressure, is more complex than the on-ground storage because is not only limited to the storage itself but also to the connected pipeline system. Indeed, for example, the safety measures involve more components than at the other types of storage and, also, the good geological conditions are limited. Taking into account these *"weaknesses"* of the geological storage, and without being it useful for our research itself, we are going to continue the project with the most common stationary types of hydrogen storage: compressed, liquid, MH, LOHC and NCT.

3.2.Conventional Storage

Nowadays, nearly all hydrogen produced nowadays is used in industrial sector but is expected that in the future it will be employed to its current chemical usage. It will be use like a versatile energy carrier in transportation or in the energy utility sector (power generation or heating). Needing, both of the utilities, an adequate infrastructure. [5]

The most common methods for stationary hydrogen are: compressed, cryogenic liquid and metal hydrides, but commonly -because of its price- the latter is used for small amounts of hydrogen [6], and is relatively new in the commerce so, in this chapter of conventional storage, we will focus on compressed and cryogenic hydrogen.

We are going to study how can we storage the hydrogen (as free molecules) in vessels that can be locate both: above ground or buried a few meters below the ground.

From the types mentioned before, we can assume that the most feasible application as a road transport fuel should be the compressed hydrogen because it has structural analogies and technical similitudes to the existing for the natural gas [7,8]. In this context, we can define two different kind of storage depending on the minimum and maximum demands: *short-term* (to compensate the hourly fluctuations in refueling station demand) and *long-term* (to compensate the seasonal fluctuations in refueling station demand and production plant outages) [9,10,11]. Consequently, we will have different sizes: small-scale (final-user level, storage capacity up to 5tons), medium-scale (up to 500tons) and large-scale, which covers everything above. [4]

The suitability of different storage methods for a certain application is best evaluated with the appropriate parameters like gravimetric and volumetric capacity, which are, respectively, amount of mass of hydrogen stored per unit weight and volume. And, this mentioned suitability is directly linked to the necessities and boundary conditions of the future application [12,13].

In the next graphic [14] we can see the difference between these mentioned densities of liquid and compressed hydrogen and common fuels:
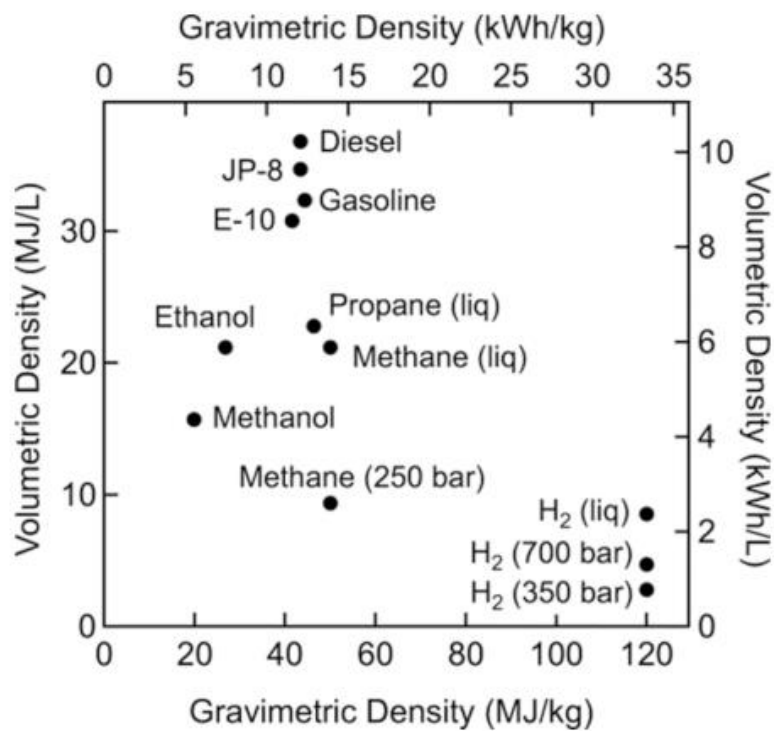

Fig. 7: Volumetric and gravimetric density of different fuels

In which is visible that hydrogen has the highest mass energy density but the lowest volumetric energy density.

3.2.1. *Compressed hydrogen*

Storing hydrogen under pressure has been used for many years and, nowadays, storing it in vessels is the most common storage form [15]. The advantages of compressing a gas is increasing its density or, setting it the other way around, reducing volume. For getting and idea, at ambient temperature (20C) and pressure (1.013bar), the hydrogen density is 0.084kg/m^3, if we increase the pressure up to 100bar, the density is 7.197kg/m^3 and if we increase it again up to 1000bar, the density is 49.938kg/m^3, corresponding to the non-ideal characteristics of hydrogen at elevated pressures [4]. The resulting deviation from the ideal gas law is because the gas occupies more space than the ideal gas law predicts [33]. One of the simplest ways of correcting is adding a compressibility factor, usually derivate from data obtained from experimentation, and now taken from the "Spanish Association of Hydrogen" [16], in order to make visible the non-linearity at high pressures.
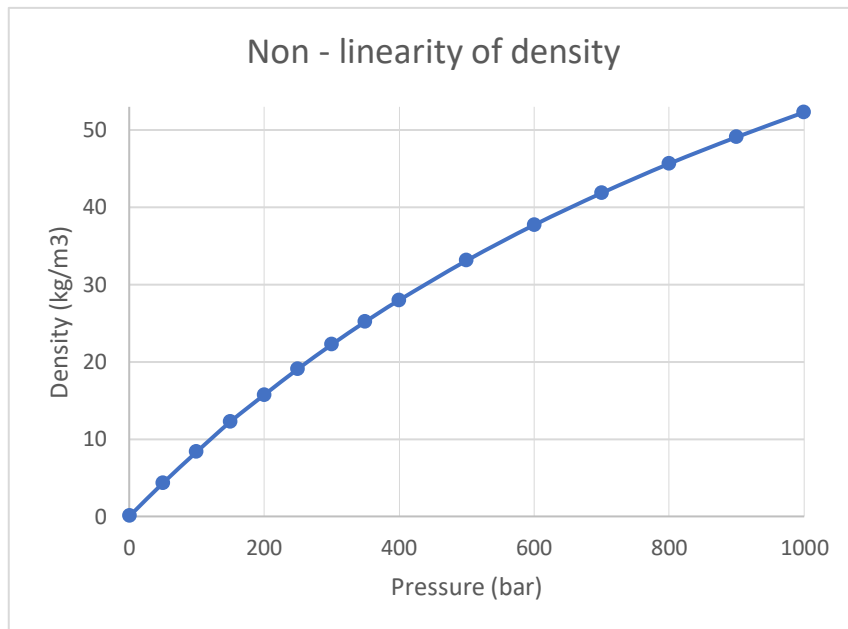
Appendix 1 is related.

Fig. 8: Hydrogen non-linearity behavior

We can see that are not precisely matching with those mentioned before but are really similar.

The necessary compression work is different depending on the type of compression and the applied cooling. Isothermal compression poses the most energy-efficient method and leads to minimum compression work but, in order to keep the temperature constant during a gas compression, is necessary to do it slowly enough to allow the heat -increased because of the increasing of internal energy- to be diffused away. With the isothermal compression, the theoretical minimum work of compression until 253 and 1013bar is 1,5 and 2,0 kWh/kg, respectively. Since in the practice there are also losses such as parasitic compression losses and the consumption of the compressor,

the power demand rises to 2,5 and 4,0 kWh/kg [17,18]. Which corresponds to 7,5% and 12% of the LHV of the hydrogen. Some researches set the values in 5% and 20% of LHV when compressing up to 350 and 700bar, [19]. Even so, we can notice that the necessary energy consumed for compressing the hydrogen in percentage of LHV, doesn't increase linearly with the pressure but parabolic. Therefore, in relative terms, we can notice that is more efficient if we work at high pressures because increasing a huge amount of pressure, the needed energy is just slightly higher than increasing less amount of pressure. In other words, the work required to compress hydrogen depends on the initial (suction) pressure: the higher it is, lower the difference between pressures, lower the energy demand for compression [33]. This fact is more visible in the figure below:
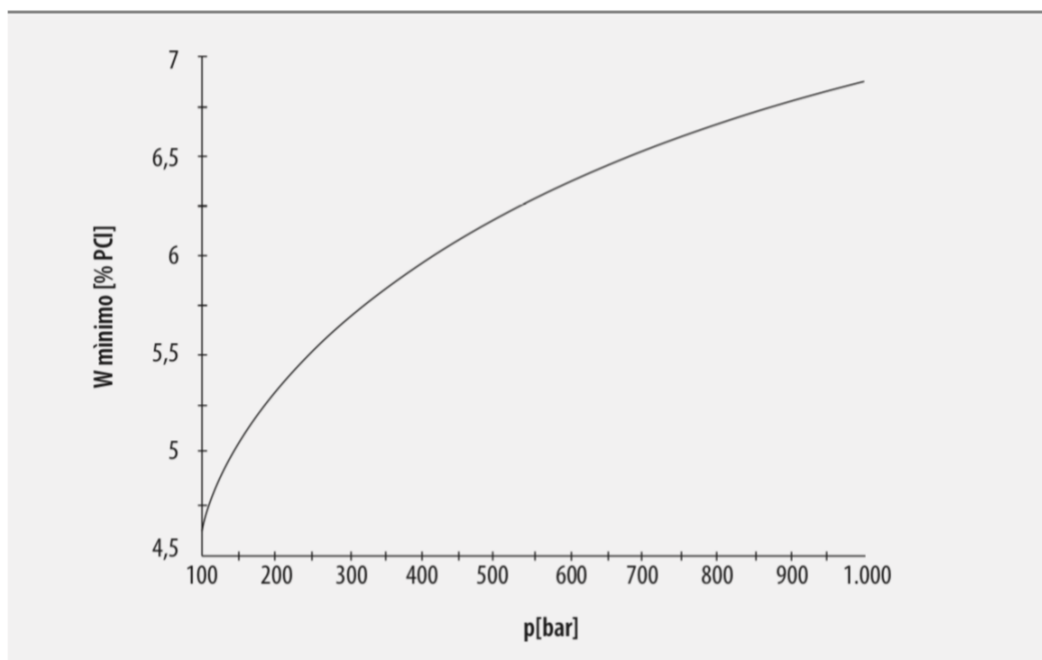

Fig. 9: Minimum needed energy in terms of LHV depending on the pressure

In the next figure [20], we can see the difference between adiabatic and isothermal ideal-gas compression of hydrogen, compared to its higher heating value, HHV. Also, it can be observed that the multi-stage compressors with intercoolers operate between these two limiting curves, getting closer to the isothermal curve (less energy required) with the number of stages [33].
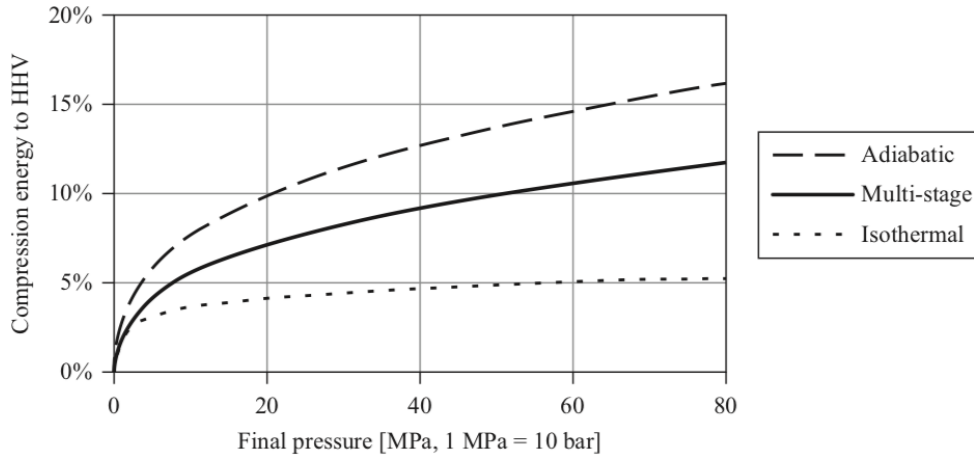

Fig. 10: Adiabatic, isothermal and multi-stage compression of ideal-gas compared with its HHV

There are different types of compressors (such as centrifugal, rotary displacement, reciprocating or the non-mechanical such as metal hydrides, electrochemical compressors and high pressure electrolyzes) but, because of the hydrogen special characteristics, only the reciprocating displacement compressors are being used in industrial and chemical applications [4]. In this category, we use reciprocating pistons for high-volume applications and pistons or diaphragms for small-volume [15]. Another interesting approach is the use of non-mechanical compressors as electrolyzes, metal hydrides and electrochemical compressors [18].

One of the applications of the compressed hydrogen is as fuel in vehicles. Actually, is a mature technology and compared to other storage methods such as liquid or chemical in metal hydrides (that we will see here after) it is most advantageous with regards to short refueling time, hermetically sealed system without boil-off, system complexity, and gas handling. Regulations for vehicle approval are already in place worldwide. Refueling technology is available; station network is currently being built up in many countries and regions.

The following paragraphs are about typical pressure vessels used for small-scale bulk storage and medium-scale bulk storage [15,21].
-Small-scale bulk storage the most common consist in a number of pressure tubes that can be accumulated together to extend storage volumes, can be established vertically or horizontally and can be sized according to customer use rates and purpose.

Generally, we can differentiate four different types of high pressure vessels:

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Type I: pressure cylinder all made with metal
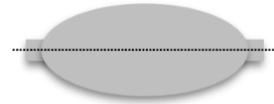
Type II: pressure vessel made of a load-bearing metal liner hoop wrapped with a fiber-resin continuous filament.

Type III: pressure vessel made of a non-load-bearing metal liner axial and hoop/polar fully-wrapped with a fiber-resin composite.

Type IV: pressure vessel made of a polymeric liner (non-load-bearing, non-metal liner axial) and fully-wrapped with a fiber-resin composite. The port is metallic and integrated in the structure.
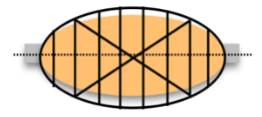
Fig. 11: Types of small-scale bulk storage.

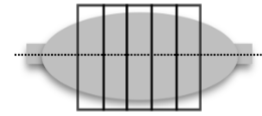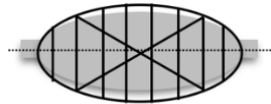For stationary gaseous storage, type I is the most common because, although is the weightiest, is the cheapest. They seem to be first linked to the high consumption of CO2 for beverage, with the necessity of keep it safely by the 1870-1880 approx. Its pressure is limited to 300bar. For stationary applications with higher pressure, type II is preferred, although they cost maybe 50% more to manufacture, can reduce the weight of storage by 30-40%. Types III and IV are more cost-effective for high pressure (up to 350bar is a mature technology) stationary storage. These types of vessels were initiated specially for military functions, which technical performances - specially weight- were important criteria. Its price is almost twice the price of type II vessels and 3,5 times greater than type I. On a typical transit bus or commercial truck, for example, the use of Type III and Type IV vessels easily could reduce the weight of the gas containment system by more than 454 kg. This weight reduction would not only improve fuel economy but also increase load-carrying capacity and introduce other operational benefits, making it possible for the more expensive tanks to buy their way onto vehicles. Second, composite vessels extend the practical limit for gas containment pressures and provide better energy storage density. For many high-pressure applications. Third, composite materials significantly improve a pressure vessel's corrosion resistance and overall safety. For composite vessels that incorporate carbon fiber tow as reinforcement, the excellent fatigue resistance of these fibers also extends the vessel's service life. Carbon fiber-reinforced Type III and Type IV pressure vessels can remain in use for as many as 30 years before they require replacement — twice the interval allowed for Type I and Type II vessels. [80]

The design of pressure vessels takes into account a lot of parameters such as: the service and test pressures, external stresses (impacts, aggressive media, vibrations, temperature of service…), real lifetime (cycling) and safety coefficients for static and dynamic conditions, which define the mechanical design and choice of materials. It is also important to note that metallic and composite vessels are very different. The metal is isotropic, the composite is anisotropic (mechanical properties concentrates in the fiber direction for the composite) and the failure modes and elderly are diverse.

Diameter, length and pressure of each tube determine the amount of hydrogen stored. Higher is the pressure, higher is the capacity of hydrogen storage per unit volume but higher is the vessel's wall thickness, so the cost increases [4].

-Medium-Scale bulk storage: in the natural gas utility sector, storage vessels are gas holders, spherical pressure vessels and pipe storage facilities. Having special attention with the consequences that hydrogen can produce in some materials, such as hydrogen embrittlement and fatigue, vessels have to be built with materials able to stand them and able to maintain mechanical integrity under high pressure cycling environments.

Gas holders were built around 1900 and 1960 [22] and, at the beginnings of the twentieth century, were used to store gas town just at a few mbar above atmospheric pressure level. For example, at operating pressures of up to 1.5bar a gas volume of 600.000-700.000 m^3 can be stored in some types [23]. Due to this low pressure, the space needed is so huge. This is one of the reasons why this technique of storage is considered obsolete (although until 2012 there were a few hydrogen storage gas holders still).

Spherical pressure vessels were built around 1930 and 1990 [22] and they offer the possibility of store amounts of gas town relatively large in small space. Their medium operating pressure is up to 20bar and can keep up to 300.000 m^3 [24,25]. In addition, the shape minimizes the ratio surface area/volume, which means minimizing losses. Comparing gas holders with these vessels, we can say that the latter, also, reduce operating costs because the thickness of the walls decreases. The literature assures the existence of a spherical pressure vessel which stores 15.000 m^3 at pressure in the range of 12-16bar [26,27,28]. Since evidences of spherical containers of hydrogen couldn't be found, researchers used the technical data from natural gas spherical pressure vessels to estimate hydrogen storage parameters.

Pipe storage facilities have been built since 1980 until today [22]. These tubes are constructed from standard diameters of about DN 1400 and are able to resist high operational pressures such as 64-100bar [29], which makes possible the storage in the range of GWh. They are normally buried under ground, protected from bad weather conditions and mechanical impacts and, also, allow the ground un-usable to be -for example- agriculturally usable [30]. Comparing it with spherical vessels is able to operate

at higher pressure ranges with small storage volumes and easier technical construction, which consequently translates in economic advantages: lower investment costs.

Is necessary to remark that the vessels have to be designed with materials resistant to hydrogen embrittlement and fatigue. In addition, they have to conserve structural integrity under high-pressure cycling environments [15].

New ideas are being created for the medium-scale bulk storage. One of them is the use of prestressed concrete pressure vessels (PCPV) that can be spherical or hemispherical or silo shaped, for the hydrogen storage up to 100bar [31]. To prevent hydrogen leakage is necessary to install an impermeable coating, which have been improving and developing using high molecular weight carbon composites and polymers.

Other approach is to use the wind turbine towers in order to store pressurized hydrogen. The ideal pressure levels are recognized to be in the range of 10-15bar [32].

3.2.2. *Cryogenic liquid hydrogen storage*

Nowadays this kind of hydrogen storage is mostly used in space exploration and science, but the volume reduction of liquid hydrogen makes it particularly attractive for bulk in transportation. The huge problem with liquid hydrogen lies in the amount of energy needed to liquefy it and to maintain it in the require conditions and the boil-off [4].

The liquefaction of hydrogen is achieved by cooling hydrogen gas below its boiling temperature of -253°C (maximum temperature in which hydrogen is liquid) [4,33], as mentioned in the first chapter. There are different processes to obtain liquid hydrogen, such as combining thermodynamic cycles with the following technics: heat transfer using heat exchangers, isenthalpic expansion following compression in reciprocating engines and cryogenic turbines or J-T throttle valves, taking advantage of the Joule-Thomson effect [33].

The minimum theoretical liquefaction power can be influenced by parameters such as feed pressure and temperature, but one of the most important parameters is the equilibrium of the hydrogen's forms: "*para-hydrogen*" and "*ortho-hydrogen*", which have different properties due to the orientation of its nuclear spin.

Para-hydrogen, whose nuclear spins turns in the opposite direction (a), has a lower energy level than ortho-hydrogen, whose electrons turn in the same direction (b). The ortho-para composition defines most of the physical properties of the hydrogen (such as liquid density, triple point temperature and pressures). At normal conditions, the most common composition is the so called "*normal hydrogen*" (abbreviation: n-H_2): the molecule consists of approx. 75% ortho-hydrogen and 25% para-hydrogen [4]. This normal composition will
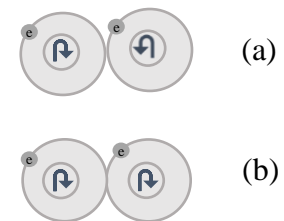
 (a)

 (b)

Fig. 12: Para-hydrogen and ortho-hydrogen spins

be obtained when the cooled down is made rapidly (Hydrogen can liquified in terms of seconds or maximum minutes). At the boiling point of liquid hydrogen, the equilibrium shifts as: 0.21% of o-H_2 and 99.79% p-H_2 [4].

In general, the equilibrium between these forms changes towards a bigger fraction of para-hydrogen (lower energy level) with decreasing temperature, as is seen in the figure below [33], or simply with time.
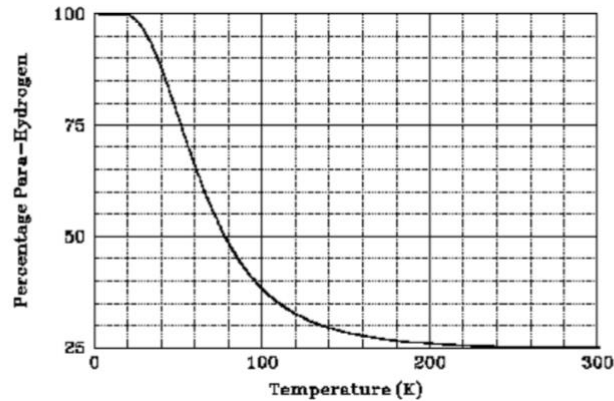

Fig. 13: Equilibrium percentage of para-hydrogen as a function of temperature

With this, is understandable that if we store for a long period liquid hydrogen that has not achieved its equilibrium point, the ortho-hydrogen existing will slowly shifts into para-hydrogen through an exothermically and slow conversion (maybe days or weeks). The slowness of this process is due to the weakness interaction between the atomic nucleus and the electrons. However, this process is not insignificant: because of its exothermic characteristics, produces a non-neglectable amount of heat, leading - irremediably- to vaporization and loss of liquid stored hydrogen. Due to this, the pressure inside the vessel will increase, so it has to be regulated by a pressure relief system that, at the same time, contributes to hydrogen losses: "*boil-off*" [4] (explained forward).

Because of the issues mentioned before, the challenge is that the liquefaction and conversion have to be accomplished simultaneously. This is possible through the modification of the *normal hydrogen* with the assistance of catalyzed reactions, which reduce up to the minimum the amount of "ortho-hydrogen" during the liquefaction process. Therefore, the ortho-para content of the liquid hydrogen will correspond to the equilibrium combination at the liquefaction temperature (mostly containing p-H_2 and being appropriate for large-term storage). Normally, the liquefaction plants operate with a minimum fraction of 95% of para-hydrogen [4].

In order to design a liquefaction process, is basic to take into account the Joule-Thomson effect. Contrary of ideal gases, that don't present a change of temperatures while isenthalpic pressure change, the real gases do. That is why the Joule-Thomson effect appears only in real gases. Throttling a real gas through an adiabatic valve, results in the reduction of its pressure with a corresponding change in its temperature (increasing

or decreasing depending on the substance and its initial temperature). Rephrasing, under certain conditions a Joule-Thomson expansion will produce heating rather than cooling, determining the design of cryogenic equipment [40]. When the JT is negative, the temperature of the gas increases in an isenthalpic expansion, and when the JT is positive, the temperature decreases in an isenthalpic expansion. The change from negative coefficient to positive one is achieved at -83°C [36] and it's called *"temperature of inversion"* (other sources settle it in -69°C [33]). This is the reason why the ideal process, shown in the figure below [33], in a liquefaction process is compressing in order to decrease temperature (negative JT coefficient) and increase pressure until the inversion point and then, expanding from this pressure to ambient pressure, to further reduce the temperature (positive JT coefficient), which, however may not be enough to liquefy hydrogen [33]. Even so, the gas that has been cooled by throttling is used to cool the feed/incoming gas, thus lowering even more the gas temperature. Hence, after successive cooling cycles, the temperature of the gas is lowered to such a temperature that, after throttling, some liquid can be formed [41].
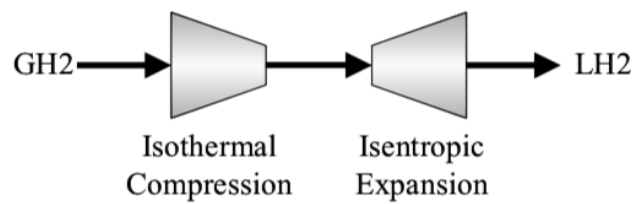
Fig. 14: Ideal liquefaction of hydrogen

The liquefaction processes are so diverse but, nowadays only few of them are applied in the plants. The conventional way to do the hydrogen liquefaction consists in: compression, cooling (with heat exchangers) and expansion (with valves).

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In the figure below [4], we can see the scheme of the conventional process with flash gas:
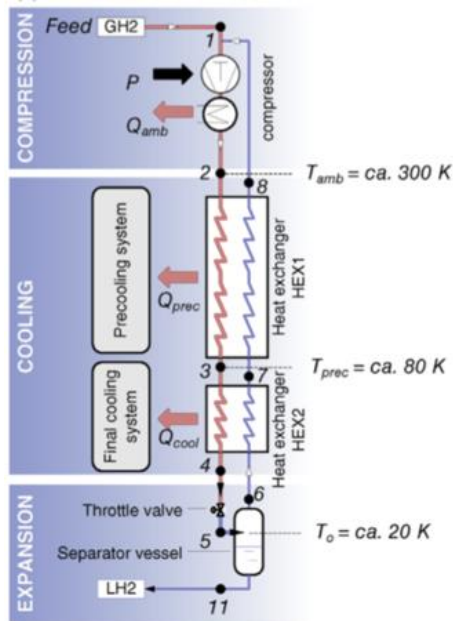
Fig. 15: Conventional hydrogen liquefaction process with flash gas

The first step within the liquefaction is compression of pure and dry hydrogen in order to increase its pressure and temperature (approximately ambient temperature) before entering in a heat exchanger (constant pressure) to cool down the hydrogen by two steps before going to the valve. The first step cools the hydrogen down to 80K and the following, down to 22-45K. After that point, the hydrogen pass through so-called "throttling valve", producing some liquid. The cooled gas (so-called *flash gas*) is separated from the liquid and returned to the compressor to undergo the same process [4, 33].

Sometimes is used a similar process but, instead of cooling the feed hydrogen only with the flash gas, we get some help from nitrogen. Is called the **nitrogen precooling**, and among the nitrogen precooling there are different processes: basic one and other ones which integrate the ortho-to-para conversion. In the following scheme we will see the **basic one** [4]:
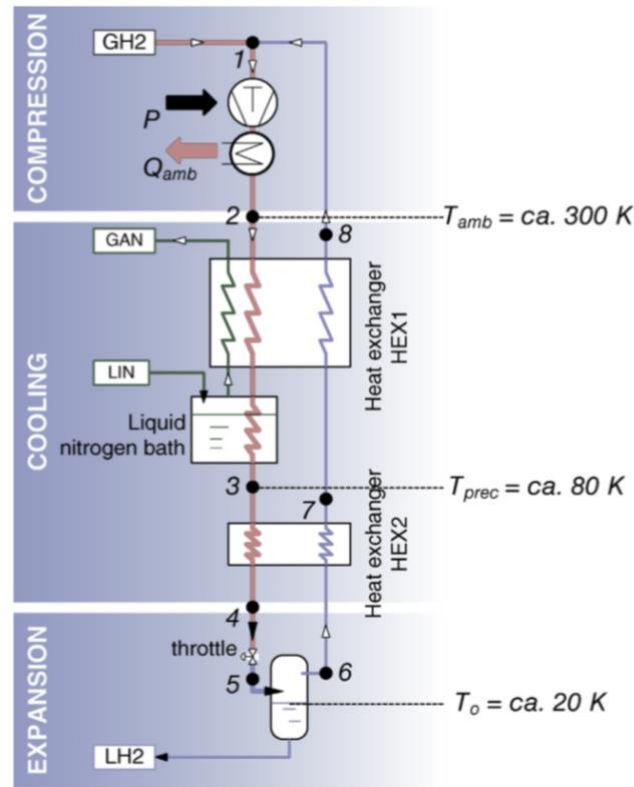
Fig. 16: Basic hydrogen liquefaction process with nitrogen precooling

At the beginning of the cool-down process, the warm compressed hydrogen flows through the liquid nitrogen bath and becomes colder. The liquid nitrogen evaporates and flows through the heat exchanger (HEX1 in the figure) and then to the ambient. Sometimes there's a vacuum pump installed at the warm end of heat exchanger HEX1. In the final cooling, the hydrogen feed is cooled with the second heat exchanger HEX2 by the cold flash to temperatures of 40K approx. and then is expanded in a throttling valve to low pressures of 1.2-1.4bar approx. and cooler temperatures. It partially liquifies and is separated (as before) from the cold vapor in a separator vessel. The cold vapor flows back through the second heat exchanger and cools the inlet feed stream [4].

Focusing in temperatures before the throttle valve, there are three different behaviors: from temperatures above 52K (dark blue line in the following figure [4]) won't occur any liquefaction, so it's not applicable in liquefaction plants. From 22-25K and 1atm (pink line), the liquid fraction at the outlet is more than 85% (having on disadvantage that the 15% of vapor remaining is not enough for cooling of the feed before the valve). And, if temperature is around 40K (red line), the liquid fraction will be around 50% (hence, there's a considerable amount of gas able to cool of the feed before throttling device, hence is auto-refrigerated process but it has higher thermodynamic losses because of the amount of liquid fraction) [4].

There are different forms of the integrated process of **hydrogen**
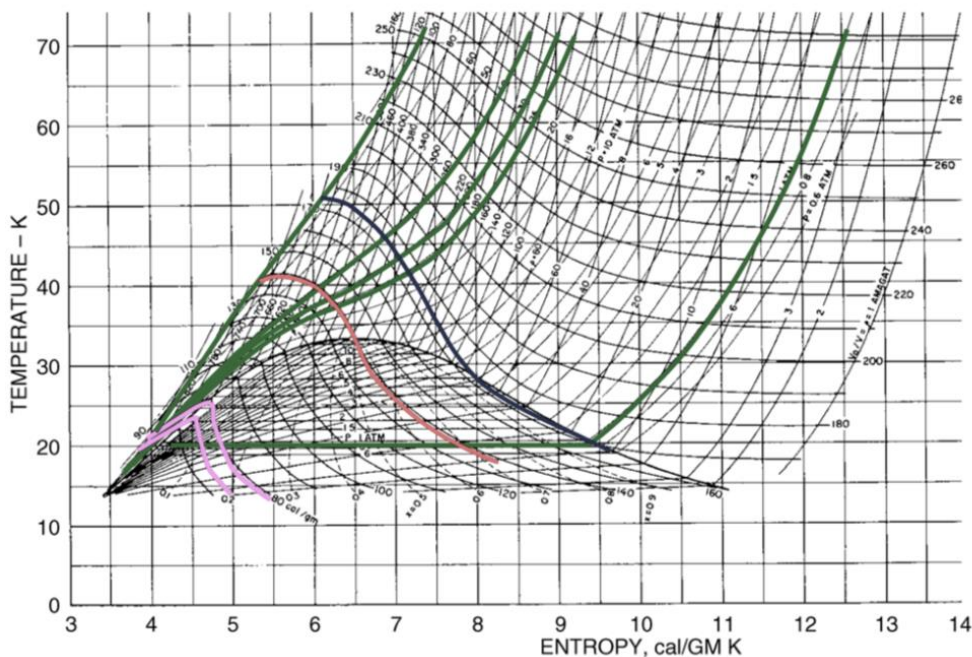
Fig. 17: Relationship between the temperature before the throttle valve and the liquefaction fraction

liquefaction with ortho-to-para conversion. As mentioned before, with the reduction of temperature ortho-hydrogen is transformed into para-hydrogen with a current release of energy, thus increasing the temperature of the liquid hydrogen and resulting iin losses due to evaporation. To overcome this issue, catalysts are used during the liquefaction processes [33]. One of them consists in three separate o-p reactors placed on three temperature levels. The transformation is focused on few positions, so it causes a relatively high local heat generation inside of reactors and therefore additional thermodynamic losses. It is one of the very early designs of hydrogen liquefiers. Another one, more sophisticated and modern, consists in catalyst placed inside of the heat changers, so the o-p conversion is made through the whole temperature range homogenously [4].

The most common option employed to cool the hydrogen feed to liquid nitrogen temperature level is the nitrogen Brayton process (compressor, heat exchanger, turbine). Strictly speaking, when referring to cooling we should call this thermodynamic cycle as "reverse Brayton cycle" as the original Brayton is a process of power generation or propulsion via gas turbine, but these terms are used indifferently. This kind of machines can be built to operate at many cryogenic temperature ranges and can range in size from tens of kilowatts in cooling power to small cryocoolers producing just a few watts of cooling [42]. In the following figure we will see the two-stage version of the Brayton process (two Brayton cycles in parallel driven by the same compressor).

Figure 18 shows the so-called two-stage version of the Brayton process (in simplified form), which consists of two Brayton cycles switched in parallel and driven by
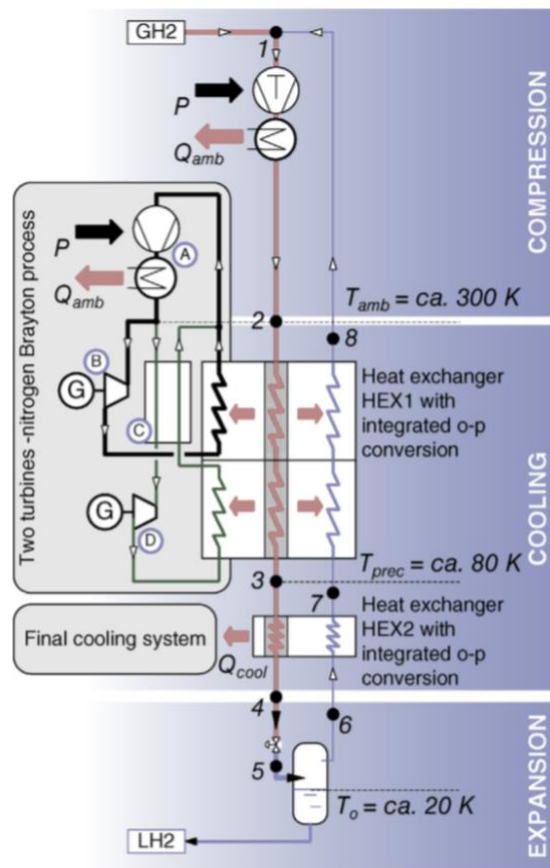
Fig. 18: Two-stage version of the liquefaction Brayton process

the same compressor. The warm cycle is marked by a black line, the cold cycle by a green line. Similar to the gas turbine process, the working fluid (air in the case of gas turbines or nitrogen in low temperature processes) is first compressed in a compressor ("A" in Figure 18) from low pressure (usually 1–6bar) to high pressure (8–80bar). After compression the gas is cooled to ambient temperature by means of cooling water or cooling air and then expanded to low pressure in a gas expander ("B" in Figure 18) producing mechanical power and driving a generator device.

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A considerable amount of mechanical power is produced during the expansion of the high-pressure gas in this expander, which means that the enthalpy of the gas at the expander outlet is lower than at the inlet. This leads to a significant temperature reduction (60–100 K depending on pressure ratio). The temperature of the gas at the expander outlet reaches 40 to 80 °C (≈190–230 K) or even colder. This cold stream flows through the heat exchanger HEX1 back to the compressor inlet and cools the hydrogen feed to the corresponding temperatures.

To produce the cold at temperatures below 80 °C another gas expander ("D" in Figure 18) in combination with heat exchanger ("C" in Figure 18) is used. A fraction of pressurized nitrogen after compression is cooled here in the heat exchanger to temperatures below 80 °C and after that expanded to low pressure in expander D resulting in a remarkable temperature reduction. The targeted temperature range for the gas after expander D is in the range of 150 and 190 °C (80–120 K), depending on the overall process design. The hydrogen feed gas can be cooled to the corresponding temperature by the cold stream from outlet of expander D. It first flows through the lower part of the heat exchanger HEX1 and subsequently through the heat exchanger C and cools the nitrogen before expansion in expander D.

The common fact is that all of the different processes have a requirement of upstream purifications in order to reduce the concentration of impurities up to 1ppm, otherwise these materials would be the reason of an obstruction in the liquefier because they are solid at 20K [4].

Nowadays, only few plants exist worldwide, and their exergy efficiencies are around 20-30%. The proposals to the future are to reach 40-50% and, in the large-scale hydrogen production, is essential to increase liquefaction capacity and decrease the specific power necessities [4].

For more than 40 years, the cryogenic tanks have existed to store medical gases like helium [21]. The storage of liquid hydrogen is similar to the latter and, nowadays, is a state-of-art [43], specially to applications in space flight because we can take advantage of its high energy density, light weight and low environmental impact by using as fuel. The tanks can be built with a spherical (more advantageous on ships) or cylindrical form -both: horizontal and vertical- (transportation via railway or truck). And, like in the case before, these tanks can also be built under/above ground and can be used in modular way. Although the costs for underground liquid hydrogen would probably be higher than for aboveground compressed tanks, this option combine the advantages of under-ground and liquid storage: the first advantage relies in its higher density, which means less space needed, and the other advantage relies in the free space above ground for other purposes.

In order to reduce losses in the system, the spherical shape is better for a long-term storage because guarantee a minor ratio surface/volume and, this is translated into the reduce of evaporation losses, as we can see in the provided graph [44]. Thus, the spherical shape is also more economic because it allows the vessel to have
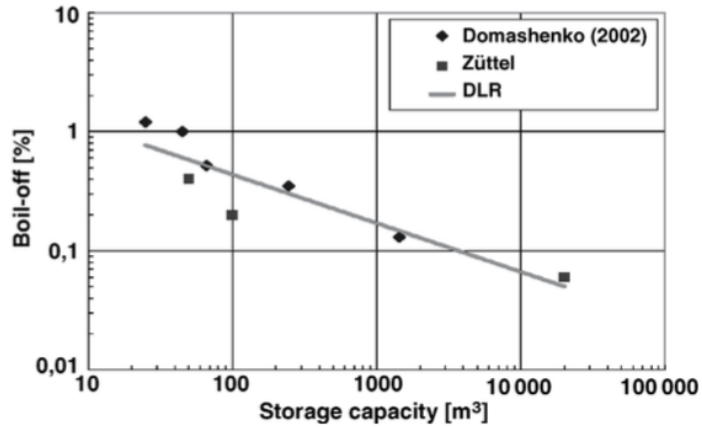

Fig. 19: Relationship between storage capacity and the boil-off

of liquid hydrogen in different tanks

low wall thickness. Additionally, attention should be given with the vessel's constructional materials not just in order to minimize the losses, but also protect them from the hydrogen embrittlement, commented at the beginning, taking into account that this phenomenon can be neglected at the boiling point because the hydrogen solubility is low [18,21].

To minimize the losses, the storage of liquid hydrogen must have great insulation to minimize heat transfer into inner (convection, conduction and radiation) [4,33]. Then, the cryogenic vessels have an external protective container with an isolating vacuum layer. There are diverse types for isolation the inner vessel which contains the cryogenic hydrogen but, the most typical are multilayer of alternating aluminum foil and glass fiber matting or perlite vacuum insulation. To protect from embrittlement (even if this process can be neglected at the boiling point, the brittleness of metals at cryogenic temperatures restricts the choice of material), the nickel ferritic steels or stabilized austenitic stainless steels and aluminum alloys, are frequently used in this form of storage [43, 21, 44, 45].

Notwithstanding an excellent isolation of the tank, evaporation occurs, so the pressure is increased [45]. Due to this extra-pressure, cryogenic vessels have to be designed with a pressure relief system which leads some hydrogen outside the vessel in order to control and return to the regular pressure. These losses are the so-called (and mentioned before): *boil-off* losses and can't be avoided but minimized. Typically, are below 0.03%. per day for large storage spherical tanks with perlite vacuum insulation, 0.4% per day for vacuum-superinsulated tanks and 1-2% per day for large tanks with vacuum powder insulation depending on their geometry [33]. The hydrogen released can be directly stored in an auxiliary system or can be returned to the liquefaction plant [18, 44]. Usually, the installation with following gaseous hydrogen use have a cryogenic storage tank, ambient air vaporizer and controls. The size and liquid storage can be

selected depending on the customer volume, desired pressure, purity level, etc. Normally the range of liquid hydrogen tank's capacity is 1500 l (100kg) to 95 000 l (6650 kg). The maximum pressure in the tank is 20-30bar.

Cryogenic storage, because of the low working pressure compared to high-pressure storage systems, has a great potential to reduce weight by using new composite materials with enhanced performance. With such systems, specific energy storage mass similar to conventional fuel tanks, can be achieved [33].

3.2.3. Cryo-compressed hydrogen storage

In the following figure [44] we can recognize different frames of hydrogen storage. The yellow frame was analyzed at the beginning of the project and is the "compressed hydrogen storage", usually made with ambient temperature and high pressure. The blue/purple zone is for cryogenic hydrogen, in which really low temperatures should be reached. There's another frame in the figure, which is painted with green, which is above 33K up to 233k and also above ambient pressure. Is the "cryo-compressed hydrogen" and is a really interesting technology for hydrogen storage, regarding to its advantageous range and combination of temperature and pressure. This kind of hydrogen storage capture the best advantages of both conventional LH2 and CGH2 vessels.
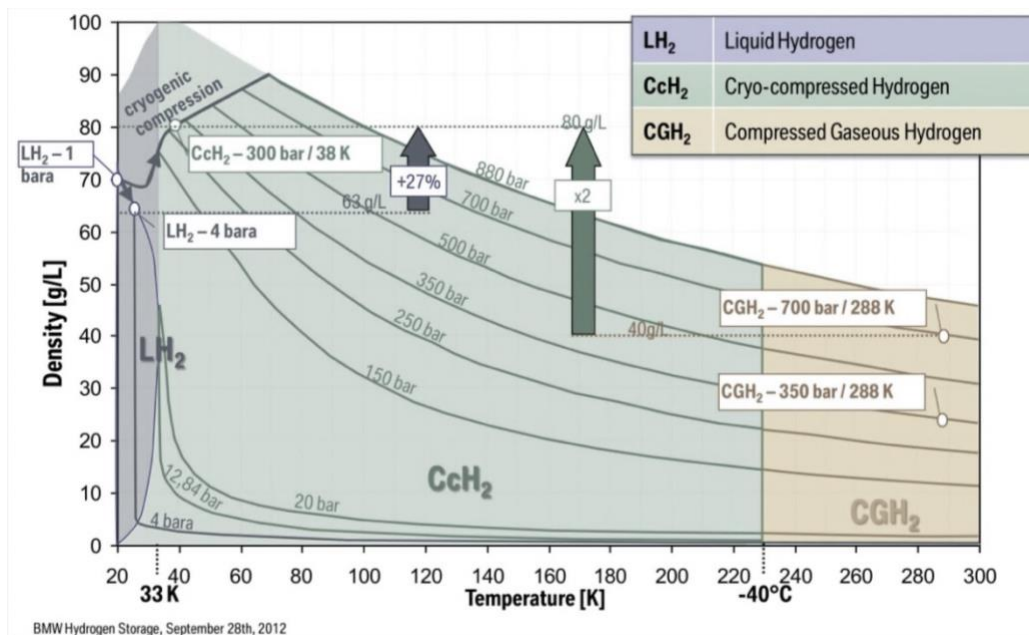

Fig. 20: Relationship pressure, temperature and density with different type of hydrogen storage

The thermodynamic opportunities of the proposed CcH2 storage system seem to be a good compromise among maximizing system energy density, refueling time, efficiency and having a high safety level.

This kind of storage compromises several essential safety opportunities that guarantee a very high level of safety under all operating conditions and failure modes: the vacuum enclosure protects the storage pressure vessel against overheating in case of a fire (even a localized fire), and also protect it against mechanical and chemical intrusion. The vacuum super insulation enables very sensitive leak detection by simple means, for example, measuring the pressure increase rate that significantly changes when the vacuum is broken by external or internal leaks. The impact of a sudden failure of the pressure vessel would be lower for a cryo-compressed storage in cold operation than in a compressed storage system because of the low adiabatic expansion energy of cold hydrogen compared with warm hydrogen gas (this adiabatic expansion energy is the measure for the energy release by sudden mechanical failure of a loaded pressure vessel).

The design of the cryo-compressed storage vessels is really similar to those of the cryogenic storage vessels. It consists of an inner vessel with a metal liner an all-enveloping layer of vacuum super-insulation with multi-layer radiation shields to minimize heat input into the inner vessel and a lightweight outer vessel which acts as a vacuum enclosure. In the following we can observe the concept of the BMW cryo-compressed storage tank:
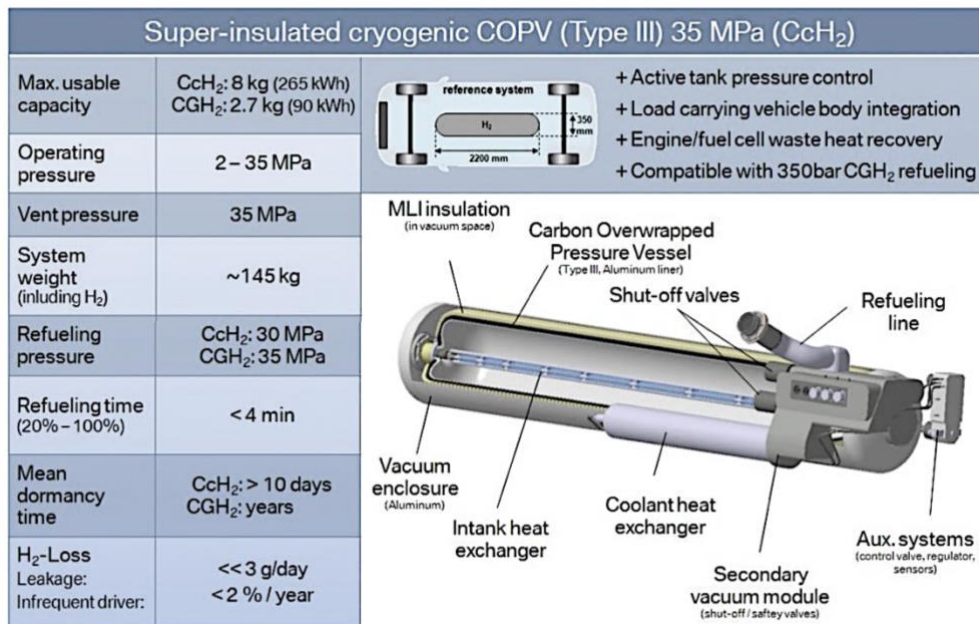

Fig. 21: Concept and performance data of the BMW cryo-compressed storage tank

Also, is important to take into account the adiabatic expansion (a measure for the energy release by sudden mechanical failure of a loaded pressure vessel) for cryo-compressed hydrogen in comparison with the compressed hydrogen. In the following figure [77], this difference is really perceptible:
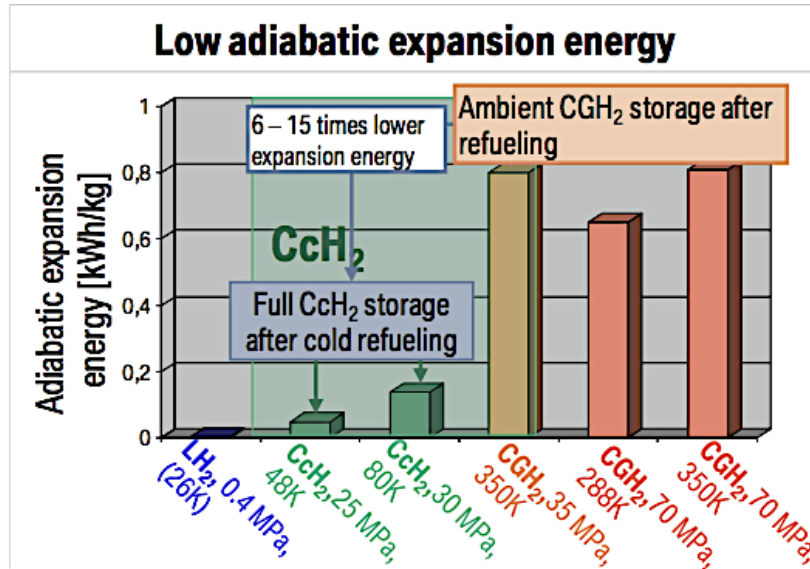
Fig. 22: Adiabatic expansion energy in function of different storage methods

3.3. Chemisorption

3.3.1. *Metal hydrides*

Hydrogen, the simplest element, is so reactive that it can't even exist by its own: when it is alone, the molecules are linked in couples. It reacts with almost ever solid when temperature and pressure are appropriate and with almost every element of the periodic table except noble gases, In y Tl. Actually, all metals (and other inorganic solids) also dissolve at least small quantities not just of hydrogen, but also of oxygen, carbon and nitrogen. The first time that these occlusions were discovered was in 1866 by T. Graham, who see hydrogen inclusions in palladium metal; since then, the research on these topics has increased a lot [4]. The reason why hydrides could be worthwhile is because is safer than compressed storage and the maintenance is cheaper than cryogenic hydrogen. Due to the safety characteristic, is used in small-scale such as rural houses, in addition, the generated heat during the absorption can be used in a heat exchanger [49].

The hydrides can be saline/Ionic, molecular/covalent and metallic, depending on which kind of element does the hydrogen react with. *Saline hydrides* are formed when the hydrogen interacts with the metal elements of the s-block (except Beryllium) and some of the d-f-blocks. All of them are solid, crystalline and electrically isolated. Other type of hydride is the *molecular/covalent*, which is formed -for example- when the hydrogen interacts with non-metallic element. The last type is *the metallic hydride*, which is formed when hydrogen interacts with metals which are from d-f-blocks. In these hydrides, hydrogen acts as a metal and forms a metallic bond [69]. Its properties are depending on the ratio M/H but usually the formed hydride is solid, hard, brilliant,

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maintain the electric conductivity of the metal which precedes, has less density than the original metal and a large diffusion capacity of the hydrogen. Even so, one of the most interesting features of this kind of hydrides is the exceptionally high volumetric density of the hydrogen atoms present in the host lattice [47].

Among these, metal hydrides are the most useful and interesting for us because they can absorb a large amount of hydrogen at constant pressure -due to the phase transition while the absorption-. Many intermetallic compounds with transition metal react with hydrogen and form reversibly metal hydrides at pressures in the range 1-10bar and 300-400K. Typically, H/M ratios are between 0,8 and 1,3; volumetric densities are at least that of 20K liquid hydrogen (usually more than that, up to 3-4 times more) and gravimetric densities range between 1,5 and 3 mass% (considered too low for automotive applications of fuel hydrogen) [4]. For stating an example, the Palladium (Pd) can absorb a volume of hydrogen up to 380 times its own volume, then, when we need the hydrogen we can heat the hydride to certain temperature to release it. Due to the small size of the hydrogen molecule, during its absorption in the metal, the molecules can occupy diverse positions in the lattice (not just within the tetrahedral and octahedral holes) producing an alteration in it. That's why the compounds are not always stochiometric.
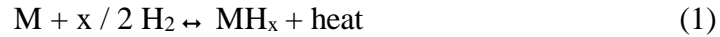
The metal hydrides can be:

-Interstitial metal hydrides: offering a storage capacity of 1.8wt.% (percentage of hydrogen by weight) at 60-70oC, or as high as 3wt.% for quasi-crystalline Zr-Ti-Ni alloys, [54,55] but with a rather poor reversible hydrogen uptake [51]

-Activated magnesium rich powders: reaching in the laboratory up to 5-6wt.% at 260- 280oC (at 1 bar) but their kinetics need to be improved using cost effective procedures [51].

-Complex light-metal hydrides (alanates and their isostructure counterparts): they absorb 5 to 8wt.% but they release hydrogen at a slow rate. Catalysed hydride complexes (with Ti or Zr catalyst) are considered to be the most promising from this category [57,58]. Lab-scale alanates are good candidates for designing hydrogen storage tanks since they can reach 5wt.%, at 180oC, 1 bar, but there is still room for improvement in their hydrogen absorption/release kinetics, via lattice distortion [51,56].

The basis of these methods consists in the possibility of some metals and metal alloys to create reversible covalent links when they react with hydrogen, establishing what is known as metal hydrides, that can be decomposed when heated or de-pressured. The hydride is formed when the metal has a "sponge behavior" and can absorb the hydrogen within its lattice. That happens when it's under pressure and it's an exothermic reaction, while desorption is an endothermic process. Initially, hydrogen dissolves into the host lattice, increasing really sharply the pressure and forming a solid solution (alpha-phase) which has the same crystal structure as the bare metal [59]. When the physical

sites are saturated, a second phase, the formation of metal hydride starts (betha-phase). The reaction (hydrating and dehydriding) of metals can be written as [60]:

$$M + x/2 \, H_2 \leftrightarrow MH_x + heat \tag{1}$$

$$M + x/2 \, H_2O + x/2 \, e^- \leftrightarrow MH_x + x/2 \, OH^- \tag{2}$$

The first one (1) is when there's a direct dissociation chemisorption of H_2 and the second one (2) is when there's an electrochemical splitting of H_2O. In the reactions written above, M refers to a metal, a solid solution or an intermetallic compound and "heat" is the heat released during the reaction. In the next figure is noticeable the relation between pressure and H/M ratio and the reversible process.
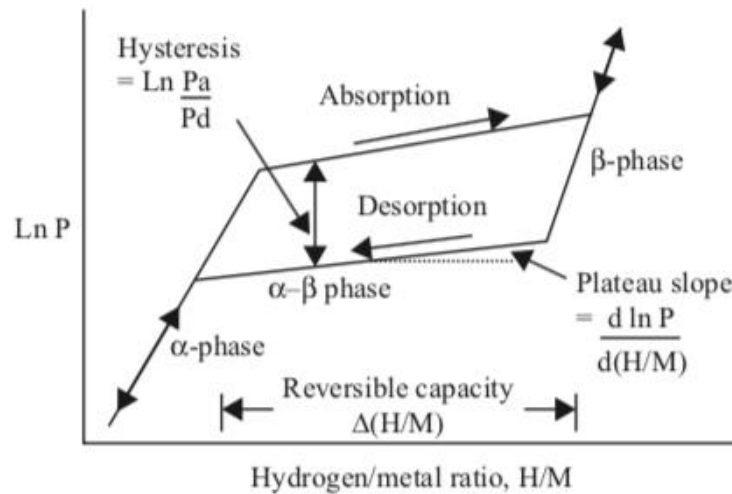
Fig. 23: Pressure and H/M ratio

The hydrides have the important characteristic of being able to store hydrogen during several cycles of absorption – desorption, without decreasing its storage capacity [49,50].

In view of energy storage, looking to these metals as sponges which are able to absorb and release the hydrogen when is needed is an interesting starting point to analyze. We have to analyze not only the capacity of hydrogen that can be dissolved, but also the properties of the "sponge". The physicochemical properties in which we have to focus are: storage density (volumetric and gravimetric) and reversibility at nearby ambient conditions [4]. For economic and sustainability reasons, abundant materials and low-cost processing are needed. The challenge is to find a way to store hydrogen in solid form with a reasonable temperature and pressure, which permits high density, security facts, economic feasibility and sustainability.

The metal hydrides are worthy to large stationary and small portable use applications. They are formed when the metals dissolve non-molecular hydrogen and create concentrated metal-hydrogen phases.

The hydrogen can be provided by molecular H_2 gas, proton providing electrolyte or acid or just H_2O (as shown below) and the maximum amount of H_2 is given by the number and size of interstitial places and the amount of energy involved for adaptation of bonding and structure.
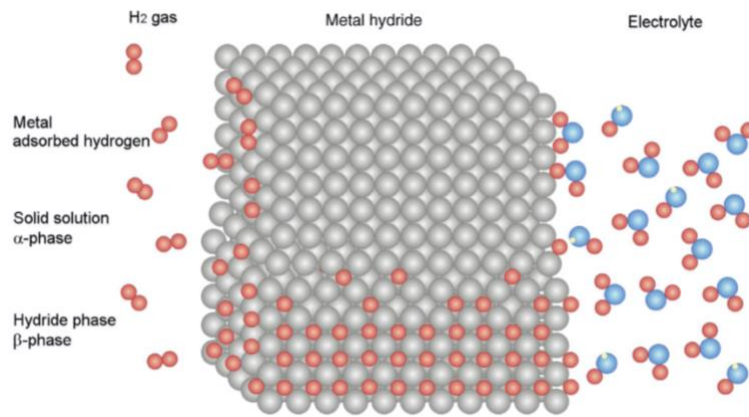
Fig. 24: Schematic hydride formation from the gas phase (left) and from the electrolyte (right)

The host metal dissolves a few % hydrogen as a solid solution. Due to the increased of the gas pressure because of the equivalent potential together, interactions become important and lead to nucleation and growth of hydride phase. While both phases coexist, the isotherms show a flat plateau, the length of which determines how much hydrogen can be stored reversibly with small pressure variations. The two phases coexist until they reach the critical temperature. At higher pressure of hydrogen, further plateaus and further hydride phases may be formed. The plateau (equilibrium pressure) depends strongly on temperature and is related to enthalpy and entropy. The entropy stays almost constant for all the studied metal-hydrogen systems, and it's 130 kJ/mol. The enthalpy characterizes the stability of the metal-hydrogen bond. To reach an equilibrium of 1bar at 300K, enthalpy should amount to 19,6 kJ/mol [4].

At the image below, we can see the pressure-composition isotherms for the hydrogen absorption in a typical metal.

Alpha-phase (solid solution)

Betha-phase (hydride phase)

Fig. 25: pressure-composition isotherms for the hydrogen absorption in a typical metal

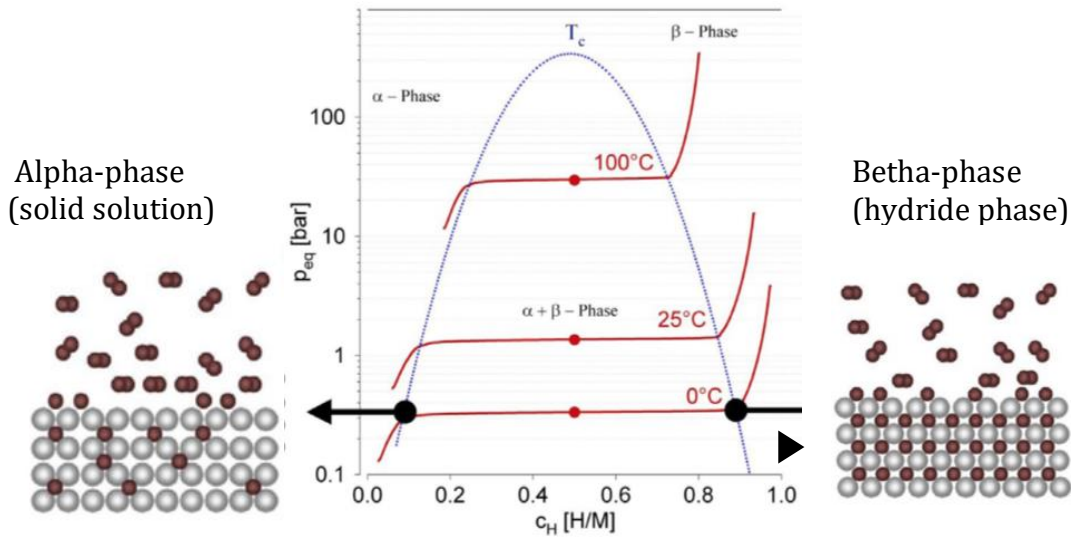Hydrogen absorption is electronically an integration of electrons and protons into the electronic structure of the host lattice. The electrons have to fill the empty states at the Fermi energy while the protons lead to the hydrogen induced s-band approximately 4 eV below the E_f[3].

The stability and concentration of hydrogen in an intermetallic hydride is explained differently depending on the empirical model. There's the Westlake criterion which exposes that the theoretical maximum volumetric density of hydrogen in a metal hydride is around 254 kg/m3 (assuming that the hydrogen is closed packing), which is almost 4 times the density of liquid hydrogen. There's also other sophisticated model called "Miedema's rule" that is based on the fact that hydrogen can only link with a neighbor metal atom if the bonds among the metal atoms are at least partly destroyed. That is to say, correctly, that: the more stable an intermetallic compound the less stable the consequent hydride, and the other way around [4].

The reaction with hydrogen is able to stabilize or destabilize a compound. In addition, crystalline lattice and the behavior of electrons and phonons is changed due to the solution of it and the formation of hydride phases. The anisotropic net expansion and the loss of symmetry are usually observed phenomena. With that variations, also the cohesion is changed. In view of energy storage, also the dynamic and kinetics of hydride formation and decomposition and the lightweight are as important as storage capacity.

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[3] The Fermi energy (Ef) is a concept in quantum mechanics that is referred to the energy difference between the highest and lowest occupied single-particle sates.

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Some researches lead us to know that the best metals to form metal-hydrides as hydrogen storage are Pd, Ti, Ni and Mg [4].

In the following figure [48] we can compare de gravimetric and volumetric hydrogen densities for various hydrogen storage methods.
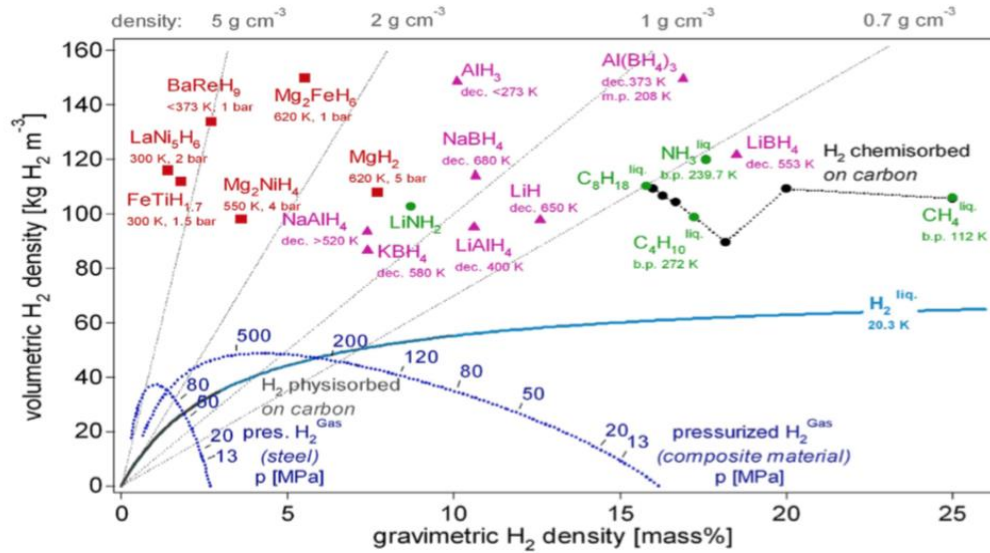
Fig. 26: Comparison of volumetric and gravimetric hydrogen density for different storage methods

3.3.2. *Liquid Organic Hydrogen Carrier (LOHC) Systems*
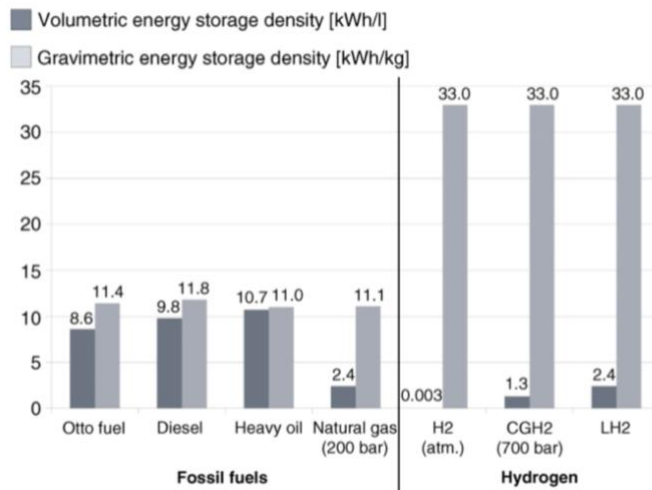
Fig. 27: Comparison between gravimetric and volumetric density of different fuels

Is already known that, despite the high gravimetric energy density, the low physical energy density of the gaseous and liquid hydrogen lowers the volumetric density of the hydrogen.   Even in the form of compressed hydrogen (typically at 700bar) or in cryogenic hydrogen (typically at 20K), the volumetric storage density is still quite low, as shown the previous figure. In addition, the processes to maintain those characteristics requires energy consumption and special/complex infrastructures as compressor stations,

pipelines and tanks of storage [4]. Also, other handicap of the conventional hydrogen storage methods is in regard to safety issues. Hydrogen has been used in its compressed and liquified forms in the chemical industry, where the people is qualified, and the environment is protected. For the broad and untrained public, the handling of a gas at very high pressures or very low temperatures requires safety mechanisms, training and some public understanding [4].

As a consequence of the challenges mentioned before of storing and handling molecular hydrogen, researches around the world are working on alternative hydrogen storage technologies as the reversible chemical conversion of hydrogen into hydrogen-rich chemicals, which also have the advantage of non-needed to construct new infrastructures. Among these researches, the MH (solid storage, explained before) and LOHC have been developed [4].

The material consists in store hydrogen in reversible hydrogenation /dehydrogenation cycles of a saturated compound, usually aromatic. The hydrogenation is a chemical bonding of hydrogen molecules to the liquid carrier via a catalytic reaction (exothermic process) and the dehydrogenation is the release of this hydrogen molecules from liquid carrier also medium via catalytic reaction (endothermic process). The energy is stored during the energy-rich times and is later released at energy-lean time. When the hydrogen is released, the compound can be reused.

LOHC enables safe and efficient storage of hydrogen through molecular binding. Density can be increased up to 57 kg/m3 [72]. They have a high efficiency due to the cycle stability of LOHC and are easy to handle. Furthermore, is a non-toxic carrier liquid and no flammable. LOHC can be stored and transported under ambient conditions in the existing fuel infrastructure without the need for high pressures or low temperatures. One cubic meter of LOHC can store more than 600 cubic meters of hydrogen gas and therefore about 2 MWh of energy [71].

Due to their high storage density, good manageability and reversible binding, LOHC substances are highly applicable for the local storage of excess energy in buildings, also for mid- to large-scale hydrogen storage and transport [72]. The long-term perspective to use LOHC systems is as over-production of energy from renewable sources available for mobile applications.

The basic storage system for buildings consists in five main elements: electrolysis, LOHC hydrogenation, storage tank, LOHC dehydrogenation and fuel cell, as shown in the following figure (adapted from [70], [4]). Thermal losses from the storage processes can be used for heating or cooling to increase the general efficiency of the system.
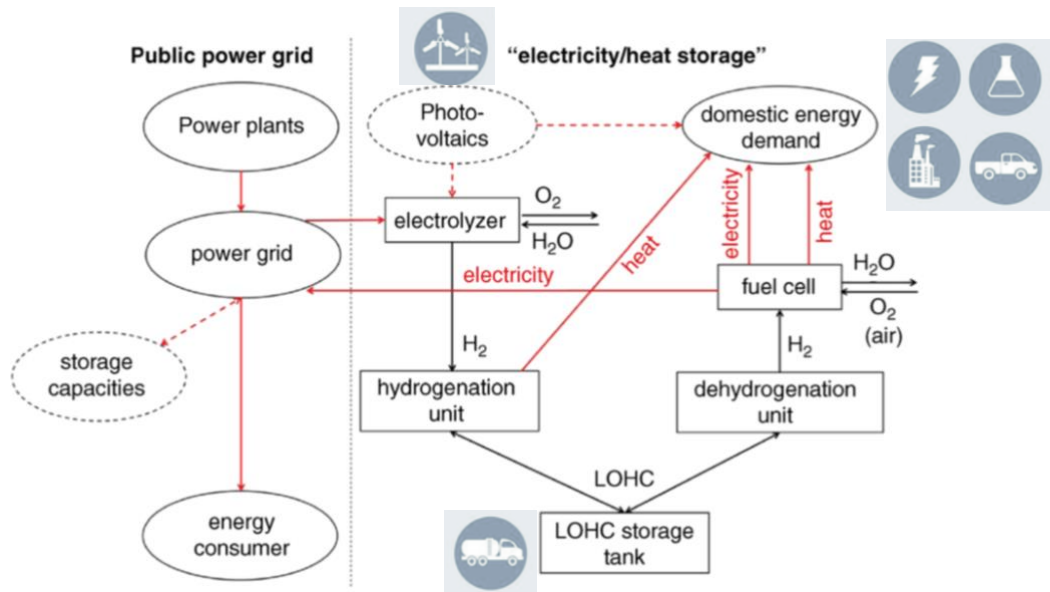
Fig. 28: Illustration of an electricity/heat storage unit used for energy supply of domestically, commercially or industrially used buildings.

The electrical efficiency of any storage system based on hydrogen is usually limited around 33-38% [4]. From power-to-hydrogen-conversion (electrolysis around 70%) and hydrogen-to-power-conversion (fuel cell, 50-55%) [4]. If the wasted heat is used, the overall efficiency can be increased (fact that is easier with LOHC systems). In addition, as we will see in the next graphic, the achievable income saving heating can exceed the costs.
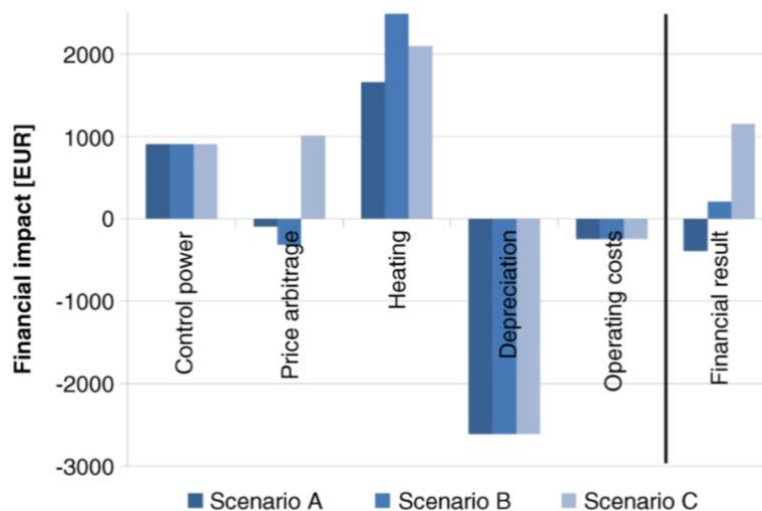
Fig. 29: Income and costs for operation of a LOHC electricity/heat storage

The three different scenarios analyzed above regarding price are: case A – 4 Ct./kWh/22%. Case B – 3 Ct./kWh/34%. Case C – 12 Ct./kWh/29%.

LOHC systems as liquid, diesel-like substances can be transported and stored in the same infrastructure as today's mineral oil-based fossil fuels. Due to the usage of an existing infrastructure (e.g., oil tankers, tank trucks, pipelines, etc.), the costs of building up this sort of "new" energy distribution system are comparably low.

There are a lot of analyzed Liquid Organic Carriers but in order to take some data from www.hydrogenious.net, we are going to focalize in the dibenzyltoluene—a liquid organic hydrocarbon that maintains a liquid state in a broad temperature range between -39°C to 390°C and ambient pressure. It is low flammability and non-toxic either explosive, even when loaded with hydrogen. There is no evaporation of stored hydrogen—multi-month storage is possible without any losses. The release of hydrogen molecules from the liquid carrier medium also occurs via catalytic reaction. This is an endothermic process with 10kWhth/kg H2 @ ~300°C [3,75].

Although energy production from solar and wind is increasing, the overall efficiency of the system is still low. There's no doubt that in the future are going to exist electric energy storage safely, cheaply and without loss over longer periods of time. Chemical energy storage is very interesting option as fuels are characterized by high storage densities.

The LOHC systems have a very high potential to become a leading concept within the different options for chemical energy storage. Hydrogen loaded on liquid organic molecules avoids the provision of a second gaseous reaction partner, prevents the formation of by-products and allows very safe handling of large amounts of hydrogen in a future hydrogen-based energy system.

4. COMPARISON

Likewise, depending on the application area, different solutions can be beneficial since each storage method has its own advantages and disadvantages. Nowadays, exist few near-surface bulk hydrogen storage facilities. They store hydrogen either in gaseous or liquid state and the applications are mainly for chemical industry or space purposes [4].

System hydrogen storage density is the most important parameter in H_2 vessels. High storage density allows long-range vehicles necessary for practical carbonless transportation. Indeed, increasing the storage density: increase the hydrogen weight fraction (Kg H2 / Kg Storage) and decreases the cost because
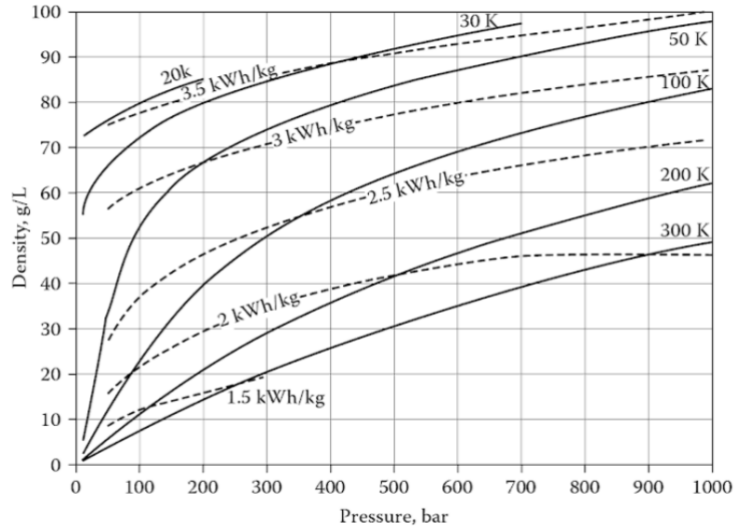

Fig. 30: Volumetric density in function of temperature, energy and pressure

demands less material (\$ / KgH2). The gravimetric density of hydrogen is function of its temperature and pressure, as shows the following figure [43]:

Increasing its density is typically a productive endeavor but, the system storage density is which really matters since thick vessel walls and thermal insulation occupy volume otherwise available for H_2 storage. The strength of practical materials and the performance of thermal insulation limit ultimate vessel storage system density [43].

To make this importance more visible, we can compare the amount of H2 that can be stored in a fixed volume of 170L (2m long, 35cm outer diameter, ellipsoidal heads). Internal vessel volume is a function of pressure since wall thicknesses increase when increases the pressure (without changing the material), to maintain stresses below the maximum (ultimate stress / safety factor of 2.25) [43].

In the next graphic, we will study the behavior of stored hydrogen in the fixed volume mentioned before but in three different situations (two different wall strengths and a vessel neglecting wall thickness): 1.5GPa (similar to composite materials) and 3GPa. Higher the wall strength, lower its thickness, higher the inner volume for store hydrogen, leading to increase the geometric volume efficiency. Compressed vessels up to 350bar made of materials with high strength (in the graphic represented as 3GPa) can

achieve 90-95% geometric volumetric efficiency. As higher pressures, since thickness wall becomes necessary, the inner volume decreases and also the mentioned efficiency [43]. If we focus our attention in the graphic at 700bar and 300K, we will see that considering a thickness wall zero, the amount of H2 stored is around 6,6 kgH2, higher than if we consider a material with a wall strength of 3GPa (6 kgH2) and the latter is higher than the one with half wall strength (5,3 kg H2). If we want to have more kgH2 with the material of 3GPa, we can increase the pressure and we will have it. With the material of 1.5GPa, even if we increase the pressure, there is going to be a moment (1000bar) in which the amount of kgH2 is not going to increase because the density is not going to change much more (we will be at the ultimate H_2 storage density as the H_2 becomes more incompressible) and the walls are necessary going to be thicker [43].
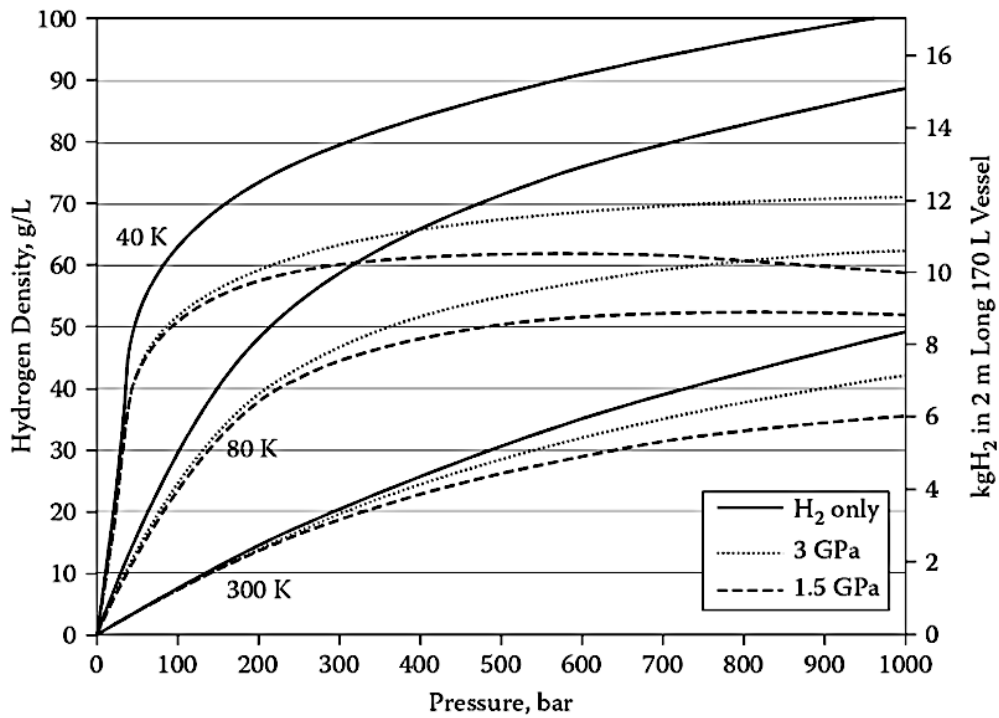
Fig. 31: KgH2 in 2m Long 170L Vessel and density, depending of the pressure, temperature and wall strength

The disadvantage of low-strength materials is made worse by the commented real-gas nonlinear relationship between pressure and density (which was also commented on the firsts chapters). These factors ultimately limit maximum H2 storage density to pressures of approximately 10% of vessel wall material strength and 60% geometric volumetric efficiency, whereas maximum economic compressed H2 pressures are likely to occur at approximately 5% of vessel wall material strength [43].

In summary, system storage density of compressed gas vessels is limited by the non-linear properties of H2 and the strength of available vessel materials. Although a maximum system density can be reached at a pressure about 10% of the wall strength, it

is unlikely that pressure vessels will operate beyond about 5% of ultimate strength because only marginal density gains are obtained at considerable increase in material cost [43].

Capital cost

In comparison with the conventional fuels, which are not at all expensive, we have a really big disadvantage with the cost of hydrogen. Its low density demands really huge vessels with expensive materials and expensive cost of maintenance.

The compression of the gas is an 80% of the total cost and the balance of the plant and processing represent the remaining 20%. Since hydrogen compressibility decreases with the pressure, is more expensive storing hydrogen at higher pressures than at lower,
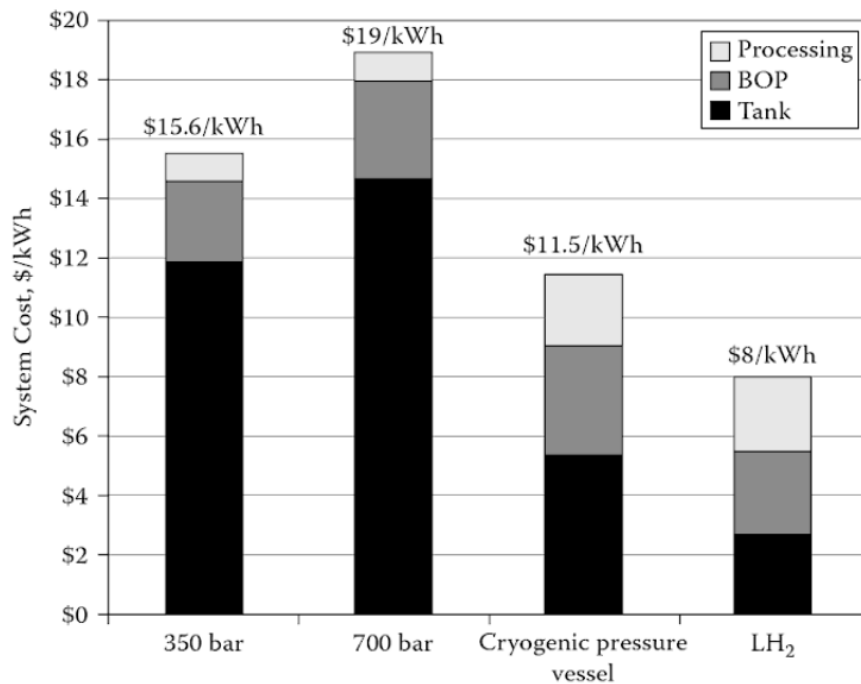
Fig. 32: Comparison of system costs

as shown in the following graphic [45,44]. Compressing hydrogen up to 350bar costs 15.3$/kWh, while compressing it up to 700bar costs 18,6$/kWh [43].

The higher density of cryogenic H2 reduces vessel size and cost (due to the low-pressure operations). In cryogenic storage systems, vacuum insulation, cryogenic valves, cryogenic regulators and pressure and temperature sensors are needed. Therefore, balance of plant and processing are larger fractions of the total cost and vessel cost are only 30% of the total [43].

 If we analyze the solution between the compressed hydrogen and the liquid one: cryo-compressed vessels, we can suppose that are more expensive than the liquid hydrogen vessels but considerably less than compressed ones. Also, the fraction of the vessels cost for total cost is 50% [43].

A really huge difference between the main storage methods that we are analyzing is: while in the compressed hydrogen the cost is almost linear with the kilograms of H2

(following graph of data taken from reference [4]) but, in cryogenic pressure vessels capacity can be almost doubled while increasing a little bit the cost.

Fig. 33: Linearity among cost and pressure in compressed hydrogen storage

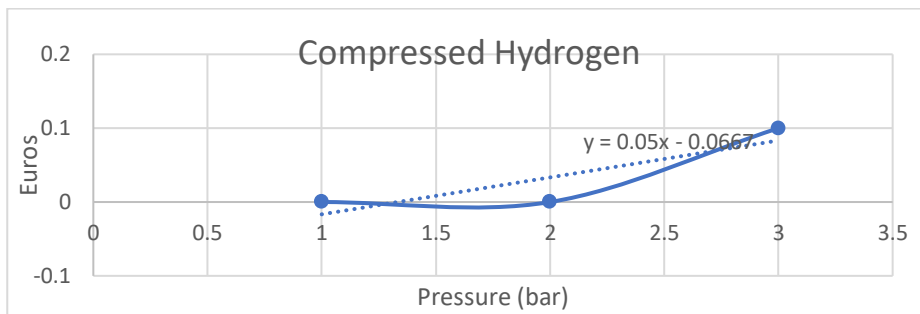In the following figure we will find a comparison between GD and VD for different storage technologies [76] and cryogenic pressure vessel prototypes (generations 1, 2, 3) vs. Department of Energy /DOE) 2010, 2017 and ultimate weigh and volume
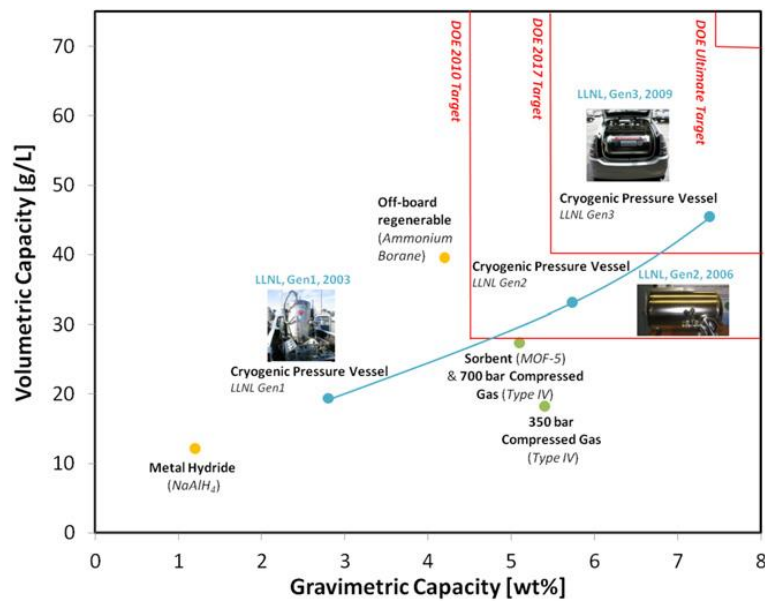

Fig. 34: GD and VD comparison taking into account vessel generation and the DOE targets for 2010 and 2017

targets. Being so visible that the 3Generations vessels for cryo-compressed hydrogen has the highest demonstrated gravimetric and volumetric capacities.

In order to compare most of the developed storage methods costs, we can analyze the following figure [4]. We can see the investment costs of different hydrogen storage options depending on the gross storage volume capacity. The economic data in the figure is an estimate on the basis of data requested from the industry (M. Altmann, Ludwig-Bölkow-Systemtechnik GmbH, personal communications 17 December 2012) and an ensemble of data from other tables given in the book [4].
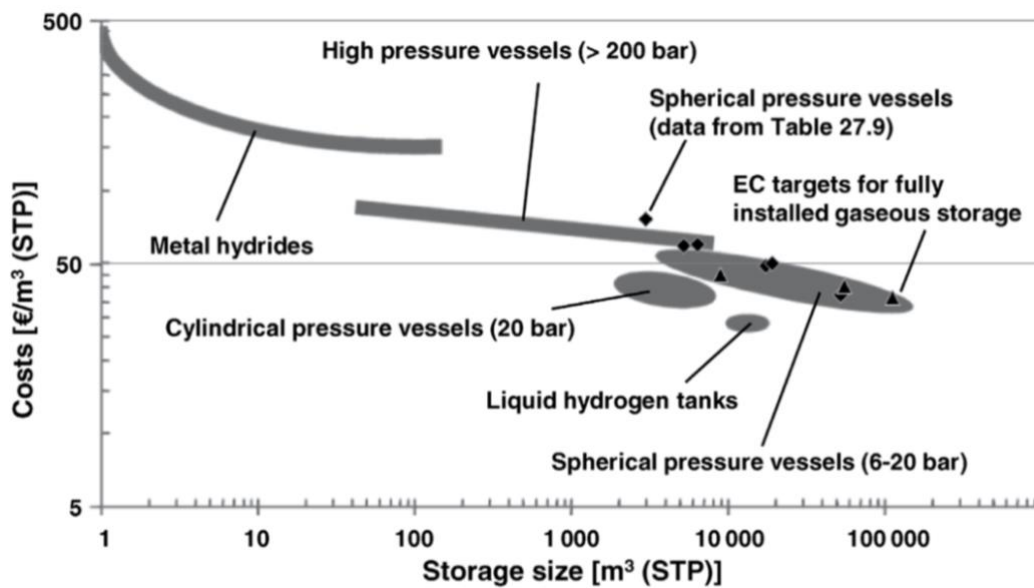
Fig. 35: Investment cost estimates of different hydrogen storage options depending on the storage size.

The high cost level of solid state storage is clearly visible. It also becomes clear that gaseous storage costs are influenced by the size, pressure range and shape of the vessel, and shows that the liquid storage tanks are cheaper than gaseous storage vessels. Though, in a complete analysis the costly and energy-intensive liquefaction process also has influence. Therefore, an economic calculation of the different storage alternatives is only realistic on the basis of a detailed application scenario taking into account all relevant parts such as the charging-discharging schedule [4].

5. EXCEL ANALYSIS

In order to draw practical conclusions from all the research done, an excel comparison tool is done with the aim of searching which is the best method of storage according to the amount of hydrogen that is needed to store.

To achieve this objective, we have make some assumptions that are going to be commented meanwhile the explanation of each storage method. Also, in order to be

accurate as much as possible, some data are taken from NIST (National Institute of Standards and Technology) and imported to excel.

For the conventional methods (compressed, cryogenic and cryo-compressed hydrogen), there's either the pressure constant and the temperature changing or vice versa. The parameters that are colored with grey-blue are which can be changed (selecting from some given options) and the parameters that are constant are colored with light green. The rest of parameters are going to change automatically. Depending on the pressure or temperature selected, the density, specific volume, internal energy and phase are read from the NIST databases exported in the rest of Excel sheets called "CH2 25C, CcH2 10bar, CcH2 250bar, LH2 1bar", which have logical names: type of storage method and constant parameter. The volume occupied for hydrogen is calculated multiplying the specific volume per the input of amount (kg) of hydrogen. The storage vessel volume is calculated in basis of the volumetric density last target of the D.O.E (Department of Energy) as well as the storage vessel weight (in basis of the gravimetric density last targets). Therefore, the vessel weight with the weight hydrogen is easily calculated. The costs are taken from different sources, trying to select the data that mostly fit with all of our references, written in the excel sheet.

Starting with the analysis of compressed hydrogen, we have assumed a constant temperature of 25C and pressures from 1 up to 1000 bar. Depending on the amount of hydrogen given, excel gives us if the scale is small, medium or large, and together with the pressure, is given the type of vessel (I, II, III or IV for small scales) or if we should store it in gas holder, spherical vessel or pipe storage in case of medium scale. Also, the GD is different depending on the pressure of the vessel, we took into account GD=3 if the pressure is less than 500bar, otherwise, GD=5. Is also considered that if the type of vessel used is Type II, the weigh is reduced in a 30-40% and the costs are different depending on the type of vessel. We found following data: Type III-IV and 350bar: 15$/kWh, which is 13,32euro/kWh, taking into account the LHV of the hydrogen, it results 439,52euro/kgH2. For type II vessels is known that the price is about the half of Type III/IV, so we assumed 6,66euro/kWh which means 219,78euro/kgH2. And, for type I vessels, we know that the price is half the price of Type II, so with the same logic we assume that it costs 109,89euro/kgH2. Also, a different calculation is done when the scale is "medium scale" instead of "small scale". For these cases, in which the pressure is low, we are following the linear relationship between pressure-cost that we took from our reference [4] and which is written in the Excel sheet called "Price CH2 Medium scale". The explanation is that, from three given points of pressure-euros, we made a graphic and a linear trend with its equation. This equation is which we apply when Excel gives us that our characteristics are for a "Medium scale" hydrogen storage.

It is important to point out that the firsts two columns are with the same programming but are split in two in order to have the graphics and data for both typical pressures of 350bar and 700bar. (If you are wondering why is written 340bar instead of 350bar, the reason is because the "increment" was each 20bar of pressure starting in 0bar, in order not to have 1000 different pressure options).

For the cryo-compressed hydrogen, two different pressures are assumed. The first one is 10bar, in order to have the advantage of storing hydrogen at low pressure. The other one is 250bar, because through the research, we have realized that the most common pressures for cryo-compressed tanks which are used in mobility applications, for example a car, are from 250bar to 350bar. With these pressures, different temperatures can be selected (from -243C till -43C, that is the range of cryo-compressed hydrogen) and depending of the temperature, the NIST database is read and required data are given. The cost per kilogram is also read from the reference that is written in the excel sheet.

With cryogenic hydrogen storage, the methodology used is the same than explained with the mentioned conventional methods. Also, is necessary to take into account if the hydrogen storage is going to be needed for long or short periods because, depending on this, the geometry of the vessel is different. For long periods, spherical vessels are used in order to reduce (minimize) the ratio surface/volume, otherwise, cylindrical are used because are cheaper to manufacture. As we know that the "typical" liquid hydrogen storage cost 8$/kWh (which is 6,83 euro/kWh = 225,03euro/kg) and we also know that the spherical vessels are about 2.3 times more expensive than the cylindrical (from reference 4), we assume that the cylindrical vessels cost 15,91euro/kWh = 525,03euro/kg.

For chemisorption methods, more assumptions had to be taken. The first of them was which metal hydride and liquid organic carrier would we analyze. In this sense, and based on the Fig.26, we first selected the LiBH4 because has a really high volumetric and gravimetric density but, supposing its high cost, we decided to opt for the NaAlH4 (that was also analyzed by the DOE in the graphic of GD-VD attached before (Fig.34) and also because is a medium-temperature complex hydride with high reversible hydrogen content at moderate conditions [82]) with a high volumetric density and a normal gravimetric density. Hence, taking the most of them with a really reasonable price. As a liquid organic carrier, we decided to analyze the dibenzyltoluene, one of the LOHC the company *Hydrogenious* is working with and which we know that has really advantageous characteristics.

Keeping in mind the constraints of finding accurate data of the specific conditions considered in our excel tool, we decided to focus in the D.O.E last data that better match with our dates. Sometimes, an approximation had to be made. Maybe this is one of the causes whereby our results are not really accurate with some of the results found during these months of research. Even so, from our point of view, it's useful to consider this

excel tool as a base tool which should be improved in order to take the most advantage of it.

In the following figures taken from the webpage of D.O.E, we can see the system cost and weight from their calculations. The acronyms 350b, 700b, LH2, CcH2, SA, LCH2 are which interest us, and their meanings are: compressed hydrogen at 350 bar, 700 bar, liquid hydrogen, cryo-compressed hydrogen, catalyzed NaAlH4 and liquid organic carrier, respectively. Also, is interesting to point out that the following graphics depict the distributions of the measures depending on processing, balance-of-plant, charge-discharge system, and tank.
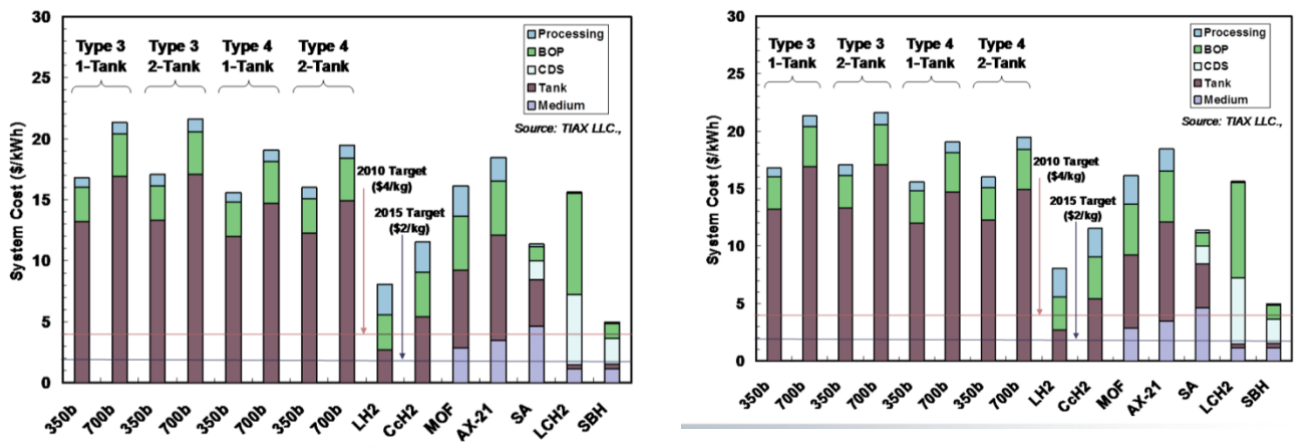

Fig. 36: D.O.E System cost and weight comparison

We think that the excel tool can be useful for giving us an idea of the path that we should take, and forward investigations and more efficient tools (maybe based in this one) are going to be necessary.

From now on, the analysis that is going to be made with the inlet of: 500 kg H2 for all of the analyzed storage methods. Also, each of them has the following characteristics: CH2 25C 340b (as is written, ambient temperature and 340bar), CH2 25C 700b (ambient temperature and 700bar), CcH2 10bar (cryo-compressed hydrogen at 10bar and -243C), CcH2 250bar (cryo-compressed hydrogen at 25bar and -233C), LH2 1bar (liquid hydrogen at -253C and ambient pressure), MH – NaAlH4 and LOHC -Dibenzyltoluene.

A locked and exclusive conclusion in this topic is impossible to make because, according to the knowledge acquired during the investigation, the best method of storage is directly linked with the final application in which it will take place and, it will have particular advantages and disadvantages comparing with the rest of the storage methods. Even so, of all the systems built and proved, the cryo-compressed hydrogen in vessels of the 3rd generation, are the ones which until the moment has demonstrated the highest gravimetric and volumetric capacities, fact that can be visible in the following figure,

taken from our developed Excel tool: the volumetric density is 35 kg/m3 and the gravimetric is 4,5% and 7%, for low and high pressure, respectively. In addition, the cryo-compressed storage method should be cheaper than the compressed and the cryogenic storages. Fact that is not really visible in our graphics. In the figure 39 we can see that for both pressures taken in the cryo-compressed vessels study, the cost is higher than for the liquified.
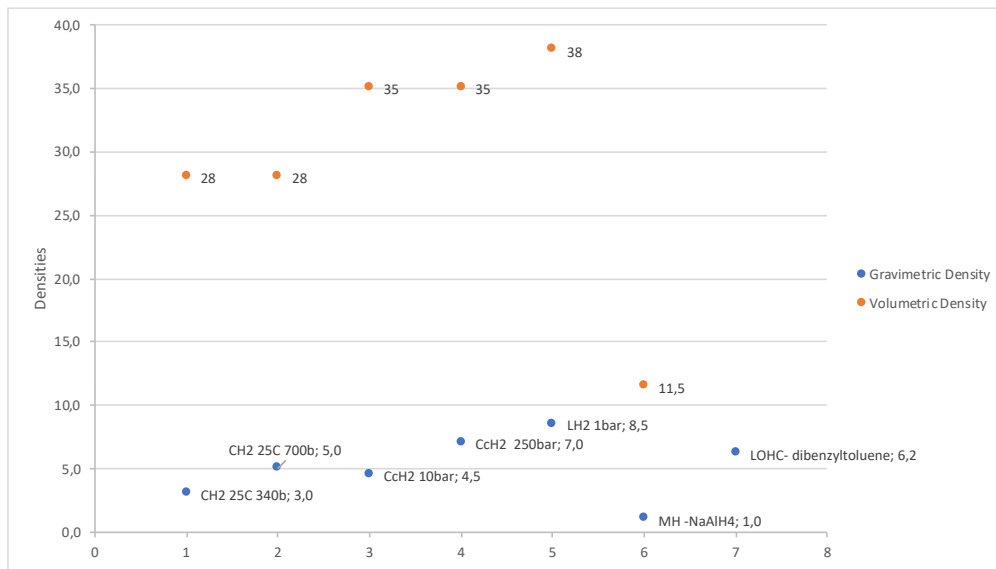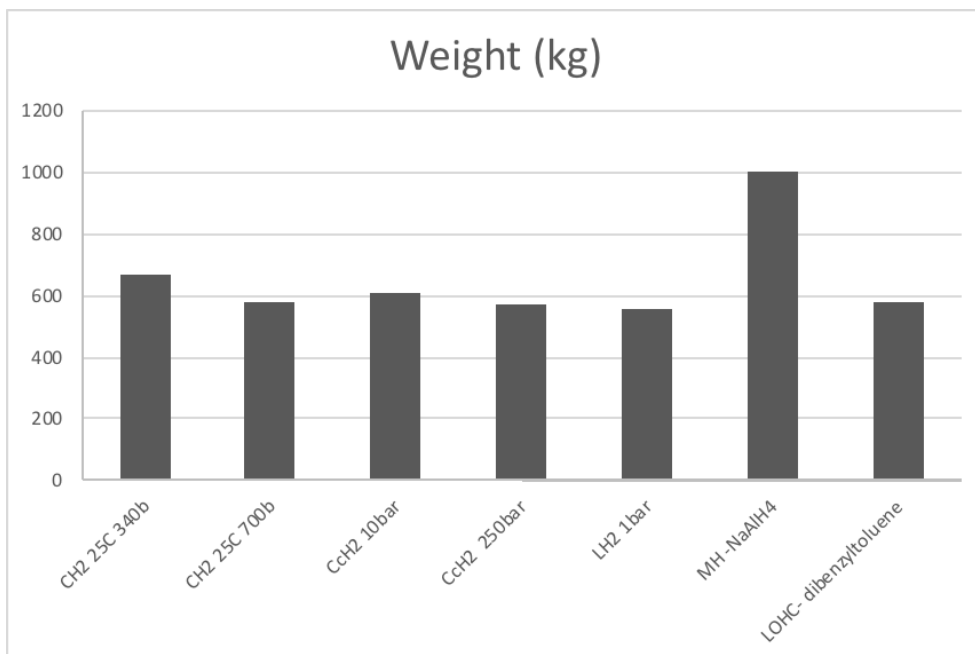

Fig. 37: GD and VD from Excel

Fig. 38: Weight comparison from Excel data

Considering the weight of the diverse storage systems, in the following figure (data also obtained from our Excel tool) is visible that the Metal Hydride storage is the most weight but, having in mind this disadvantage, is good to point out the advantage that is the only one of our research that is in solid-state storage which gives it safeness.
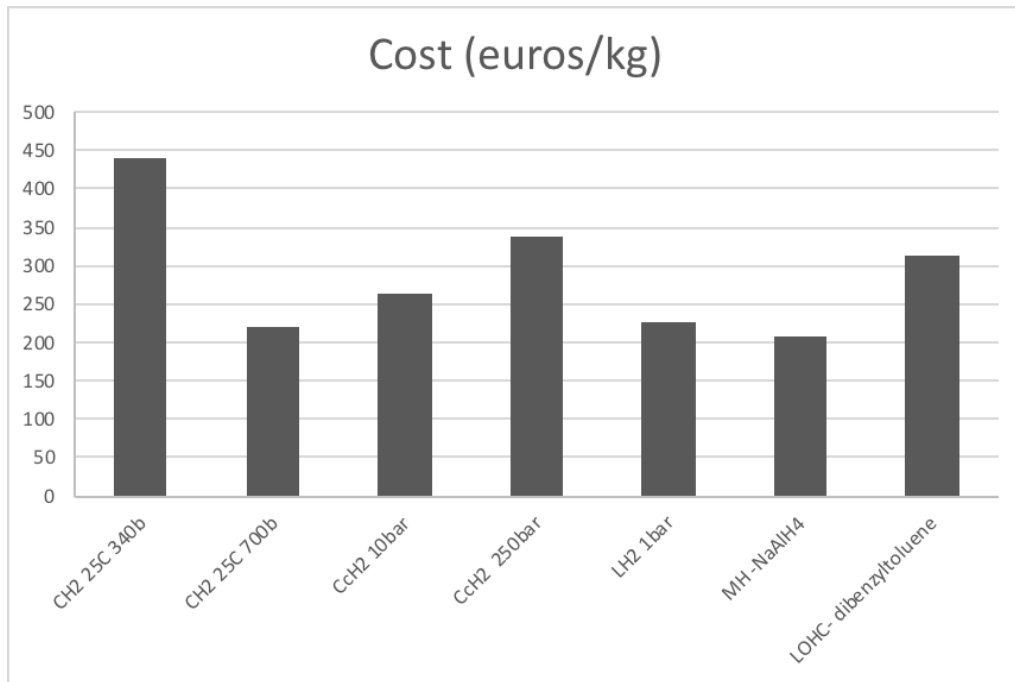
Fig. 39: Cost comparison from Excel data

In general, is evident that the compressed gas vessels are well known and kind of optimized because have been used during more time than the rest of storage methods. Up to 200bar (low pressure, low density, small amount of hydrogen stored) is a really well understood technology but at high pressures (high densities, higher amounts of hydrogen), are technologies under development. Even though, in these figures we are able to see that even if the CH2 700b should be weightier than CH2 350b, it is not due to the type II vessel used in the first one, which gives it 30-40% less weight.

The liquid tanks have a good storage density and are also well-understood technology but, they require a super insulation for maintain the cryogenic temperatures, there is used a lot of energy to make the hydrogen cool down until those conditions and, in addition, they have losses that are not really neglectable and that could be critical for efficiencies and safety reasons. From our point of view, LH2 should be more expensive than CcH2 and in our results is not like that.

The metal hydrides are currently quite expensive, with big volumes as shown in the figure below, really heavy and they can degrade with time but, its study and knowledge

in the future, will optimize their positive characteristics (such as the safeness, commented before).

The liquid organic carriers are also a promising alternative and, based on the results, is the best solution. Its weight is within the average, the cost is slightly higher than the average cost and the volume is the lowest. In addition, we know that they are not inflammable, not toxic, non-explosive and can exist at ambient pressure.
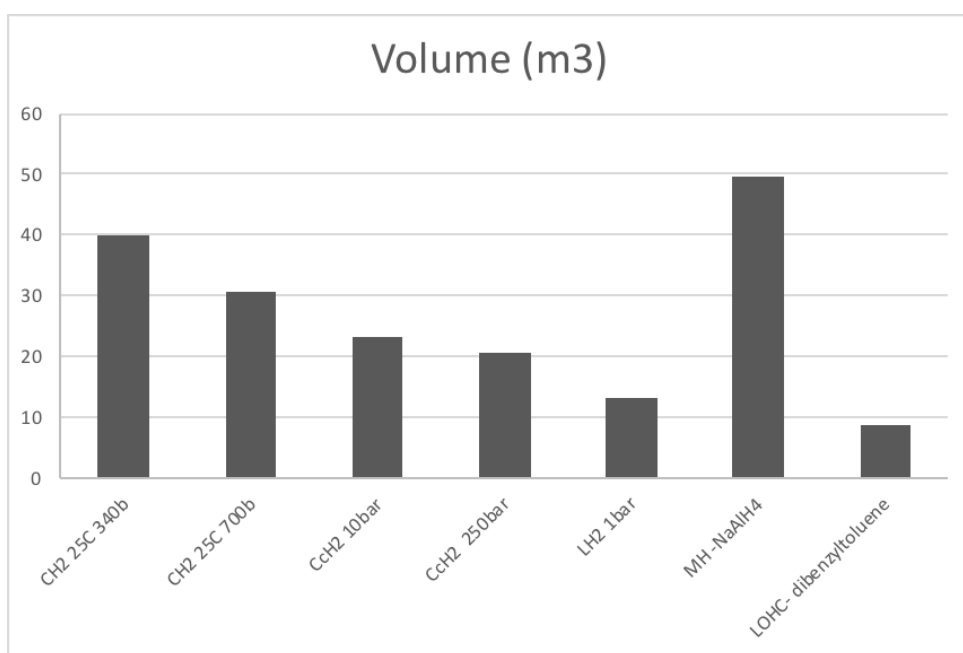
Fig. 40: Volume comparison from Excel data

It is important to be reiterative in the point that there is not a unique conclusion for our project. Occupied/needed volume, weight, safeness, cost and materials that can be used, are ones of the various parameters that should be taken into account while trying to figure out which is the best hydrogen storage method. Even so, is satisfactory to know that these researches are being more developed every time and so, the hope of a green-energy system and economy is every time closer.

6. CONCLUSIONS

In recent years, environmental concerned has enhanced and Scientifics around the world are trying to find environmental-committed solutions. One of the solutions that has been investigated is the energy production/storage/utilization and the objective is to find feasible alternatives energies which allow us to renounce to fossil fuels.

Thereby, there is a lot of investment in clean energies, such as solar and wind (main sources of hydrogen production through electrolysis) but the main problem of clean energies is their versatility. This problem could be solved if energy storage is possible and practical. For years, energy has been stored in batteries but, as mentioned at the beginning of this research (Fig.1), the hydrogen is more promising because it has a higher specific energy. Hydrogen: one of the most abundant chemical substance in the universe, is going to be our future clean fuel.

We will handle the hydrogen not like a source of energy (because is not found in the universe in its molecular form) but like an energy vector: this is the reason why its storage is a key issue that should be optimized in our way to the hydrogen economy.

Although hydrogen has the potential to be generated from renewable energies, is necessary to use intense energy technologies producing it, as well as storing it. Despite this difficulty, taking into account the fact of its high specific energy (three times the specific density of conventional fuels), the scale may be tipping towards it.

Known that the gravimetric density is really beneficial, is good to remember that the volumetric density is a weakness that should be dealt, and this is where the different hydrogen storage methods take place.

The early solution for increasing the volumetric density is increasing the storage pressure or switching gaseous hydrogen to liquid hydrogen. Unfortunately, even compressed and liquified hydrogen have still low densities and both present significant risks, technical challenges and require big amounts of energy. This is why alternative storage methods such as MH and LOHC have been investigated. Both of them offer advantages in safeness because of the non-extreme temperatures or pressures, but they also have their disadvantages such as the weight, volume or cost increasement.

Considering the figures screenshot before from the excel tool for a certain amount of hydrogen, we can see that depending on the needs that we have on the application of the hydrogen storage, we should maximize space, budget or weight.

The case of the metal hydrides is not really beneficent nowadays because although the price is really accessible, its volume and weight are really high. From our point of view, this technology is really promising but it has to be still developed until a point in which we can optimize at least two of these three characteristics.

In our case of using the hydrogen storage for a forthcoming electricity production, those which have less volume or weight are which are going to maximize the efficiency

of the ship. In this case we may focus in the liquid organic carriers because even if their price is slightly higher than the rest, their small volume and their characteristic of safeness are really interesting. Also, the cryo-compressed hydrogen at 250bar because it's a little bit more expensive but has approximately the same weight and low volume.

To sum up, we know that the Excel tool could be still really small or under-developed, but it could be the base of a better tool which could give results with more precision and reliability. Regardless this, we think that it is a good beginning to have a rapprochement in order to find an idea of a convenient solution.

7. APENDIX

APENDIX 1: Table needed to calculate the different densities of gaseous hydrogen depending on the pressure. Calculations were made with excel.
Data of RC [16]

Pressure (bar)	RC	Density (kg/m3)
1	1	0,089
50	1,032	4,312015504
100	1,065	8,356807512
150	1,089	12,25895317
200	1,132	15,72438163
250	1,166	19,08233276
300	1,201	22,23147377
350	1,236	25,20226537
400	1,272	27,98742138
500	1,344	33,11011905
600	1,416	37,71186441
700	1,489	41,84016118
800	1,56	45,64102564
900	1,632	49,08088235
1000	1,702	52,29142186

Table 1: Density-pressure for compressed hydrogen

APENDIX 2: for compressed hydrogen is known that there is a lineal relationship between pressure and cost. Therefore, a graph was constructed with the cost-pressure data taken from [16] and a trend line was assumed as linear. The equation of this trend line was calculated in order to have the cost in function of the pressure.

	Dollars	Euros
Pressure (bar)	1	0,76
160	700	532
430	750	570
860	1000	760

Table 2: Pressure-cost for compressed hydrogen

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