

HYDROGEN STORAGE: STATE-OF-THE-ART AND FUTURE PERSPECTIVE



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HYDROGEN STORAGE: STATE-OF-THE-ART AND FUTURE PERSPECTIVE

The objective of SETRIS is to collect, harmonise and validate information on sustainable energy technologies and perform related techno-economic assessments to establish, in collaboration with all relevant national partners, scientific and technical reference information required for the debate on a sustainable energy strategy in an enlarged EU, and in the context of global sustainable development.

In the particular field of hydrogen, the objective of SYSAF (Systems for Alternative Fuels) is to provide independent technical expertise and validation of storage performance, efficiency and safety of competing technologies. It aims at harmonising, validating and standardising test procedures for safety and operational performance of hydrogen storage systems.

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Executive Summary

The EU aims at establishing a sustainable energy supply, able to provide affordable and clean energy without increasing green house gas emissions. Hydrogen and fuel cells are seen by many as key energy system solutions for the 21st century, enabling clean and efficient production of power and heat from a broad range of primary energy sources. To be effective, there is a crucial need for well-coordinated research, development and deployment at European Level.

The particular segment of hydrogen storage is one key element of the full hydrogen chain and it must meet a number of challenges before it is introduced into the global energy system. Regarding its energy characteristics, the gravimetric energy density of hydrogen is about three times higher than gasoline, but its energy content per volume is about a quarter. Therefore, the most significant problem for hydrogen (in particular for on-board vehicles) is to store sufficient amounts of hydrogen. The volumetric energy density of hydrogen can be increased by compression or liquefaction which are both the most mature technologies. Still the energy required for both compression and liquefaction is one element to be properly assessed in considering the different pathways in particular for distribution. As far as on-board vehicle storage is concerned all possible options (compressed, liquid, metal hydrides and porous structures) have their own advantages and disadvantages with respect to weight, volume, energy efficiency, refuelling times, cost and safety aspects. To address these problems, long-term commitments to scientific excellence in research, coupled with co-ordination between the many different stakeholders, is required.

In the current state-of-the-art in hydrogen storage, no single technology satisfies all of the criteria required by manufacturers and end-users, and a large number of obstacles have to be overcome. The current hydrogen storage technologies and their associated limitations/needs for improvement are:

- Compressed hydrogen: it is the most mature technology; nevertheless improvements in weight, volume storage efficiency, conformable shapes, system integration and cost-reduction are needed. New tank design methodologies are necessary for increased strength-to-weight ratio materials, optimised safe structures and versatile shapes (700 bars pressures).
- Liquid hydrogen: a major concern in liquid hydrogen storage is to minimize hydrogen losses from liquid boil-off. Because liquid hydrogen is stored as a cryogenic liquid that is at its boiling point (-253°C), any heat transfer to the liquid causes some hydrogen to evaporate. The source of this heat can be the ortho-to-para hydrogen conversion, mixing or pumping energy, radiant heating, convection or conduction heating. This storage technology has good volumetric storage efficiency, however the special handling requirements, long-term storage losses, and cryogenic liquefaction energy requirements are penalties. Here the physico-chemical properties of hydrogen are important and there is a need to better understand the macroscopic heat transport of hydrogen.
- Metal hydrides: metal hydrides store hydrogen by chemically bonding the hydrogen to metal or metalloid elements and alloys. Hydrides are unique because some can adsorb hydrogen at or below atmospheric pressure, then release the hydrogen at significantly higher pressure when heated. There is a wide operating range of

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temperatures and pressures depending on the alloy chosen. Each alloy has different performance characteristics, such as cycle life and heat of reaction. Metal hydrides offer the advantages of lower pressure storage, conformable shapes, and reasonable volumetric storage efficiency, but have weight penalties and thermal management issues. There is a need to rationalise overall research efforts by sharing expertise, specific equipment and modelling tools for systems validation and improvements concerning weight and activation treatments.

- Carbon-based materials/porous structures can also store significant amounts of hydrogen at room temperature because of their high surface area and abundant pore volume. The most recently discovered nanomaterials such as single-walled nanotubes and graphite nanofibers have renewed attention on carbon as an adsorbent, which has the advantage of being inherently safe. Nevertheless, on a fundamental level there are still challenges on understanding the exact adsorption/desorption mechanism and the volumetric capacity of porous structures. It is also recognized that there is a need for comparison and validation of hydrogen storage measurements in order to avoid dissemination of unreliable results.

Storage systems still need to be analysed in a comprehensive way, cross cutting the above-mentioned possibilities and integrating all of the storage functions to go towards optimised storage systems. It is also worth exploring the feasibility of innovative concepts with novel materials. Due to the crucial problems still facing each of the above storage methods, considerable research is still needed in the short and medium term (2010-2015) and it is essential to take into account the different requirements of stationary and transport applications. A great deal of research effort in the United States (Grand Challenge) and Japan is actually directed towards developing the next generation technologies of hydrogen storage.

However, hydrogen as a fuel cannot become an economically viable option unless its cost is comparable to those of conventional fuels. The cost of storage vessels, of hydrogen conditioning (compression, liquefaction), of auxiliary equipment and the overall cost of hydrogen storage are key issues.

Introduction

Hydrogen is seen as a major energy carrier for the future. An energy economy based on hydrogen (especially when produced from renewable energy sources), with fuel cells as a major energy conversion technology could then resolve the major concerns about security of energy supply, source diversification and reduction of greenhouse gas emissions. The European Commission has drawn attention to alternative fuels caused by concerns over meeting increased energy demand, in particular in the transport sector.

The policy framework documents of the Commission, the Green Paper on the security of energy supply (COM (2000)769) and the White Paper on a common transport policy (COM(2001)370), suggest a target of 20% use of alternative fuels in road transport by 2020 in order to provide improvement in security of energy supply (by source diversification and oil substitution) and reduction of greenhouse gas emissions. In the Communication on alternative fuels (COM (2001)547) this suggestion has been further developed, identifying three main lines: biofuels, natural gas and hydrogen/fuel cells. Each fuel, as a prerequisite, should have a market share potential of at least 5% by 2020 to ensure a reasonable perspective for infrastructure and product developments. Techno-economic aspects of a broader market introduction of alternative fuels have been investigated by experts and stakeholders in the Alternative Fuels Contact Group established by the Commission in 2002. An interim report has been presented in March 2003.

In addition, the important role that technology plays in achieving a sustainable energy future is well recognized by the Commission as reflected in its Communication “Environmental Technology for Sustainable Development” of March 2002, proposing the development of an Action Plan for Environmental Technologies due to be adopted by the Commission by the end of 2003. The aim of this Action Plan is to identify promising environmental technologies, any barriers holding them back and appropriate measures to overcome these barriers. As far as promising technologies are concerned, hydrogen and fuel cells technologies have been identified as one of several examples of key areas that require a continued and strengthened research and development support. This is fully in line with priority areas covered in the 6th Framework Programme, in particular in promoting research, development, demonstration and market introduction of cost-effective technologies for hydrogen production, transport, storage and end-use from fossil, renewable and other sources. The consensus is that the overall policy of the Union on sustainable development has to include a robust strategy on alternative fuels, hence on hydrogen and fuel cells.

The most recent Commission initiative, in its effort to promote better energy systems, was the set-up of a High Level Group (HLG), made of top-level stakeholders from across Europe, with the aim of proposing an integrated European vision on the role that hydrogen and fuel cells could play in achieving sustainable energy, and on how to gradually transform this vision into a reality. The key recommendation action of setting-up a “European Partnership”, associating all relevant actors, public and private, interested to deliver and implement an integrated strategy for hydrogen, was strongly endorsed on 16-17 June 2003 at the major European conference “The hydrogen economy – a bridge to sustainable energy”, under the aegis of President Prodi. On 10 September 2003, President Prodi, Vice President de Palacio and Commissioner Busquin presented a Communication on actions towards the launch of the H₂/FC European

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Technology Partnership that was endorsed by the Commission. This is the strongest move yet by the Commission since its June Conference. It demonstrates the political will of the Commission to meet the challenge. The European Partnership will be constituted by the end of 2003 and its main goal should be *“to facilitate the development and deployment of cost-competitive, world class European hydrogen and fuel cell based energy systems and component technologies for applications in transport, stationary and portable power.”*

These policies and initiatives outline the efforts of the Commission to promote better energy systems and the key potential of hydrogen as a promising energy vector. According to President Prodi *“our goal is to achieve step-by-step a shift towards a fully integrated H₂ economy within the next few decades”*. However a number of challenges associated with the production, the storage, the transportation and distribution and applications have to be solved by the identification of appropriate research and development and development of technical standards.

A key precondition for the realisation of a hydrogen economy is the development of a hydrogen infrastructure which, by definition includes the system needed to produce hydrogen, store it, and deliver it to its users. This encompasses hydrogen production systems, for converting primary energy sources or other energy carriers to hydrogen; hydrogen storage needed to match time (and space, location) varying demands to hydrogen production output and finally distribution systems.

The wide use of hydrogen thus necessitates resolving its storage issue. This ranges from large-scale storage of hydrogen down to small-scale use near at the point of use, for example, onboard hydrogen storage in vehicles. For the large-scale storage there are solutions and options applied today by the industry utilizing hydrogen as a chemical commodity that could be used in future energy systems. However, it is the small-scale storage of hydrogen that poses a great number of challenges and remains a high priority.

Unlike gasoline or diesel, easily handled liquids at ambient conditions, hydrogen is a lightweight gas and has the lowest volumetric energy density of any fuel at normal temperature and pressure. Regarding its energy characteristics, the gravimetric energy density of hydrogen is about three times higher than gasoline, but its energy content per volume is about a quarter. Therefore, the most significant problem for hydrogen (in particular for on-board vehicles) is to store sufficient amounts of hydrogen. All possible options (compressed, liquid, metal hydrides and porous structures) have their own advantages and disadvantages with respect to weight, volume, energy efficiency, refuelling times, cost and safety aspects.

In the current state-of-the-art in hydrogen storage, no single technology satisfies all of the criteria required by manufacturers and end-users, and a large number of obstacles have to be overcome. Storage systems need to be analysed in a comprehensive way, cross cutting the various possibilities and integrating all of the storage functions to go towards optimised storage systems. It is claimed that if a breakthrough hydrogen storage technology were successfully developed, it would speed the introduction of hydrogen as transportation fuel.

In this report the current technical and economic status of technologies for hydrogen storage are reviewed and the likely areas for technological progress are described. Research efforts devoted to these issues worldwide are highlighted and options under development are discussed along with commercially available hydrogen storage technologies. Although all applications for hydrogen are addressed, emphasis is given more to the use of hydrogen in transport.

1. Fundamentals of hydrogen

Hydrogen (chemical symbol H) is the lightest of all elements (atomic weight 1.00794 a.m.u), with atomic number $Z=1$. Its name comes from the combination of the Greek words ‘*hydor*’ meaning ‘*water*’ and ‘*geinomai*’ meaning ‘*to bring forth*’, i.e. the element that brings forth water. It is the ninth most abundant element on Earth’s crust (1400 mg/kg) and the second most abundant element in Earth’s sea after oxygen (1.08×10^5 mg/l). Furthermore, it is the most abundant element of the universe, accounting for 91% of our solar system by weight. Under normal conditions of temperature and pressure¹ it is a colourless, odourless, tasteless, non-poisonous² and flammable gas. It was discovered by Henry Cavendish in England in 1766 and named by Lavoisier [1].

Its atom is the simplest of all elements, mostly consisting of a single proton nucleus and an orbiting electron³. The hydrogen molecule consists of two atoms (H_2) and appears in 2 forms, ortho-hydrogen and para-hydrogen; their difference being in the orientation of their nuclear spins. In ortho-hydrogen both atoms have the same (parallel) spin, while in para-hydrogen, molecules have opposite (anti-parallel) spins, see Figure 1. Under normal conditions hydrogen molecules are present both in ortho- state (75%) and para-state (25%)⁴; this equilibrium composition is referred to as *normal hydrogen*. However, this equilibrium composition of hydrogen states varies with temperature, see Figure 2. As temperature decreases, ortho-hydrogen transforms into para-hydrogen and finally at the liquid state, hydrogen is present practically exclusively in the para- state (99.8%). This state transformation is accompanied by heat release: the energy released during the conversion of ortho-hydrogen to para-hydrogen at 20K is 703 J/g [2] while the energy required to transform normal hydrogen (75% ortho-) to pure para-hydrogen is reported as 527-670 J/g, depending on the literature source [2, 3]. This state conversion has significant consequences to hydrogen liquefaction and storage, since it leads to release of energy that is higher than the heat of evaporation (445.6 J/g [2]) ultimately leading to hydrogen losses due to boil-off.

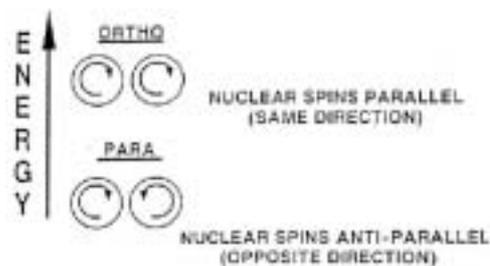


Figure 1 – Drawing representation of ortho- and para- hydrogen [3]

¹ Normal conditions are at temperature of 20°C and pressure of 1 atm.

² Hydrogen is non-toxic nor is listed as carcinogen; however it is an asphyxiant. The potential for asphyxiation in unconfined spaces is negligible due to the high buoyancy and diffusivity of hydrogen. Concerns should be raised about large leaks in confined spaces.

³ There is also an isotope of hydrogen with a nucleus that contains both a proton and a neutron, called *deuterium* or *heavy hydrogen*. One atom of deuterium is found in about 6,000 atoms of normal hydrogen atoms. *Tritium* is another unstable isotope.

⁴ Under normal conditions, hydrogen has 3 quantum ortho- states and 1 para- state.

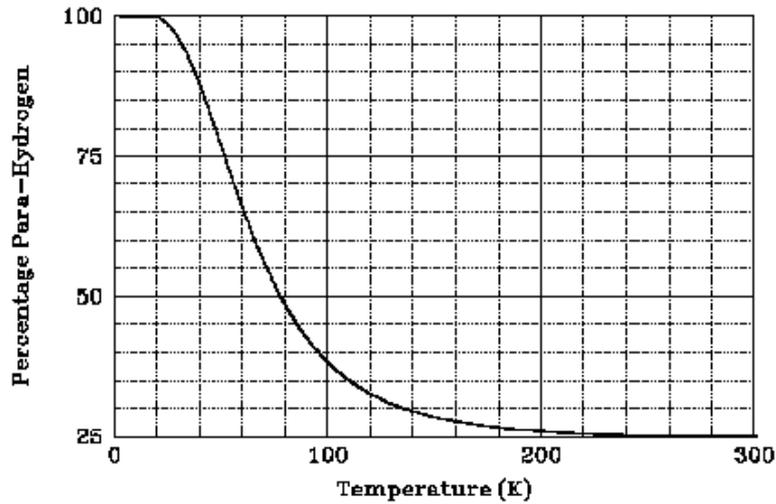


Figure 2 – Equilibrium percentage of para-hydrogen as a function of temperature [2]

1.1 Basic Properties

1.1.1 Thermo physical properties

A phase diagram of hydrogen is shown in Figure 3. At normal conditions hydrogen is in a gaseous state. At atmospheric pressure hydrogen is liquefied at -252.87°C , having the second lowest boiling point among all elements after helium, and solidifies at -259.34°C . The boiling point of hydrogen is increased with the application of pressure, up to its critical point of -240°C at 13 atm. However, the application of higher pressure does not have any further influence to the boiling point [4].

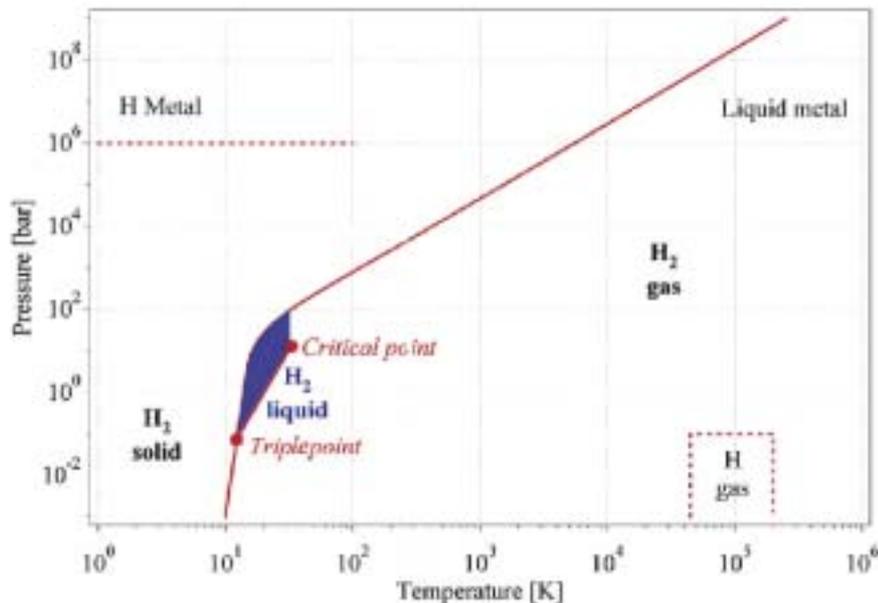


Figure 3 – Simple phase diagram for hydrogen [5]

Hydrogen has a very low density both as a gas and a liquid. Its density is 0.08988 g/l in gaseous state, i.e. 7% of the density of air; 70.8 g/l as liquid (at -253°C), i.e. 7% of the

density of water; and 70.6 g/l as solid (-262°C). For comparison, the density of typical fuels is shown in Table 1. At normal conditions, gaseous hydrogen is about 8 times less dense than methane; in liquid state hydrogen is 6 times less dense than liquid methane and 55 times less dense than liquid gasoline. Furthermore, the volume ratio between gas and liquid hydrogen at ambient pressure for a given mass is 848; and the volume ratio between hydrogen at 1 bar and compressed hydrogen at 700 bar is 440. Therefore, compressed hydrogen cannot reach the density of liquid hydrogen under any practicably achievable pressure conditions. Finally, it is interesting to note that more hydrogen is contained in a given volume of water or gasoline than in pure liquid hydrogen (111 kg/m³, 84 kg/m³ and 71 kg/m³ respectively).

Table 1 – Density of fuels in gaseous and liquid state [4]

<i>Substance</i>	<i>Gas (vapour) at 20°C, 1 atm</i>		<i>Liquid at boiling point, 1 atm</i>	
	<i>Absolute (kg/m³)</i>	<i>Relative to hydrogen</i>	<i>Absolute (kg/m³)</i>	<i>Relative to hydrogen</i>
Hydrogen	0.09	1.00	70.8	1.0
Methane	0.65	8.13	422.8	6.0
Gasoline	4.4	55.0	700.0	9.9

The density of hydrogen at elevated pressure can be estimated using the principles of thermodynamics. While the behaviour of most gases can be approximated with a high accuracy by the simple equation of state⁵ attributed to the *ideal gas*⁶, the behaviour of hydrogen deviates significantly from the predictions of the ideal gas model (although its predictions are practically accurate at low pressures - below 100 atm). This deviation is mainly due to the peculiar nature of the substance; the hydrogen molecule is highly polarised so that attraction forces between molecules are applied changing slightly the gas pressure. This change is always expressed in the form of compression. The behaviour of hydrogen at elevated pressure can be described more accurately with a more appropriate equation of state than the ideal gas model. A number of such equations of state have been proposed for *real gases* including the *van der Waals* model, the virial function, the Berthelot equation and the *compressibility* factor. Herein, the first and the last of the aforementioned approaches are briefly discussed.

The equation of state for the van der Waals model has the form:

$$\left(P + n^2 \frac{\alpha}{V^2} \right) \left(\frac{V}{n} - b \right) = RT \quad \text{Eq.1}$$

where, P, V and T represent the pressure, volume and temperature of the gas respectively, n is the number of moles of gas present, and R is the universal gas constant (8.314 N·m/mol·K). The equation also uses two constants (α and b) that are

⁵ An equation of state is an equation that relates the pressure, the volume and the temperature of a given substance.

⁶ A gas is considered as ideal when (i) it obeys the equation of state $P V = n R T$ (where P is its pressure, V its volume, n the number of moles, R the universal gas constant and T its temperature); and (ii) its internal energy is a function of the temperature only and not of the pressure and volume [6].

experimentally determined. For hydrogen, they take the values of $0.0244 \text{ Pa}\cdot(\text{m}^3)^2\cdot\text{mole}^{-2}$ and $0.0266\cdot 10^{-3} \text{ m}^3\cdot\text{mole}^{-1}$ for α and b respectively [6].

The compressibility factor approach introduces a variable, Z , to represent the deviation of a real gas from the ideal gas model. The corresponding equation of state is:

$$PV = nZRT \tag{Eq. 2}$$

Compressibility factors are experimentally determined and presented in charts and tables (see [97]). They depend on the temperature, pressure and the substance. The compressibility factors for hydrogen are shown in Figure 4 and Table 2.

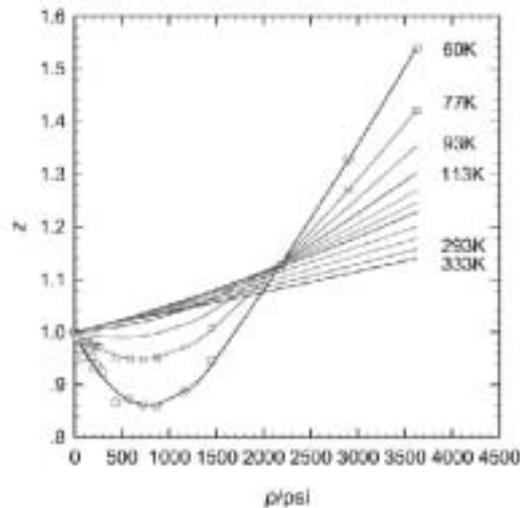


Figure 4 – Compressibility factors of hydrogen [7]

Table 2 – Hydrogen compressibility factors (Z) at 20°C [8]

Pressure (MPa)	0.1013	5	10	20	30	35	40	50	70	100
Z	1	1.032	1.065	1.132	1.201	1.236	1.272	1.344	1.489	1.702

The use of the different equations of state leads to diverse predictions of the behaviour of hydrogen at high pressure. Figure 5 shows the density of hydrogen with pressure as calculated by considering the ideal gas model, the van der Waals model and the compressibility factor of hydrogen. For pressures up to 150 bar, the predictions of the 3 models are practically identical. However, at higher pressures the ideal gas model overestimates the density of hydrogen, compared to the real gas models; the deviation increases with pressure. The predictions of the 2 real gas models are identical for pressure up to 400 bar; however, at higher pressure, the predictions differ. It is not possible to state which model is correct, given that both real gas models considered above are generic models developed to characterise all real gases. The values of their variables (α , b and Z) have been selected so that their predictions are close to experimentally measured values for hydrogen. This issue of uncertainty in the predictions of behaviour of hydrogen at high pressure can be overcome only with the formulation of a new set of equations that describe fully and accurately the behaviour of hydrogen. This set of equations comprises: (i) an equation of state that relates pressure,

temperature and volume devised exclusively for hydrogen, based on actual experimental data, and (ii) a calorific equation that describes the change of the internal energy of a gas as a function of pressure, temperature and volume, see footnote 6. To date, the authors are not aware of such equations.

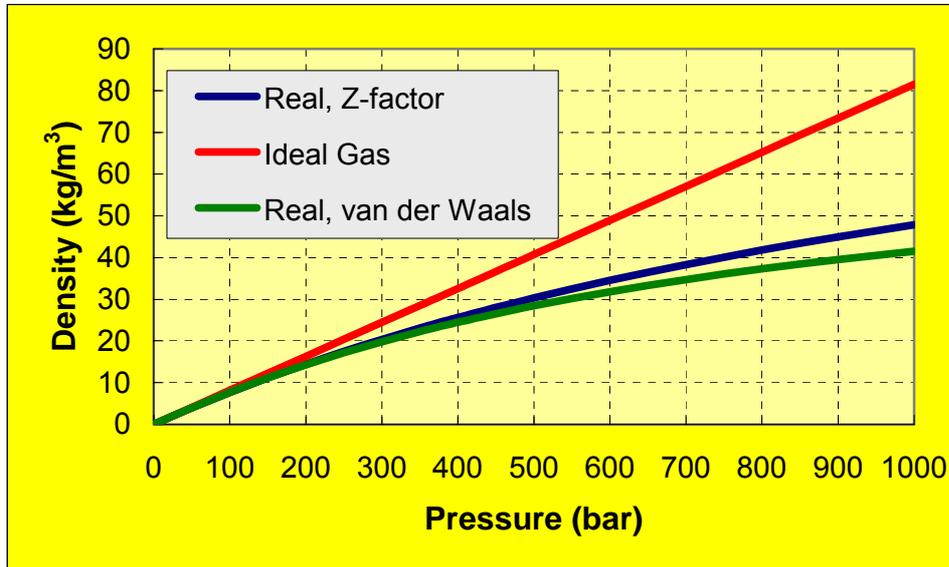


Figure 5 – Hydrogen density as a function of pressure

1.1.2 Energy Content

When hydrogen reacts with oxygen, H_2O is formed and energy is released. This amount of energy when normalised with the quantity of hydrogen reacted represents the *energy density* of hydrogen which is distinguished between the low heat value (LHV) and the high heat value (HHV). The differentiation between HHV and LHV is based upon the state of the H_2O products of the reaction. If the H_2O is in the vapour phase the normalised energy released is called the LHV (or net calorific value). On the other hand, if the H_2O is in the form of liquid water then the normalised energy released is called the HHV (or gross calorific value) that is higher than the LHV by about 10% accounting also for the heat of condensation of water vapour into liquid. In most applications, such as high temperature fuel cells, H_2O is produced as steam, therefore the LHV represents more accurately the energy available to do external work. However, in certain applications, such as proton exchange membrane fuel cells, H_2O is produced in liquid form (water); in such a case the use of the HHV of hydrogen is more appropriate.

The energy density of hydrogen can be expressed either on a weight basis (mass energy density) or on a volume basis (volumetric energy density). The energy density of hydrogen as reported by various sources is shown in Table 3 and Table 4. There is some discrepancy in the reported values, which can be the result of rounding or of measuring at different reference conditions.

Table 3 – Mass energy density of hydrogen as reported by various sources

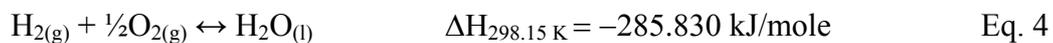
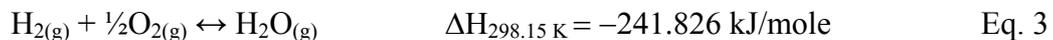
<i>HHV (MJ/kg)</i>	<i>LHV (MJ/kg)</i>	<i>Source</i>
141.86	120.0	[8]
141.86	119.93	[4]
142	120.2	[9]
142	120	[10]
141.6	119.6	[11]

Table 4 – Volumetric energy density of hydrogen as reported by various sources

<i>HHV (MJ/m³)</i>	<i>LHV (MJ/m³)</i>	<i>Source</i>	<i>Conditions</i>
<i>Gaseous Hydrogen (GH₂)</i>			
12.75	10.8	[8]	At normal conditions
	10.1	[4]	At 15°C
12.71	10.8	[9]	At normal conditions
11.7	9.9	[10]	At 25°C
<i>Liquid Hydrogen (LH₂)</i>			
10.04*10 ³	8.495*10 ³	[8]	At boiling point
	8.491*10 ³	[4]	At boiling point
10*10 ³		[10]	

The energy density of hydrogen can easily be calculated based on basic thermodynamic principles:

Mass energy density: The energy released during the ‘combustion’ of hydrogen, i.e. the heat of formation of H₂O, is given by the following equations [1]:



Equation 3 is applicable when H₂O is produced in a form of vapour and can be used for the calculation of the LHV of hydrogen, while Equation 4 is applicable when H₂O is formed as liquid, thus this heat of formation can be used to calculate the HHV of hydrogen. The mass energy density of hydrogen at 298.15 K or 25°C is simply the division between the above-mentioned heats of formation and the molecular weight of hydrogen (i.e. 2.02*10⁻³ kg). Therefore, the mass energy densities of hydrogen at 25°C are 119.716 MJ/kg (LHV) and 141.500 MJ/kg (HHV). Typically, hydrogen properties are reported at 25°C, at 20°C (normal conditions), at 15°C (standard conditions according to ISO 2533) or at 0°C (standard conditions according to IUPAC). The mass energy density at these temperatures can be obtained via simple thermodynamic

calculations. At 0°C the mass energy densities of hydrogen are 120.131 MJ/kg (LHV) and 141.686 MJ/kg (HHV).

Although the discrepancies between the reported values of the volumetric energy density of hydrogen at low pressures are insignificant, reported values at high pressures may vary significantly. This variation in the reported values is the result of the inaccuracy of calculating the density of hydrogen at higher pressures (see Figure 5), given that the volumetric energy density is the product of hydrogen's density with the mass energy density. Figure 6 shows our calculated values (at 20°C) plotted against values reported in the literature. It is clear that the volumetric energy density of compressed hydrogen (LHV) cannot reach the energy density of liquid hydrogen (LH₂) within the practically acceptable storage pressures. Furthermore, the assumption of ideal gas behaviour leads to significant errors in estimating the volumetric energy density of hydrogen.

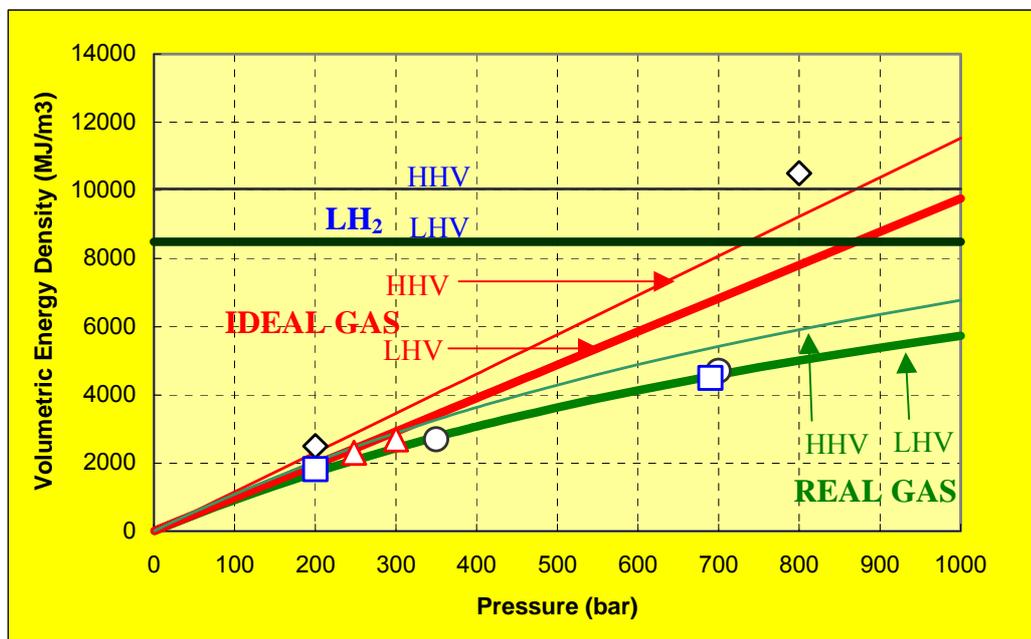


Figure 6 – Calculated values for the volumetric energy density of hydrogen (in continuous lines) plotted against reported values. LH₂ stands for liquid hydrogen.

Compared to other conventional fuels, hydrogen has the highest mass energy density, almost 2.5 times the energy released during the combustion of conventional hydrocarbon fuels (Figure 7). Therefore, on a weight basis, the amount of fuel required to deliver a given amount of energy is significantly reduced when hydrogen is utilised. More importantly, hydrogen has the lowest volumetric energy density when compared with conventional fuels (Figure 8). To put these figures in perspective, a 50 l gasoline tank is equivalent on an energy basis to a 460 l tank of compressed hydrogen at 350 bar, or a 340 l tank of compressed hydrogen at 700 bar, or an 185 l tank of liquid hydrogen.

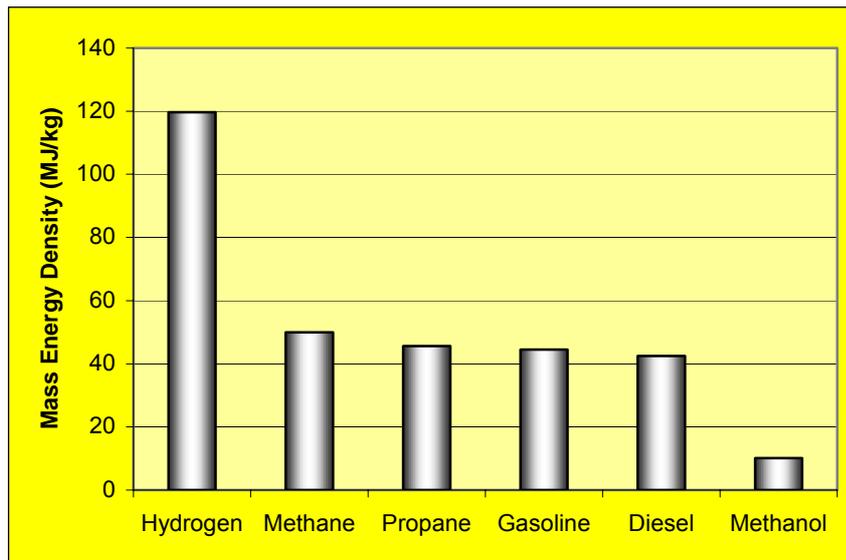


Figure 7 – Mass energy density of fuels (LHV)

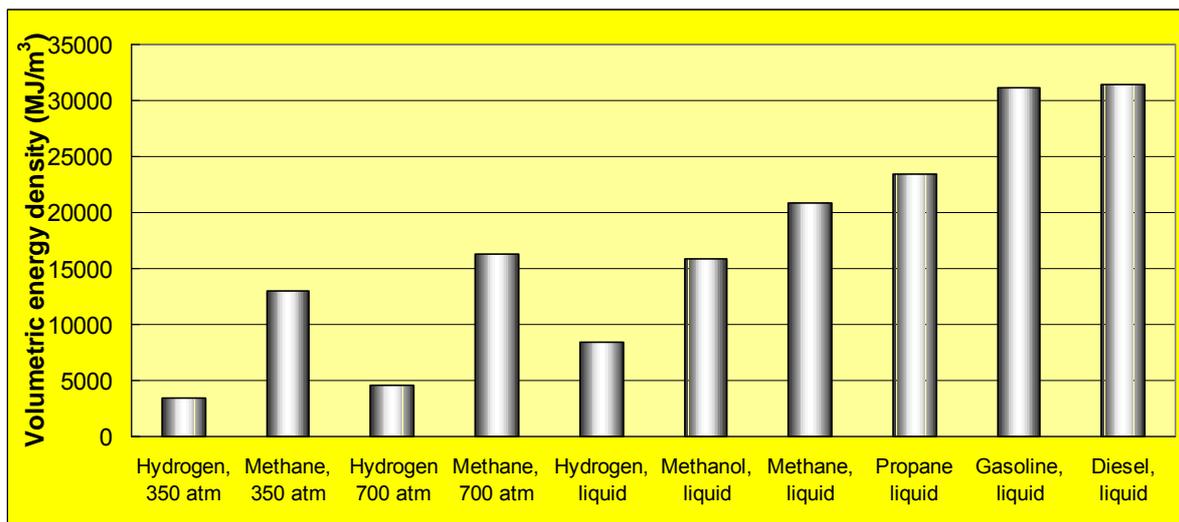


Figure 8 – Volumetric energy density of typical types of fuel (LHV)

1.1.3 Physicochemical properties of hydrogen related with its storage

Hydrogen is a flammable gas and can feed a fire or an explosion under specific conditions, such as mixed with oxygen in certain composition ranges with a concurrent presence of an ignition source. The concentration range in air in which hydrogen is capable of supporting a self-propagating flame when ignited is called the flammability range. Under ambient conditions, hydrogen is flammable over a wide range of concentrations (4-75%) and explosive in a narrower range (15-59%) [4]. The flammability ranges for a number of conventional fuels is shown in Figure 9. The upper flammability range of hydrogen, i.e. the highest concentration of hydrogen in air (75-85% depending on the temperature) has important consequences for hydrogen storage: it becomes evident that hydrogen is not flammable when stored (due to the lack of oxygen). Hydrogen becomes flammable only in the peripheral areas of a leak, where the mixing of hydrogen with air is within its flammability range. Given that hydrogen

diffuses very fast, increased chances for a fire and explosion may be encountered when leakage is in an enclosed environment.

Another important property of hydrogen is the auto-ignition temperature, i.e. the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of an ignition source. This temperature for hydrogen is 585°C, higher than any other conventional fuel such as methane (540°C) and gasoline (230-480°C). In the absence of such a high temperature, an appropriate hydrogen mixture can be combusted only by an ignition source such as a flame or a spark. However, the minimum energy required to initiate combustion (the ignition energy) is 0.03 mJ, almost an order of magnitude lower than that of conventional fuels. Therefore, hydrogen can ignite more easily than other fuels. It is claimed that the energy generated by static electricity discharge or even by the agitation of compressed or liquid hydrogen may generate enough energy to cause ignition [4].

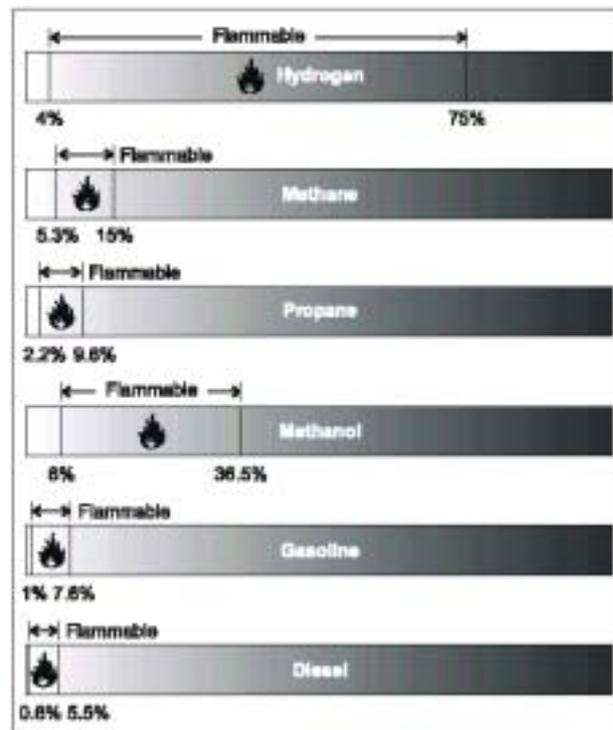


Figure 9 – Flammability limits of conventional fuels [4]

1.1.4 Hydrogen embrittlement

Hydrogen may degrade the mechanical behaviour of metallic materials used in the hydrogen infrastructure (e.g. storage tanks, pipelines, etc.) and lead them to failure. The embrittlement of materials used in hydrogen-related applications is a major practical issue. The reasons that cause it are still debated in the scientific community, which is a reason for the presence of numerous studies devoted to the effect of hydrogen on material behaviour⁷. In brief, the accumulation of hydrogen in a solid metal results in

⁷ At least 25 papers have appeared in the scientific literature since 2001 with the words ‘hydrogen embrittlement’ in their title (based on a search on Science Direct in September 2003).

the reduction of its ductility thus increasing the probability of brittle fracture. Such failures may have catastrophic results (see Figure 10).



Figure 10 – Factory after rupture and explosion of a hydrogen storage tank [12]

It is understood that hydrogen can cause embrittlement when present in a metal or alloy in its atomic form and not as a molecule. Solute hydrogen atoms in metals tend to concentrate in defects of the crystal structure (dislocations and grain boundaries among others), imposing a barrier to the movement of dislocations, effectively impeding the plastic flow of the material. As a result, the ductility of the metal decreases and the material becomes brittle. Furthermore, the concentration of hydrogen at grain boundaries, possibly in molecular form, and the potential of formation of hydrates after the reaction of hydrogen with the metal, are additional mechanisms that may lead to embrittlement.

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

The latter two processes are also responsible for failures in hydrogen-related process plants, a phenomenon known as hydrogen attack. Hydrogen attack has been reported in plain carbon steel, low alloy steels and even some stainless steels operating above 200°C. It is one of the major causes of problems in refineries, where hydrogen and hydrocarbon streams are handled under conditions of up to 200 atm and 500°C [124]. In this context, failure is the result of the formation of intermetallic phases from the host metal and hydrogen dissolved in the metallic matrix via chemisorption and electrochemical reactions, changing the properties of the material, degrading its mechanical properties and forming methane gas that concentrates in the grain

boundaries of metallic components leading them to failure caused by void growth assisted by creep.

Finally, in the presence of hydrogen, stressed components may fail due to hydrogen-induced stress corrosion cracking, a type of damage understood as the formation of cracks by tensile stress in the presence of a corrosive hydrogen atmosphere. For more information on these failure mechanisms the reader may consult standard metallurgical references such as [13].

1.2 Principles of Hydrogen Compression and Liquefaction

1.2.1 Hydrogen Compression

When hydrogen is utilised in a gaseous form it usually has to be compressed to an elevated pressure, a process that requires work to be done on the gas. However, the precise calculation of the work of hydrogen compression requires the knowledge of an appropriate equation of state and of a calorific equation, as was mentioned earlier, information that is not widely available. To overcome this obstacle and simplify calculations, many investigators consider the compression of hydrogen as an isentropic (adiabatic) process⁸, i.e. they assume that during compression there is no heat exchange between the compressor and the environment and the process is reversible. The work required to increase the pressure of a gas, P, is:

$$W = \int_{V_1}^{V_2} PdV \quad \text{Eq.5}$$

where V is the volume of the gas. Based on the assumption that hydrogen behaves as an ideal gas, the work of isentropic (adiabatic) compression for 1 mole of hydrogen (or 2.02 g) from pressure P₁ to pressure P₂ (P₁<P₂) is given by:

$$W_{\Delta S \rightarrow 0, ideal} = \frac{\gamma}{\gamma - 1} RT_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad \text{Eq. 6}$$

where T₁ is the temperature of hydrogen at P₁ and γ is the specific heat ratio of the gas (C_p/C_v) assumed of being independent of temperature. For hydrogen and all other diatomic gases, γ has the value of 1.4. The work of adiabatic compression as a function of the final compression pressure is shown in Figure 11. Furthermore, since the adiabatic compression of hydrogen is not a reversible process, deviation from the ideal behaviour is accounted for by introducing an isentropic compressor efficiency. Then the actual work of compression is given by:

$$W_{actual} = \frac{W_{\Delta S \rightarrow 0}}{\eta_{adiabatic}} \quad \text{Eq. 7}$$

⁸ Under adiabatic conditions PV^γ is constant and under isentropic conditions $\Delta S=0$, i.e. the process is reversible.

where $\eta_{\text{adiabatic}}$ is the adiabatic efficiency of the process typically of the order of 75-85% [14]. Ultimately, the electrical consumption of the compressor is calculated considering that the efficiency of the electrical motor is of the order of 90%.

However, as was shown in the previous section, significant errors may be induced by considering that hydrogen behaves as an ideal gas at high pressure. However, none of the real gas generic equations of state (such as Eqs. 1 and 2) have been used to derive an expression similar to Eq. 6.

Another simplification made for the calculation of the work of compression of hydrogen is to consider the whole process isothermal, i.e. the temperature of hydrogen, T , does not change during compression. Then, the work of compression for one mole can be calculated, based on the ideal gas model and real gas models (Eqs 1 and 2):

(a) for an ideal gas:

$$W_{\text{isothermal,ideal}} = RT \ln \frac{V_2}{V_1} \quad \text{Eq. 8}$$

(b) for a van der Waals gas [6]:

$$W_{\text{isothermal,Waals}} = RT \ln \frac{V_2 - b}{V_1 - b} + \frac{\alpha}{V_2} - \frac{\alpha}{V_1} \quad \text{Eq. 9}$$

(c) for a compressible gas (Z-factor):

$$W_{\text{isothermal,Z}} = ZRT \ln \frac{V_2}{V_1} \quad \text{Eq. 10}$$

The results of these 3 approaches are shown in Figure 11. Clearly, in the case of isothermal compression, the results depend on the gas model assumed. Independent of the model used, the relationship between the work of compression and the final (discharge) pressure is not linear but parabolic. Therefore, the work required to compress hydrogen by a given pressure increment depends on the initial (suction) pressure: the higher the suction pressure, the lower the energy demand for compression. In other words significantly less energy is needed to increase the pressure of hydrogen from 350 bar to 700 bar, than to increase it from ambient pressure to 350 bar. This relationship between work and pressure highlights the energy efficiency advantage that is offered by hydrogen production methods that deliver hydrogen at elevated pressures, such as pressurised electrolyzers and reformers.

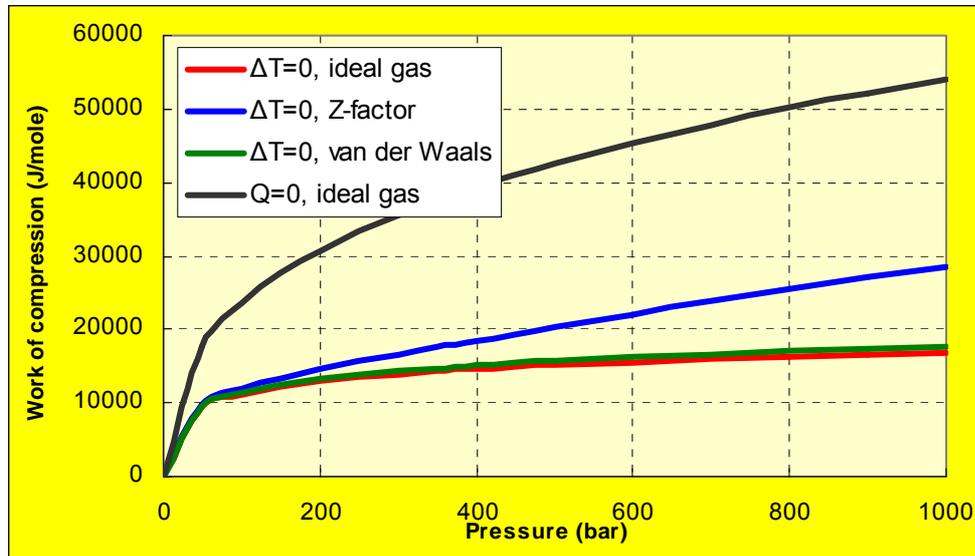
According to thermodynamics, the actual form of compression will usually be between the theoretical conditions of isothermal compression and isentropic compression, which represent a low limit and an upper limit of the work of compression respectively [16]. In practical applications the compression of hydrogen is neither isothermal⁹ nor isentropic¹⁰ nor adiabatic¹¹. The actual work of compression lies between the predictions of the two aforementioned assumptions. Such a process is better approached by thermodynamics using a reversible polytropic path, where PV^n is constant (vis-à-vis

⁹ Typically, the temperature of the gas increases during compression despite the fact that cooling to the gas is provided to keep the temperature as close as possible to its initial value.

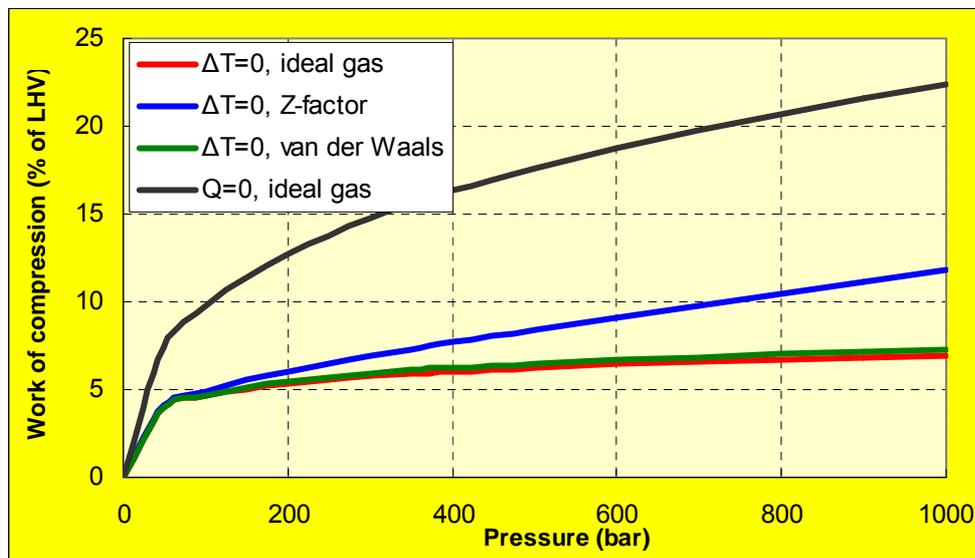
¹⁰ The process is not reversible due to energy losses from mechanical friction and viscous dissipation.

¹¹ As explained above, heat is exchanged during compression between the gas and the surroundings to reduce the gas temperature.

footnote 8). n is the polytropic index that depends on the nature of the gas and the details of the compression process. When the polytropic index, n , is greater than γ , heat is supplied to the gas during compression.



(a)



(b)

Figure 11 – Work of compression of hydrogen based on different assumptions: isothermal conditions ($\Delta T=0$) assuming that hydrogen behaves as an ideal gas (red), a van der Waals gas (green), and a compressible gas using the Z factor (blue); and adiabatic compression ($Q=0$) assuming that hydrogen is an ideal gas (black). Absolute values are shown at the top graph, and relative values normalised to the LHV of hydrogen at the bottom graph.

On the other hand, when $n < \gamma$, heat is rejected by the gas during compression. The work of polytropic compression of 1 mole of hydrogen from a suction pressure P_1 to a discharge pressure P_2 is¹²:

$$W_{polytropic} = \frac{n}{n-1} RT_1 \left[\left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} - 1 \right] \quad \text{Eq. 11}$$

As with isentropic compression (Eq. 6), the actual work of compression is larger than the above-calculated amount of work. The actual work can be calculated when the polytropic efficiency of the process (η_p) is known. The polytropic efficiency is often the efficiency quoted by the equipment manufacturers and can be used to link the polytropic index (n) to the specific heat ratio (γ) [15]:

$$n = \frac{\eta_p \gamma}{1 + \eta_p \gamma - \gamma} \quad \text{and} \quad \frac{n}{n-1} = \frac{\gamma}{\gamma-1} \eta_p \quad \text{Eq. 12}$$

As shown in Figure 11 the work required for isothermal compression is lower than that for isentropic (or polytropic) compression for a given compression ratio and initial pressure. However, since the compression of hydrogen is a polytropic process, the temperature of the gas changes during the process from T_1 to T_2 according to the equation:

$$T_2 = T_1 \left(\frac{P_2}{P_1} \right)^{\frac{n-1}{n}} \quad \text{Eq. 13}$$

A direct consequence is that the final temperature increases with the pressure ratio (P_2/P_1). Therefore, cooling during the compression process can reduce the actual work required¹³. The case of ideal isothermal compression can only be achieved if cooling is continuous throughout the compression process. This is practically difficult to obtain [16], as it would require the uniform removal of heat in the compressed gas at the same rate that heat is generated, while at the same time, guaranteeing a uniform temperature distribution in the compressed gas. Furthermore, this would necessitate complicated cooling systems (with concurrent penalties in cost and energy efficiency), especially for the larger capacity compressors (see Chapter 2). As a more practical solution, multi-stage compression can be used to cool the gas between the compression stages, using an intercooler. If intercooling is perfect, the temperature of the gas is reduced to the initial temperature after each compression stage. The isentropic work of the 2-stage compressor is:

$$W_{\Delta S \rightarrow 0} = \frac{\gamma RT_1}{\gamma-1} \left[\left(\frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] + \frac{\gamma RT_1}{\gamma-1} \left[\left(\frac{P_3}{P_2} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right] \quad \text{Eq. 14}$$

¹² The equation is similar to the one that gives the adiabatic work of compression (Eq. 6), however γ has been replaced by n .

¹³ Cooling offers additional advantages such as an improvement of the volumetric efficiency of the compressor [16].

where P_1 and P_3 are the suction and the discharge pressures and P_2 is the optimal intermediate pressure, being of such a value ($P_2 = \sqrt{P_1 \cdot P_3}$) so that the pressure ratio is the same in each compression stage; a necessary requirement to achieve the conditions of minimum work.

Figure 12 shows the calculated electrical work required for compressing hydrogen with multi-stage compressors. Two families of cases were examined, differentiated by the suction pressure being 2 bar and 35 bar respectively. It becomes evident that the required energy is reduced with the increase in the number of stages, although no significant energy efficiency gain is expected if the number of stages exceeds 3. However, as will be shown in chapter 2, 3 stages may not be adequate to deliver hydrogen at a required discharge pressure due to limitations in pressure ratios for every compression stage. This graph also highlights the importance of the suction pressure in the energy required to achieve a desired discharge pressure.

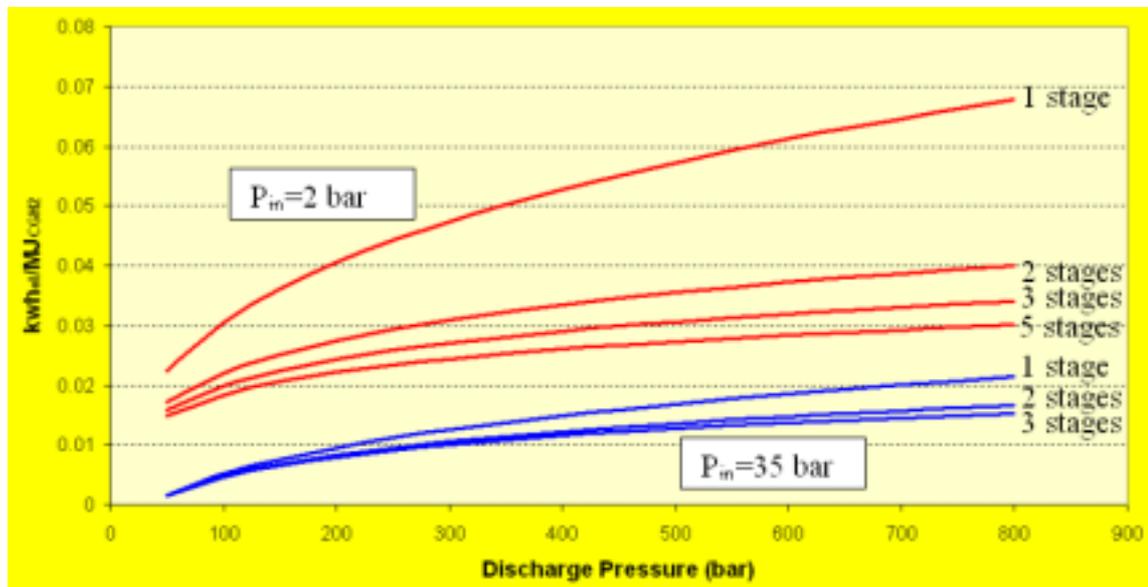


Figure 12 – Electrical work required for the compression of hydrogen, based on multi-stage compression. Assumptions for the calculation: Ideal intercooling, $T=25^{\circ}\text{C}$, $\eta_{\text{isentropic}}=75\%$, $\eta_{\text{electrical}}=90\%$.

1.2.2 Hydrogen liquefaction

The liquefaction of hydrogen is achieved by cooling hydrogen gas below its boiling temperature of -253°C . There are many different pathways that can be followed so that such low temperatures are achieved. Heat transfer using heat exchangers, and isenthalpic expansion¹⁴ following compression in reciprocating engines and cryogenic turbines or J-T throttle valves taking advantage of the Joule-Thomson (JT) effect are combined in thermodynamic cycles to transform gaseous hydrogen into liquid. The theoretical background of liquefaction is reviewed in brief next, while the characteristics

¹⁴ Isenthalpic expansion is the process of expanding a previously compressed and cooled gas through a calibrated orifice valve without heat or work exchange with the surrounding environment.

of the equipment required (compressors, expanders and heat exchangers) are discussed in the following chapter.

The JT effect is of special interest to the liquefaction process. Throttling a real gas through an adiabatic valve, results in the reduction of its pressure with a concurrent change in its temperature. The temperature may increase or decrease depending on the substance and its initial temperature. The JT inversion curve, a locus of points in a pressure-temperature plot at which the drop in pressure has no effect on the temperature dictates whether the temperature will increase or decrease during expansion. The inversion curve for hydrogen is shown in Figure 13. At temperatures below the inversion point hydrogen cools upon expansion, while, at temperatures above the inversion point, the temperature of hydrogen increases with expansion. Actually, hydrogen and helium are among few of the gases that undergo an increase in temperature upon expansion under ambient conditions. Therefore, hydrogen needs to be pre-cooled below the maximum JT inversion temperature (-69°C) being at a pressure that corresponds to a point on the inversion curve. Expanding from this pressure to ambient pressure results in the maximum decrease in hydrogen temperature, which however may not be sufficient to liquefy hydrogen. However, the gas that has been cooled by throttling is used to cool incoming gas, thus lowering even more the gas temperature. After successive cooling cycles, the temperature of the gas is lowered to such a temperature that, after throttling, some liquid is formed [17].

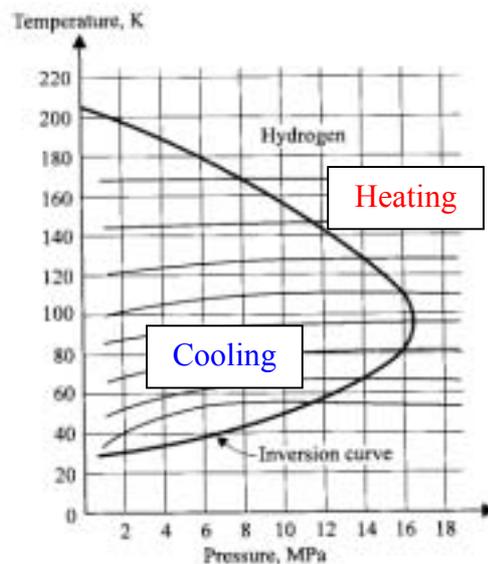


Figure 13 – The J-T inversion curve for hydrogen [17]

Precooling is typically done using cold or liquid nitrogen. In a next step, hydrogen is cooled even further in one or more stages using neon, helium, or hydrogen itself as a working fluid, depending on the liquefaction process (see next). Ultimately, the gas is expanded using a JT valve (in small plants) or a cryogenic turbine (in larger plants) to reach the liquefaction temperature.

The most commonly used liquefaction processes are the Linde cycle and the Claude cycle. However, it is instructive first to review the case the *ideal liquefaction process*, a theoretical process that consumes the least energy for liquefaction when compared with real cycles and thus is used as a measure to compare the efficiency of liquefaction

processes. The process comprises an isothermal compression followed by reversible isentropic expansion to cool the gas and transform it into liquid, see Figure 14. The work needed in this theoretical process is called the *ideal work of liquefaction* and has been calculated as 11.620 MJ/kg by [18, 5] and 11.88 MJ/kg by [19]. The ideal work of liquefaction takes into account the energy required to reduce the temperature of the gas to its boiling point, the energy of the phase transformation from gas to liquid and the energy for the transformation from ortho- to para-hydrogen during cooling. In comparison, the ideal work of nitrogen liquefaction is about 15 times less than the ideal work of liquefaction of hydrogen. The work of ideal liquefaction depends on the initial pressure and temperature of the gas, and the initial and the ultimate concentration of para-hydrogen.

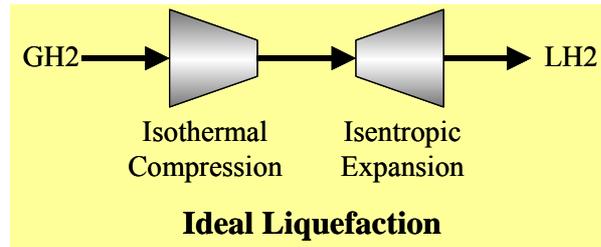


Figure 14 – The ideal liquefaction process: gaseous hydrogen (GH₂) is initially compressed and then expanded in a J-T valve resulting in the drop in its temperature, below its boiling point, forming liquid (LH₂)

The simplest liquefaction process is the pre-cooled Linde cycle, or Joule-Thomson cycle. Initially, the gas is compressed at ambient pressure and subsequently cooled to 80 K in a counter-flow heat exchanger using liquid nitrogen. Heat exchangers are used to lower the temperature even further, below its inversion temperature by transferring heat from the hydrogen stream to the returning cooled hydrogen. Ultimately, the cooled and compressed gas is forced to pass through a throttle valve or a mechanical expander where it undergoes an isenthalpic expansion to ambient pressure, producing some liquid. The liquid is removed and the cooled gas is returned to the compressor via the heat exchangers, Figure 15.

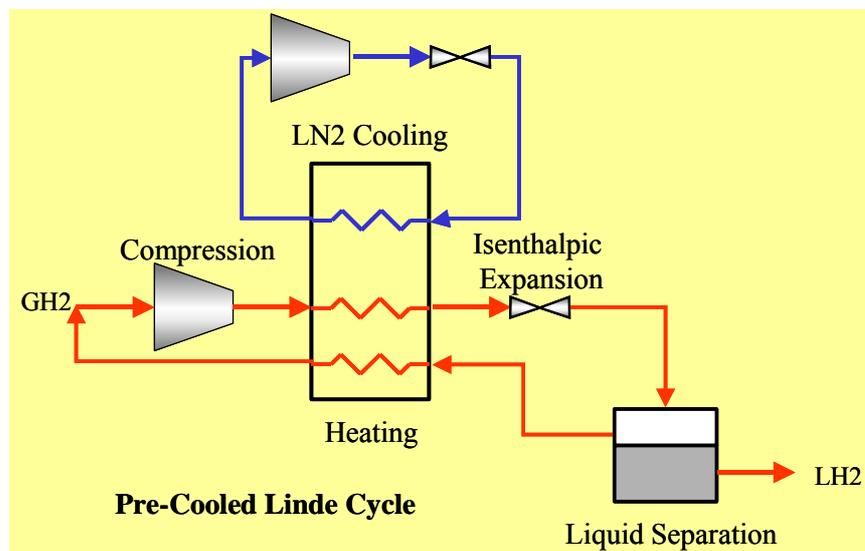


Figure 15 – Liquid nitrogen pre-cooled Linde cycle

Modern high volume liquefaction plants rely on the Claude cycle, a hybrid of the Linde cycle and the Brayton cycle where heat exchangers and mechanical expanders are used to cool the compressed and pre-cooled hydrogen below its inversion temperature, see Figure 16. Other liquefaction processes include the Haylandt cycle, the dual-pressure Linde process, and the dual-pressure Claude cycle. The selection of a liquefaction process depends on the availability of equipment and the costs (both discussed in later sections of this report).

A major problem associated with the liquefaction process is the transformation of hydrogen from the ortho- to para- state during cooling. As was mentioned earlier, with the reduction of temperature, ortho- hydrogen transforms into para-hydrogen with a concurrent release of energy. If ortho-hydrogen remains after liquefaction in concentrations above the equilibrium concentration, see Figure 2, it will eventually be converted into para-hydrogen, releasing energy, thus increasing the temperature of the liquid hydrogen and resulting in losses due to evaporation. To overcome this difficulty, catalysts are used in the liquefaction process (typically embedded in the heat exchangers) such as iron oxides, rare earth metals and oxides, etc. to promote the hydrogen transformation during liquefaction. The heat raised during the transformation is absorbed typically by liquid nitrogen.

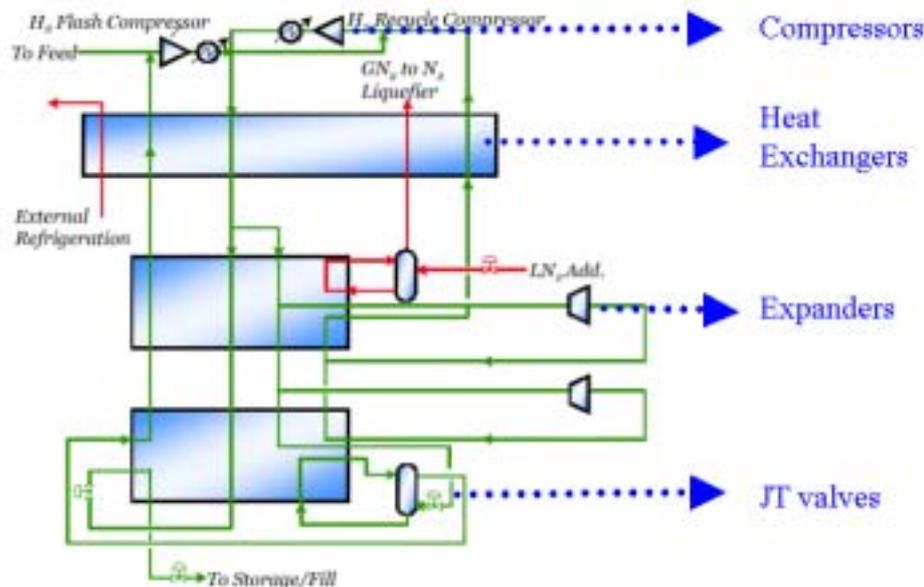


Figure 16 – A schematic of the Claude cycle [14]

2. HYDROGEN STORAGE STATE-OF-THE-ART

Storage is a challenging issue that cuts across production, delivery and end-use applications of hydrogen as energy carrier. It constitutes a key enabling technology for the realisation of a hydrogen-powered economy. Hydrogen can be stored in gaseous form (compressed gas), as a liquid (20K or -253°C) and also in solid media. The first two methods are rather established technologies with several limitations [20] the most important of which is their energy intensive character. Hydrogen solid-state storage, still at its infancy, appears as a possible attractive alternative. This is particularly due to its improved safety and volumetric energy density. Nevertheless, if this solution is chosen there are penalties to be paid in terms of weight efficiencies, thermal management and up-scaling. Intense research is ongoing to overcome the limitations of existing hydrogen storage technologies and to develop viable solutions, in terms of efficiency and safety. The section that follows gives a brief summary of the state-of-the-art of hydrogen storage technologies concentrating on the most promising storage solutions for the short and medium term (2020), depending on the application. It also presents highlights of the main research and development programmes currently running on hydrogen storage related issues, throughout the world.

2.1 Storage in gaseous form

This is currently one of the simplest, most common and efficient storage technologies in use. High-pressure hydrogen is stored in thick-walled tanks (mainly of cylindrical or quasi-conformable shape) made of high strength materials to ensure durability. The storage tank design, which is based on classic deterministic engineering approaches, is not yet optimised: the tanks are actually over-sized; there is inefficient use of material and a rather poor assessment of the pressure vessel lifetime [21, 22].

According to the European Integrated Hydrogen Project EIHP [reference www.eihp.org], which is leading the development of global regulatory standards for hydrogen testing and certification of hydrogen refuelling infrastructure components and systems, compressed gas hydrogen storage vessels can be classified in four types as:

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

The most advanced lightweight storage system for the case of compressed gas consists of a vessel, which is actually an advanced composite tank using a non-load-bearing metallic (Type III) or plastic (Type IV) liner axial and hoop wrapped with resin-impregnated continuous filaments (Figure 17). These pressure vessels are attracting most of the interest of the scientific community. Their structure is based on two fundamental components: the liner, essentially a barrier for hydrogen permeation and the composite structure that ensures the mechanical integrity of the tank. Research is

directed towards the development of new methodologies for reliability design and safety qualification of these high-pressure storage systems. Also, efforts are concentrated on the extension of these techniques to the next generation of compressed hydrogen storage systems: tanks with complex shapes, optimal use of materials and of high safety level [23].

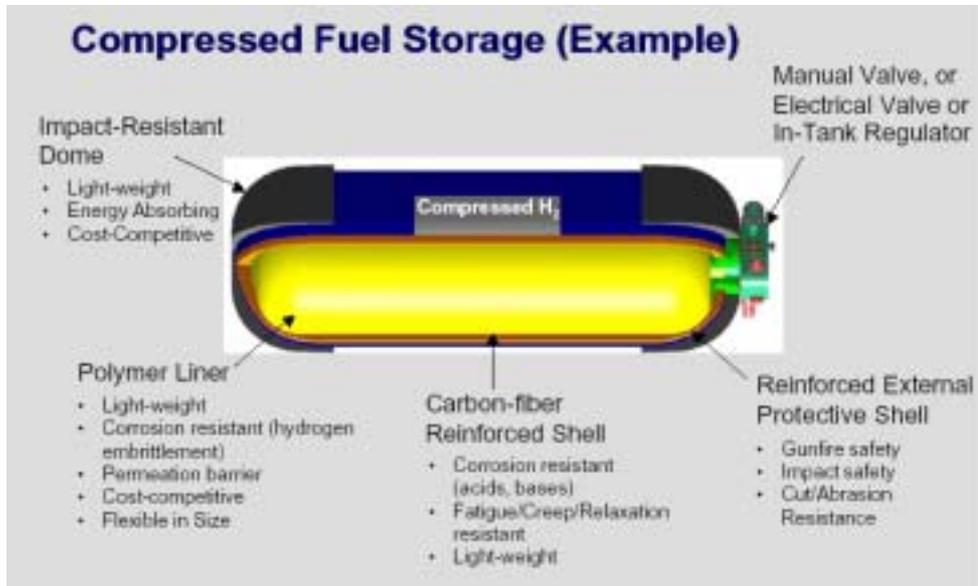


Figure 17 – Schematic of a compressed gas storage tank and its components [22]

There are some European companies working in this area mainly using their experience from compressed natural gas developing compressed gas hydrogen composite tanks. Some examples are: Dynetek GmbH a subsidiary of Dynetek Industries working on Type II cylinders with stainless steel liner; Composites Aquitaine (EADS group) in France; Faber in Italy using metallic liners; CEA and Ullit in France, and also COMAT GmbH in Germany who are developing Type IV cylinders [24]. Japan is not actively involved in R&D programmes on compressed gas storage. However, several Japanese car manufacturers such as Toyota, Honda, Nissan and Suzuki are launching pre-series of Fuel Cell Vehicle fleets equipped with compressed gas tanks at 350 bar designed by Dynetek Industries Ltd. and Quantum Technologies. These are companies linked to car manufacturers actively involved in the research and development on Fuel Cell Vehicles (FCV) [24]. Dynetek Industries have recently reported that their latest high-pressure hydrogen storage cylinders have been tested to 825 bar [25]. These cylinders will be used for storing hydrogen for stationary applications. According to the manufacturer, they have a nominal storage capacity of 170 litres (water content), a service pressure of 825 bar and a maximum fill pressure of 1094 bar. They consist of a thin-walled liner made from aerospace-grade aluminium, they are seamlessly formed, with no welds or other bonding points. This method, as claimed by the manufacturing company, promises good sealing performance of the liner. Quantum Technologies under its partnership with General Motors recently claimed having designed a 700 bar composite tank allegedly increasing to 270 km the driving range of hydrogen-powered fuel cell vehicles. This is a 60-70% improvement, compared to an equivalent-sized 350 bar system, with the refuelling process taking less than 5 min. It is noted that for large commercialisation a 480-560 km range is required [26]. This system was approved by TÜV, and it is said to be validated according to the EIHP.

2.2 Storage in liquid forms or media

Hydrogen in liquid form has a considerably higher energy density than in its gaseous form, making it an attractive storage medium. In terms of application, liquid hydrogen and the enabling technology have already been used in space (Space Shuttle, Ariane) but also in military aircrafts. Considering surface transport, a number of cars running with hydrogen in newly designed vessels with losses by evaporation to below 1.5 mass% per day have been developed and tested. Also, automated liquid-hydrogen filling stations have been built [28].

This hydrogen storage technology is rather effective but has disadvantages, mainly the energy required to liquefy the gas and the strict control needed on the container temperature stability to avoid any risk of overpressure. It also requires cryogenic vessels and suffers from hydrogen losses through evaporation from the containers, particularly the smaller ones (they have a larger surface to volume ratio than large containers, hence larger losses of hydrogen). The continuously evaporated hydrogen may be catalytically burnt with air in the overpressure safety system of the container or even collected again in a metal hydride.

The cryogenic vessels used to store liquid hydrogen, sometimes also called cryostats, are metallic double-walled vessels with insulation, sandwiched between the walls. To minimise if not eliminate thermal losses, effects of thermal radiation, thermal convection and thermal conduction have to be taken into account when designing the vessels (Figure 18) [27]. The inner vessel that contains the cryogenic hydrogen is insulated with a multi-layered material with spacers between each layer acting as thermal barriers. This inner vessel is mounted within the outer vessel by means of specially designed internal fixtures. The resulting volume between the two vessels is evacuated to avoid possible heat leaks ('vacuum super insulation') by thermal convection. Deep knowledge of cryogenics is required to properly design and select the materials for the internal fixtures of the vessel/tube system for injecting and extracting the hydrogen, in order to minimise heat leaks by thermal conduction. The complex design of a liquid hydrogen vessel system is schematically illustrated in Figure 18.

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. These designs will meet the higher requirements regarding environmental conditions and vehicle safety but also cost-effectiveness for subsequent series production. Taking into account market constraints, development of composite tanks may yield cost effective materials and processes [24].

Even though there is so much caution on the design part of these storage tanks to ensure protection from unwanted heat entry, cryogenic liquids and therefore hydrogen do evaporate ("boil-off") due to the impact of heat on the tank system. This phenomenon cannot be avoided, but only minimised. If a vehicle equipped with such a system is not used for a rather short time (about 3 days), the tank pressure rises as a result of the heat ingress. A critical pressure value is finally reached that triggers unacceptable hydrogen evaporation losses. This situation may improve by using a re-cooling system (developed by Linde AG) that allegedly minimises evaporation losses. As a result, the critical time before boil-off occurs may be extended (more than 12 days) [27].

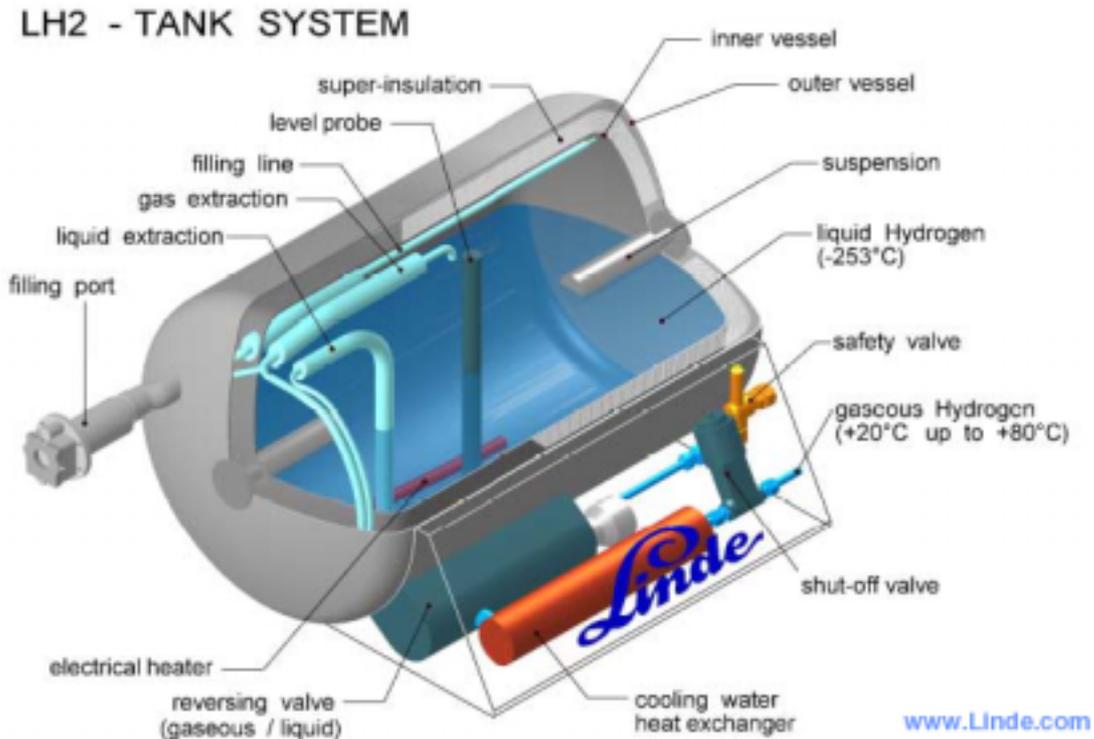


Figure 18 – Schematic representation of a cryogenic vessel – design and components
 [Reference: Linde AG]

Other issues associated with liquid hydrogen are the fuelling equipment and transferring lines, which have to be properly insulated to avoid losses. The weakest link in the whole process is the dismantlable part known as “cryogenic coupling” in the connection region of the two cryogenic transfer lines. Linde AG claims that it has an improved design for this component with potential for further optimisation. It promises an easy and safe handling operation, with minimised liquid hydrogen losses, high filling rate and short filling/refilling and coupling/decoupling times.

2.3 Storage in metal hydrides

Metal hydrides are based on metallic alloys and they act like a sponge absorbing gaseous hydrogen. Through a chemical reaction, solid metal hydrogen compounds are formed, under hydrogen pressure, and heat is released. Conversely hydrogen is released when heat is applied to the materials, through, for instance, heating of the tank and by reducing the pressure. The hydrogen molecule is first absorbed on the surface and then dissociated as strongly bound, individual hydrogen atoms. The metals are alloyed to optimise both the system weight and the temperature at which the hydrogen can be recovered. When the hydrogen needs to be used, it is released from the hydride under certain temperature and pressure conditions. This process can be repeated many times without loss of storage capacity [28].

Storing hydrogen in solid materials is, in principle, an alternative, high volume and safe (the hydrogen release is exothermic and heat is needed to proceed) but also efficient storage method. The key element is the ease of hydrogen recovery that is reflected in the dissociation pressure of the material, a temperature dependent property. The

mechanisms and the thermodynamics involved in hydride formation from gaseous hydrogen should be better understood though. Tackling kinetics and performance in hydrides has proven to be a rather challenging issue, particularly when these materials must demonstrate high hydrogen capacities and reversibility in the temperature range of 270-360K and at pressures of 1 to 10 bar – see Figure 19 [20, 28-30].

Metal hydrides can be classified in:

Interstitial metal hydrides: offering a storage capacity of 1.8wt.% (percentage of hydrogen by weight) at 60-70°C [31] and [32], or as high as 3wt.% for quasi-crystalline Zr-Ti-Ni alloys, [33, 34] but with a rather poor reversible hydrogen uptake [24].

Activated magnesium rich powders: reaching in the laboratory up to 5-6wt.% at 260-280°C (at 1 bar) but their kinetics need to be improved using cost effective procedures [24].

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 [35, 36]. Lab-scale alanates are good candidates for designing hydrogen storage tanks since they can reach 5wt.% at 180°C, 1 bar, but there is still room for improvement in their hydrogen absorption/release kinetics, via lattice distortion [37, 24].

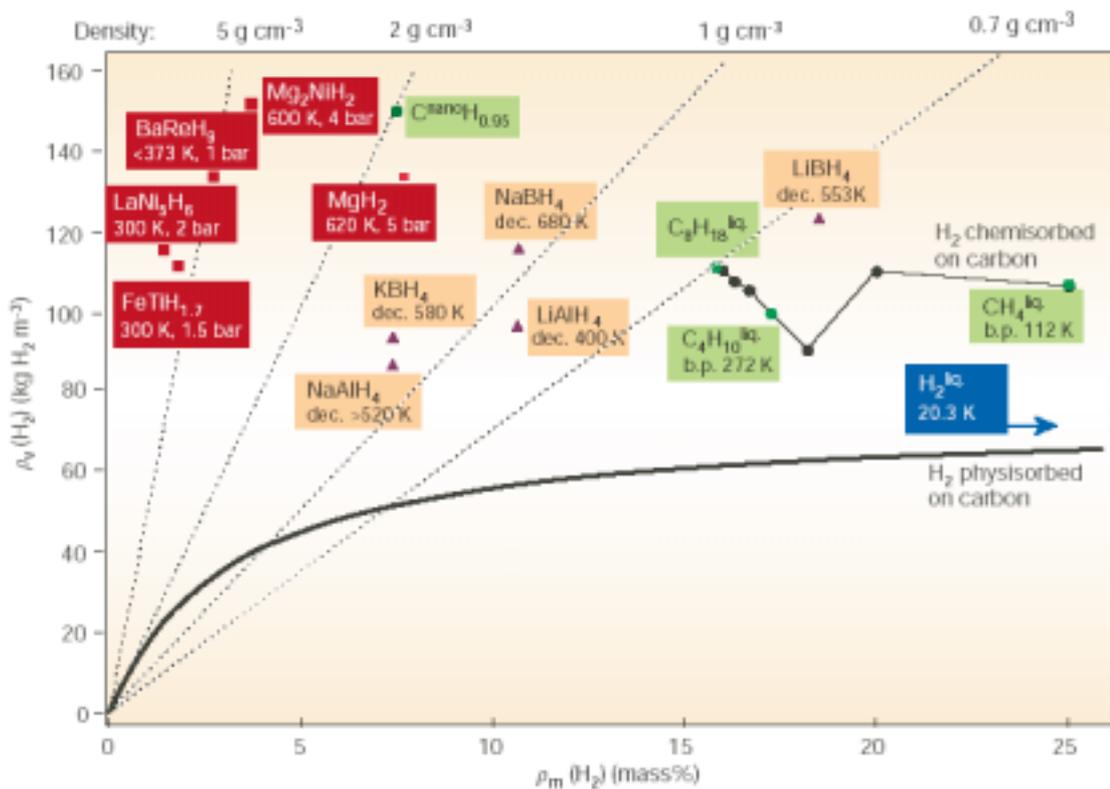


Figure 19 – Hydrogen storage capacity (considering mass and volume) for metal hydrides, carbon nanotubes, petrol and other hydrocarbons [28]

Under the International Energy Agency Task 17 project, a hydrides database has been created. It includes more than 2400 hydrides forming metals and alloys. The results at this stage indicate that systems based on reversible middle or low temperature complex

hydrides of light metals such as Na, Li and Al can be considered promising hydrogen storage media. Their performance though is still hampered by unsatisfactory rates of the hydrogenation/dehydrogenation¹⁵, cyclic instability and the need to operate at relatively high temperatures above 150°C and at pressures of 60 to 150 bar [38 - 41].

2.4 Storage in porous systems

Porous systems compared to gaseous and liquid media offer the advantage of lower pressure hydrogen storage, increased safety, design flexibility and reasonable volumetric storage efficiency. However, the technology is not yet mature. Also, there are no imminent solutions for avoiding weight/cost penalties, and tackling thermal management issues associated with this option. The materials included in this category are:

- Carbon based materials, nanotubes, nanofibres, activated carbons, activated fibres, carbons from templates, powders, doped carbons and cubic boron nitride alloys.
- organics, polymers, zeolites, silicas (aerogels), porous silicon.

2.4.1 Storage in carbon-based materials

Hydrogen, depending on the applied pressure and temperature, can be adsorbed and reversibly stored on solid surfaces as a result of physisorption (van der Waals forces) or chemisorption (as in metal hydrides). Materials with large specific area like nanostructured carbon and carbon nanotubes are possible substrates for physisorption. In terms of their storage capacity, curved structures such as carbon nanotubes appear to be more efficient as compared to high surface area graphite (25% extra at low temperatures) (Figure 20).

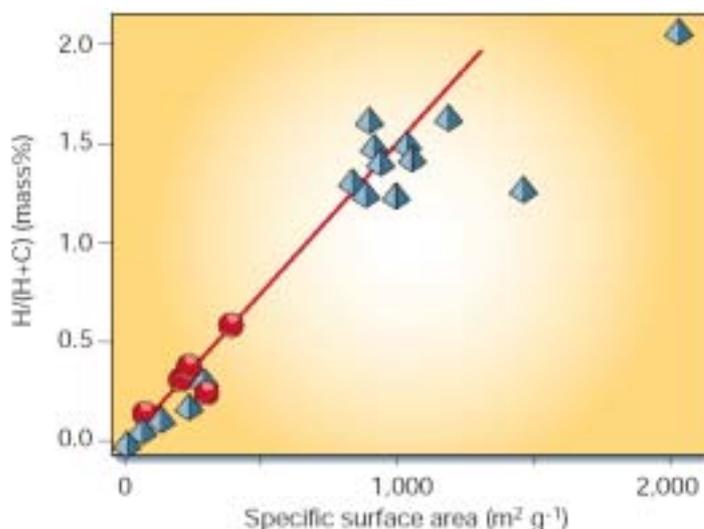


Figure 20 – Reversibly stored hydrogen in carbon structures as a function of their specific area – circles indicate nanotubes (best-fit line given) while triangles correspond to other nanostructured carbon samples [28]

¹⁵ *Hydrogenation*: a chemical reaction between molecular hydrogen and an element or compound (adding hydrogen to the molecule), ordinarily in the presence of a catalyst. *Dehydrogenation* – removing hydrogen from the molecule.

This behaviour is due to their structure interacting with the hydrogen molecule and to the greater attractive forces acting compared to the open flat surface structures [5, 28]. Such an effect diminishes with increasing temperature.

Looking into the research results that have been reported over the last years, there are conflicting data on the reversible storage of hydrogen in carbon nanotubes. This is mainly caused by insufficient characterisation of the carbon material used [28]. Extraordinary hydrogen storage capacities of an order of a magnitude higher than anything known to date, were reported in 1998 [42]. These capacity values could be questionable and may have to be seen with some scepticism since they are rather inconsistent and not reproducible. Hydrogen storage properties of nanotubes are not yet fully understood and explored. Nevertheless, there is still scientific interest particularly on Single Walled NanoTubes (SWNTs) that could be seen as a promising medium for the safe storage of hydrogen. Most researchers agree that careful and systematic investigations should be undertaken concentrating on the development in order to improve the sorption behaviour and also on the adequate characterisation of these materials. Procedures such as ball milling and pre-treatment appear to increase the number of defects such as dangling carbon bonds and can result in highly defective structures where hydrogen is weakly chemisorbed and easily released.

2.4.2 Storage in other non-carbon porous materials

Self-assembled nanocomposites/aerogels are essentially nanostructured highly porous solids with very low densities. They are in fact a special class of open-cell foams with an ultrafine cell/pore size (<50 nm), high surface area (400-1100 m²/g), and a solid matrix composed of interconnected colloidal-like particles or fibres with characteristic diameters of 10 nm. The hydrogen sorption in these materials is done by physisorption and through an acid-base reaction. They are inexpensive, light (3 – 500 kg/m³), rather stable and may have the ability to be commercially manufactured while their properties are easily controlled and so is the hydrogen sorption. Silica aerogels (produced by liquid-to-gas drying of wet silica gel) are the most promising. Work is currently targeted towards possible modifications in their chemical structures to optimise hydrogen sorption properties.

Zeolites are crystalline nanoporous materials and are considered as an advanced storage method for hydrogen with a maximum capacity measured to date of 2.5wt.% (5 kg/m³). They are available at low cost, chemically and thermally robust, with a rather good structural reproducibility, environmentally friendly and are considered to be safe. Research and development concentrates on optimising their structure (small versus large pores) and improving their adsorption of hydrogen via chemical modifications of their surfaces [36].

Metal organic materials are zeolitic materials using carbon as backbone, or materials using carbon and metals or even organic microporous or polymer synthesis materials. They have a flexible composition with a large pore structure with tailored properties and thus potential for high volume hydrogen storage when appropriate chemical modifications are made [36].

2.5 Storage in other media & latest developments

2.5.1 Other storage media

There follows a brief summary of other hydrogen storage methods. A number of these materials are categorised by some researchers as porous systems, but here are classified as “other”.

Glass microspheres: Tiny hollow glass spheres can be used for safely storing hydrogen [36, 43]. These glass spheres are warmed, and their walls permeability is increasing. Then, they are filled by immersion in high-pressure hydrogen gas. Following this, the spheres are cooled down to room temperature and the hydrogen is trapped inside the glass balls. Subsequent increase in temperature releases the hydrogen locked in these spheres. The challenge is to figure out how to activate/deactivate the whole process [43]. They have the potential of being a portable, rather safe (they contain hydrogen at a low pressure), inexpensive and rechargeable/recyclable hydrogen storage medium [36]. There is a research activity ongoing in Europe in this area, whereas the Department of Energy of the United States had chosen in 1999 to suspend research on microspheres following a cost and performance analysis [44].

Hydride slurries are a pumpable mixture of fine, solid metal hydride particles and a liquid (usually a mineral oil). Hydrogen stored as a metal hydride in slurry with an organic carrier (calcium and lithium hydrides) can be of high-purity. It can be released from the metal complex through chemical reactions while the organic carrier is recovered and recycled. Work focuses on optimising slurry production, pumping, storage, and organic recovery and thus exploring the degree of viability of this technology [35].

Boron Nitride Nanotubes: These are roughly equivalent to carbon nanotubes in terms of advantages, but are based on boron nitride rather than carbon. They are currently being investigated to verify their high hydrogen storage capacity and better understand the related adsorption/desorption mechanisms [36].

Bulk Amorphous Materials (BAMs) are new promising metallic materials based on multicomponent alloy systems, e.g. Ti-Al-Fe based BAM (maximum 6wt.%). They are loosely packed with porous defects (interstitial holes for hydrogen storage) of controlled size and distribution, in super cooled liquid phase. They appear to have fast sorption kinetics, embrittlement and disintegration resistance and may also have the possibility for low cost mass production. Work is concentrating on verifying their storage capacity and hydrogen release [36].

Hydrogenated amorphous carbon: These are composed of stressed graphitic “cages”/nanotube sponges able to store 6-7wt.% hydrogen, are rather stable at 300°C with a potential for high hydrogen content and alleged potential to rapidly release hydrogen between 200-300°C. The reversibility and the understanding of their sorption kinetics and their respective structure are still open questions [36].

Chemical storage media (methanol, ammonia etc): The hydrogen is often found in stable chemical compounds and it can then be released by a reaction the exact nature of which depends on the type of storage compound. In this case hydrogen is produced on demand by various techniques such as ammonia cracking, partial oxidation, methanol cracking, and there is no need for storage.

Hybrids: The hydrogen research community is also considering the option of combining storage solutions to create systems that are known as ‘hybrids’ (for example:

hydrides/high pressure, porous/hydrides hybrid systems). The aim is to fully exploit the major advantages offered by some of these storage options while easing a number of the problems and drawbacks associated with them [21].

2.5.2 Latest developments in hydrogen storage media

There is a lot of new activity in the hydrogen storage research area and various articles in scientific journals and magazines are frequently reporting on new findings and promising results.

Scientists from the Research Centre of Karlsruhe (FZK) [45], have managed to charge nanoparticles with hydrogen in only 7-8 minutes using a custom-made catalyst from titanium nano clusters. Currently the time it takes for the hydrogen to be absorbed and released results in a refuelling process of more than an hour, during which the fuel quality suffers. The material may also be employed in applications such as camcorders or laptops.

A new class of nanoporous materials [46, 47] have recently been developed. They are like “crystal sponges” from metal and organic blocks made by molecular design showing potential for hydrogen storage. These materials – Metal-Organic Frameworks (MOFs) – made from low-cost ingredients (zinc oxide and terephthalate), are reported as superior to metal hydrides. They are said to be capable of storing large amounts of hydrogen molecules at normally encountered temperatures and pressures, without much energy cost. MOFs are scaffolds of linked rods, which can be modified to increase the material’s storage capacity. Such a structure makes for maximum surface area; just 1g of a MOF has the surface area of a football field.

A new technology to store hydrogen in a safe, rather compact way in a chemical called sodium borohydride (“Hydrogen on Demand”) has been recently reported (Millennium Cell Inc. – [48]). Sodium borohydride is created from borax (a common ingredient in some detergents) that is dissolved in water to produce a stable and non-flammable liquid. When the liquid is combined with a specific catalyst, an instant chemical reaction produces liquid borax and pure hydrogen gas. The hydrogen can then be immediately burned in an engine or used in a fuel cell, which converts the gas directly into electricity and water. It is quoted that the borohydride powder holds more hydrogen than the most densely compressed air tank. As sodium borohydride releases its hydrogen, it turns back into borax so it can be recycled. This is still though a rather costly storage solution since the catalyst used is composed of a very rare and expensive earth metal called ruthenium. Also the sodium borohydride “fuel” is itself expensive –to produce pure hydrogen to use for converting borax into borohydride requires significant amount of energy. As a storage solution though it seems to have potential but more research is needed to make it competitive with gasoline production costs.

2.6 Utilisation

2.6.1 Transport Applications

Storage is an important issue for making hydrogen an economically competitive fuel solution for mobile and transport applications against today’s rather inexpensive liquid hydrocarbons. It has to comply with a number of requirements dictated by the manufacturers and end-users. The automakers are asking for a hydrogen storage

solution that is safe, economical, with no weight penalties [49]. Quite importantly assurances must be given that the refuelling infrastructure will be there. On the other hand, consumers are looking for vehicles that are at least comparable to today's conventional gasoline vehicles in terms of performance, efficiency, cost, vehicle range, comfort, convenience, reliability, refuelling ease, and cost-competitive fuel.

A hydrogen-run road vehicle can either burn hydrogen rapidly in an internal combustion engine (ICE) with oxygen from air, or 'burn' it electrochemically. In the latter case, the 'burning' is done with oxygen from air in a fuel cell; the fuel cell then produces electricity (and heat) and drives an electric engine [50]. In the first 'solution', the efficiency of the transformation from chemical to mechanical through thermal energy is limited by the Carnot efficiency. It is actually slightly higher for hydrogen-air mixtures (around 25%) than for petrol-air mixtures. In the case of the electrochemical 'burning', the efficiency of the direct process of electron transfer from oxygen to hydrogen is quoted as being able to reach 50–60%, twice as much as the thermal process [28]. In practice, a modern, commercially available car with a range of 400 km burns about 24 kg of petrol in a combustion engine. For a similar performance, 8 kg hydrogen are needed for the ICE version or 4 kg hydrogen for an electric car with a fuel cell. In this case, hydrogen will occupy a volume of 45 m³ (at room temperature and atmospheric pressure), requiring a tank with considerable storage space (Figure 21). So the big challenge is to find a solution for compacting hydrogen; issues such as materials, technology and safety should also be addressed (Figure 21) [28]. In general, the optimal hydrogen storage solution involves lightweight storage systems with conformable tank shapes adaptable to the space available in various vehicle structures. New concepts have recently emerged and led to shape geometries more suited to vehicle design, like the free-form tanks, but require expensive reinforcement measures to reduce the weight of the storage system. This is not always feasible.

Considering high-pressure hydrogen gas, for 4 kg hydrogen an internal volume of 225 litres is required or 5 tanks of 45 litres each. The novel tanks today are designed to be lightweight, are tested up to 600 bar and are able to be filled up to 450 bar. They are made of high tear resistant carbon fibre composite materials with a special inert inner coating to prevent the high-pressure hydrogen reacting with the polymer [28]. These liners can combine hydrogen chemical compatibility and low permeation. Another solution involves using hydrogen-inert aluminium tanks reinforced with external carbon fibre coatings. Prototype vessels and tanks that are built need to undergo full-scale tests for hydrogen leak/permeation rate, burst pressure limit and pressure cycling fatigue [24]. According to several car manufacturers, there are a number of Fuel Cell Vehicle (FCV) prototypes that have been demonstrated with such composite tanks filled at 350 bar, allegedly able to store between ~3,5 kg and ~4,0 kg of hydrogen, for driving distances of about 300 km for a 70 kW_e fuel cell. The problem is that these tanks are as heavy as 90 kg. Automation and scaling effects in mass production, are also issues that need to be faced since they are directly related to cost.

Cylindrical shape designs are usually considered. However, the main disadvantage in this case is that the fuel would be available at a pressure dropping from 450 bar to zero overpressure, so additional pressure control would be needed. Safety is therefore an important issue and strict safety requirements are currently discussed and debated under the European Integrated Hydrogen Project (EIHP-II).



Figure 21 – Volume of 4 kg of hydrogen (needed to run an electric car with a fuel cell) compacted in different ways as schematically illustrated here; size relative to car size [28]

Compression itself is a dangerous and complicated part of the hydrogen storage question. The latest targets that the hydrogen community is setting for tanks for compressed gas hydrogen storage in fuel cell vehicles, are dictating volumetric energy densities higher than 1400 kWh/m^3 and operating conditions of -40 to $+85^\circ\text{C}$, at pressures as high as 700 bar, but designed for a filling pressure of 875 bar. Challenging requirements are set too for short re-fuelling times of less than 3 to 4 min. Problems such as overheating of the composite vessel structure due to quasi-adiabatic compression, need also to be tackled. Pre-cooling of the hydrogen or the use of heat exchangers may be required to overcome this barrier [21]. Another important parameter is also the gravimetric energy density of the tank. However there is a trade-off between improved gravimetric performance from using higher-grade carbon fibre and the overall cost per tank [21]. In addition, compression itself consumes energy and adds to expense. Further work may be required on the compressors development considering new materials, improved efficiency, and more compact designs. Finally, concerns such as recycling processes for carbon fibre reinforced composite material need to be thoroughly investigated in line with environmental constraints and requirements of the car manufacturing industry and European Directives.

Addressing the case of liquid storage for mobile applications, the latest design cryogenic tanks have a hydrogen storage capacity up to 10 kg, are double-walled, cylindrical in shape, with a shell from stainless steel or aluminium alloy. Both materials are hydrogen brittleness-resistant and show limited if not negligible hydrogen permeation. However aluminium also offers extra advantages such as low specific weight, high strength and good characteristics on heat conductivity. On the other hand, stainless steel results in a tank-system (including valves and heat exchanger) weight of about 150 kg [24]. When new fibre composite materials are used for the production of these tanks significant weight reduction and greater strength may be achieved over the conventional fuel tank for similar energy storage capacity. Several layers of specially designed insulation foils are also put using state-of-the-art technology in between the inner and outer vessel to reduce the heat entry by thermal radiation. Support structures,

keeping the inner tank in position to the outer tank, are made of materials with low thermal conductivity (e.g. glass- or carbon fibre reinforced plastics) with special active cooling systems that may increase the time before considerable evaporation losses occur to more than 10 days [24].

Europe is rather well placed in the market of cryogenic vessels. Prototype liquid hydrogen tanks for fuel cell and combustion engine powered vehicles are built in Europe by Air Liquide, Linde AG, Messer-Griesheim (also supplying the USA market) and Magna Steyr. To the knowledge of the writers of this report, there are no manufacturers of cryogenic systems for automotive application within the USA or Japan. Concerning applications of this technology, several car prototypes, such as the BMW 750hL (8 kg LH₂) and the Opel HydroGen3 (4.6 kg LH₂) are using state-of-the-art liquid hydrogen tanks [24]. According to a recent announcement [51], General Motors (GM) and BMW plan to join forces to develop refuelling devices for liquid hydrogen vehicles.

There exist a number of materials that are currently being investigated, under national and international research programmes, as potential solid storage media (hydrides, porous materials) for hydrogen in transport applications. The list includes magnesium based alloys, alanates, borohydrides, lithium amides, conducting polymers, derivatives of traditional storage alloys, metal hydride/organic slurries and carbon-based materials. In Europe, many research groups are actively involved in the research and development of hydrogen solid storage materials [24]. The International Energy Agency (IEA) is also directing its research programmes towards the development of solid storage media. The targets that IEA is setting is materials with at least 5wt.% hydrogen capacity and a decomposition temperature of less than 373K [52]. The Japanese WE-NET (World Energy Network) was aiming some years ago at solid storage materials demonstrating more than 3wt.% hydrogen storage capacity, desorption temperature below 393K, operating pressure below 10 bar and retention of more than 90% of the initial capacity after 5000 cycles [53]. In the USA, the Department of Energy goal was originally set for vehicular hydrogen storage systems with 6.5wt.% but will soon be revised to a higher value [54] – see “Targets” under the “Utilisation” section of present report. International companies active in the hydrogen research are joining forces to address solid storage issues. As an example, Shell Hydrogen, Hydro-Québec CapiTech (HQ CapiTech) and GfE Gesellschaft für Elektrometallurgie (GfE), have established a joint venture - HERA Hydrogen Storage Systems Inc. Their aim is to develop, manufacture and market hydrogen storage products with a special interest on metal hydrides that they see as the most promising hydrogen storage technology [55, 56].

2.6.1.1 R&D issues and priorities

Considering the transport sector, to achieve a comparable driving range and performance as with modern diesel vehicles, a breakthrough in on-board vehicle hydrogen storage technology may still be required. Conventional storage such as compressed gas cylinders and liquid tanks can be further improved and strengthened, become lighter and less expensive. Additional research and development work is also required to appropriately evaluate and further advance the performance of hydrides and porous systems (see table below with list of barriers and potential of various storage options) [57, 58].

Table 5 – Benefits and barriers of hydrogen storage solutions – Reference [57].

Hydrogen storage technology	Benefits	Barriers
<i>Compressed gas cylinders</i>	Well-understood up to pressures of 200 bar; generally available; can be low cost	Only relatively small amounts of H ₂ are stored at 200 bar; fuel and storage energy densities at high pressure (700 bar) are comparable to liquid hydrogen, but still lower than gasoline and diesel; high pressure storage still under development
<i>Liquid tanks</i>	Well-understood technology; good storage density possible	Very low temperatures require super insulation; cost can be high; some hydrogen is lost through evaporation; energy intensity of liquid hydrogen production; energy stored still not comparable to liquid fossil fuels
<i>Metal hydrides</i>	Some technology available; solid-state storage; can be made into different shapes; thermal effects can be used in subsystems; very safe	Heavy; can degrade with time; currently expensive; filling requires cooling circuit
<i>Carbon structures</i>	May allow high storage density; light; may be cheap	Not fully understood or developed; early promise remains unfulfilled

Gaseous storage

Near future research with respect to the design of compressed gas cylinders may focus on improvements in existing fabrication concepts for mass application. Work could also be directed towards meeting the car manufacturers’ requirements of using high pressure 700 bar compressed gas vessels. These requirements include improvements in terms of operation conditions, energy density, fractional mass (weight percent) of hydrogen, compatibility with filling process in hydrogen fuelling stations, safety and on-board monitoring, and finally recycling of hydrogen storage vessels.

With respect to the liner materials and design, metallic (for Type III cylinders) and thermoplastic liners (Type IV) as well as different polymer manufacturing solutions could be subjects for thorough investigation. Work is already focussing on the evaluation of modified steels for the manufacturing of seamless steel liners resistant to hydrogen embrittlement [24]. Research may also concentrate on the performance

assessment of different liner materials and components with respect to their hydrogen permeation rate, particularly through plastic liners for type IV vessels, and to the hydrogen compatibility, especially for steel liners and metallic valves and bosses at the ends of the liners [24]. In addition, a better understanding of the material properties' influence upon the functional lifetime of each component (liner, composite structure) is required. Material properties' variability with mechanical loading and 'environmental conditions' encountered in public and industrial use (weather, vibrations, chemical aggression, installation errors) or even with gas parameters (nature, temperature, pressure) is an important element in the development of improved reliability design tools for novel high-pressure storage systems [21]. Researchers then will need to undertake full-scale tests on tank prototypes or parts manufactured using new risk design assessment methodologies in order to test their validity and degree of sensitivity to various parameters (statistical load distributions, environmental conditions and permeation, material properties and life time performance). Such design techniques may be used to guide the engineers and regulators to develop design standards, process control regulations and in-service inspections.

There is already a concentrated effort for optimising manufacturing processes of plastic and steel liners, of the liner 'wrapping' material as well as of the multi-cylinder fabrication concepts, in an attempt to move from prototypes and small quantities into mass application and a high grade of automation in cylinders production.

To meet the requirements of safety, reliability and fast re-fuelling of cylinders up to 700 bar, new components/modules may need to be designed and 'fast filling protocols' must be validated. The risk of the vessel overheating due to fast quasi-adiabatic compression and the limitations imposed by the liner material properties need to be carefully addressed. A number of potential solutions to overcome this problem can be investigated and tested 'in action' at fuelling stations on prototype cars equipped with the latest high pressure hydrogen storage tanks [24].

To answer to environmental concerns and efficiently and economically address the issue of recycling, particularly for composite vessels, innovative methods may need to be developed. During recycling, separation of materials and components entering the fabrication of a compressed gas composite vessel must be ensured. A global approach of the materials life cycle assessment and of the quality and re-use of recyclates should be adapted [24]. The whole process though should take into account chemical engineering issues, the car manufacturers industry needs and life cycle analysis results. Also the recycling concepts to be used must comply at the European level with the existing requirements of the End-of-Life Vehicle Directive 2000/53/EC [59]. On-board sensor technologies and novel diagnostics systems whose design is compatible with mass production and recycling standards may also be developed for assessing the pressure vessel structural integrity.

In parallel with the fast filling option, the so-called 'exchangeable rack' concept and its possible implementation should be investigated [24]. It is actually the scenario of having in cars exchangeable tanks of compressed hydrogen as an alternative to static vessels that need fuel station infrastructure and a fast filling procedure.

Storage in liquid forms/media

At the moment, it is rather difficult to accurately predict the liquid hydrogen behaviour and its safe handling outside the laboratory, under non-controlled conditions (when in use by the public). Existing risk assessment analyses (see EIHP programme) for liquid-hydrogen powered vehicles are based on classical fluid dynamics modelling and are not

entirely applicable to the quantum mechanical liquid hydrogen. Therefore there appears to be a need for developing appropriate and validated simulation codes/models for quantum mechanical molecular dynamics. These models must then be up-scaled and finally extended to a macroscopic dynamic model for improved engineering design and safety of liquid hydrogen storage tanks [21].

With respect to the tank, several research teams are concentrating on the actual design and ultimately the cost-effective manufacturing of a novel composite cryogenic tank. This should be even lighter than currently achievable, of a conformable shape and with a storage capacity of 170 l. It should also have a reduced boil-off time holding more than 10 kg ensuring a range of 400 to 700 km autonomy. The final product should satisfy legal, technical, physical and automotive requirements while complying with recycling standards. Obviously, new design concepts may have to be used for these free-form tanks and the manufacturing processes from the raw material to parts will have to be accordingly modified to satisfy mechanical requirements, quality and economic aims of a large production line [24].

Storage in metal hydrides

This class of materials is said to still suffer from lack of systematic, validated data on their main characteristics (stability, gravimetric and volumetric density, temperature of operation, etc.) [21, 24].

In the short to medium term, researchers prefer to concentrate their efforts on alanates and the improvement of their kinetics and in particular on the study of NaAlH_4 that has adequate reversibility and could serve as a ‘model system’. Mg-alanates are also an attractive new storage material candidate for vehicle applications but they have not been yet investigated for reversible hydrogen storage. Nevertheless, these materials may have the potential to overcome the “commercialisation barrier” of 6wt.%, and possess a sustainable elemental composition since Mg and Al are abundant in the earth crust. This is particularly interesting when large fleet of automobiles would have to be equipped with this storage material. [24].

In general, improvements may be needed with respect to metal hydrides sample-preparation and doping for optimising their hydrogenation /dehydrogenation kinetics in order to be able to satisfy performance targets specified by the automobile industry. An issue of concern is also the actual up-scaling of material production processes and the design and development of operational prototype tanks which are safe and easy to handle [24].

Based on current research, solid storage may be a viable storage option for stationary but not for transport applications. Also, hydrides can be seen for use in a hydrogen system towards a premium power end user application (banks, IT centres, hospitals). Hydrides can also be considered as a buffer in renewable energy resources, due to their lower volume demand and higher safety compared to conventional storage alternatives (mainly compressed hydrogen). Obviously, their performance needs to be evaluated against results from conventional methods like compressed gas hydrogen. In a recent scientific presentation on the hydrides potential, the hydrogen storage challenge is seen to be translated into 10wt.% and decomposition at 100°C for AlH_3 , 7.7wt.% and decomposition at 175°C for $\text{Mg}(\text{AlH}_4)_2$, 14.8wt.% for $\text{Mg}(\text{BH}_4)_2$, 14.6% wt.% for $\text{Al}(\text{BH}_4)_3$, while the development of other promising hydrides could also be an option [58].

As stated earlier, porous storage media and in particular carbon-based materials have attracted a lot of attention over the last years and triggered heated discussions on their potential. This is particularly due to the fact that no reproducible data exist to justify the really high, rather unrealistic, hydrogen storage capacities claimed in the past by several investigators. The results obtained so far on carbon nanotubes as hydrogen storage media seem conflicting and suffer from rather insufficient characterisation of the materials used [20, 60-62]. Therefore, marketing of carbonaceous materials as hydrogen storage media should be seen as a long-term option. This is also confirmed by the fact that recent industrial & commercial efforts (see joint ventures on hydrogen) are at the moment concentrating on metal hydrides systems [28, 63].

Research for this class of materials is still at the laboratory stage targeting materials development with optimal hydrogen storage capacity, under low pressure-temperature. Specific requirements in terms of cost, non-toxicity, recycling and re-use are also taken into consideration. A better understanding of the fundamentals of hydrogen adsorption/desorption processes and of the relationship between material properties and process parameters, may be required. Standardised characterisation procedures, validated materials data and qualified preparation processes are still lacking. This is the reason that many researchers are claiming that at this point ‘round robin’ and benchmarking exercises leading to the actual definition of standardised material production and characterisation procedures, are needed [21]. A number of papers and reviews recently published on the stage of the knowledge of the hydrogen uptake by carbon nanostructures [64, 65] agree on the most recommended methods. Nevertheless, there is still controversy [66] on the questions related to the sample purity. In any case, more coordinated and conjugated efforts may be essential for understanding the hydrogen sorption mechanism in carbon nanostructures [67].

Several groups have reported theoretical modelling results and simulations on hydrogen adsorption in carbon materials and are in most cases more favourable than experimental results. However, these simulations need refining to identify a ‘working combination’: an adsorption mechanism compatible with the hydrogen storage requirements of 6.5wt.% and a volumetric density for adequate hydrogen storage capacity for practical applications (see transportation), at room temperature. To ensure efficient hydrogen storage in carbon nanotubes, two issues still need to be resolved [68]. The first is whether hydrogen adsorption in Single Wall NanoTubes (SWNTs) is less or greater than in slit pores. If it is greater, then the ‘ideal’ micropore volume fraction, size/shape and ‘suitable’ pore diameter for reaching the targets set for mobile applications must be identified [69]. The other important issue is whether hydrogen adsorption occurs in the interstitial channels between adjacent nanotubes in a rope of SWNTs. As a next step, future efforts can focus on developing experimental procedures to provide carbon materials with tailored-made structures for maximum hydrogen storage capacity.

Research work is already directed towards optimisation of the development and post-production routes (purification, grinding, activation, conditioning, doping...) for yielding, in a cost-effective way, reproducible materials [21]. In parallel, efforts are also concentrating on transferring these processes to mass production at a reasonable cost. As a next step engineering solutions will need to be found for the design and manufacturing of prototype tanks using different porous materials.

For other storage media, there are some common research and development issues that may be addressed. These issues include maximum storage capacity, energy balance versus life cycle analysis, also better understanding of their absorption/desorption kinetics and their potential for low cost, high volume and above all safe storage [36].

2.6.1.2 Targets

In order to set a strategy for the penetration and actual implementation of the hydrogen technologies into the energy market, national/international institutions, industrial bodies and governing authorities have been involved in the establishment of hydrogen related programmes. As a result, roadmaps have been drawn and milestones have been decided whereas in several cases specific targets for the individual hydrogen technologies, including storage, have been determined.

A major European initiative, in line with the EU policy support to clean energy technologies, is the establishment of the High Level Group for Hydrogen and Fuel Cells. It was formally launched in Brussels on 10th October 2002 by the Vice President of the European Commission Mrs Loyola de Palacio, responsible for Energy and Transport, and the Research Commissioner Philippe Busquin. This is an action supported by the European Research Area [70] that fosters a structured, cohesive European approach for fuel cell and hydrogen technology acquisition and deployment. This High Level Group is actually an informal advisory body, with the mandate to provide expert opinion on determining the prospects for and economic impacts of moving towards a sustainable energy hydrogen-based economy. It consists of 19 stakeholders, senior representatives from major European automotive and energy companies, small and medium enterprises, research centres, utilities, policy makers and users associations. Their aim is to formulate a shared integrated EU vision on the hydrogen economy potential and outline the research and deployment strategy, the actual steps and the timescales required for delivering it. As a first deliverable, this High Level Group (HLG) has recently prepared a vision report – “Hydrogen energy and fuel cells - a vision for our future” [57], outlining the research, deployment and non-technical actions that would be necessary to move from today's fossil-based energy economy to a future sustainable hydrogen-oriented economy with fuel cell energy converters. This summary report was presented as a communication to a major European conference “The hydrogen economy – a bridge to sustainable energy” held in Brussels on 16-17 June 2003 [71].

According to the recommendations of the HLG, Europe should be taking five specific actions to a hydrogen energy future. Firstly, a political framework should be put in place for enabling the new technologies to penetrate the market. A strategic research agenda at European level concentrating and integrating research efforts at community and national level should also be drawn up. This should be accompanied by a deployment strategy with prestigious demonstration and “lighthouse” projects that would form the backbone of a trans-European hydrogen infrastructure. A European Roadmap for hydrogen and fuel cells, considering different options and setting corresponding targets for research, demonstration, investment and commercialisation will be the tool for guiding the transition. For implementing the above the HLG is recommending the formation of a Hydrogen and Fuel Cell Technology Partnership steered by a European Hydrogen and Fuel Cell Advisory Council, to provide advice, stimulate initiatives and monitor progress, based on consensus among the stakeholders [57, 71]. Such a partnership is expected to set clear objectives and commercialisation targets but also to assist in establishing a centre for consolidating and disseminating information to effectively co-ordinate the shift towards hydrogen and fuel cells.

The HLG is advising on pursuing an enhanced international co-operation. Working in partnership with North America and the Pacific Rim, as well as with the developing

world, will speed up the introduction of sustainable energy technologies by co-operating on technology bottlenecks, codes and standards, and technology transfer. Finally, in their report the HLG members are presenting a preliminary, skeleton proposal for the main elements and timescales of the European roadmap on the production and distribution of hydrogen, hydrogen systems, and fuel cells – see Figure 22.

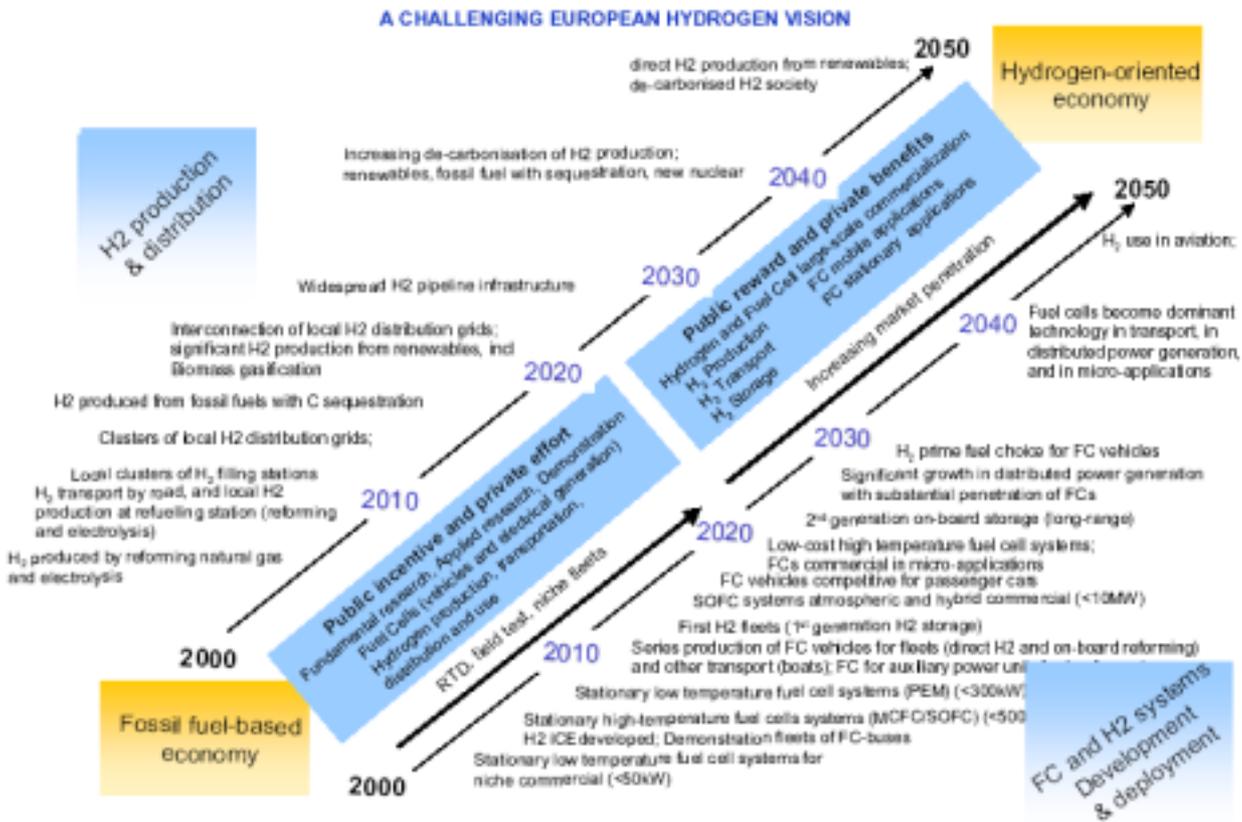


Figure 22 – Proposal for the European hydrogen and fuel cell roadmap – extracted from reference [57]

The Department of Energy of the United States (US DoE), has also been fostering the penetration of hydrogen technologies into the energy and transport market by means of various actions, one of which is the specific “Hydrogen, Fuel Cells and Infrastructure Technologies Program” [<http://www.eere.energy.gov/hydrogenandfuelcells/>]. Under this programme, road maps have been drawn and strategic steps have been decided. In terms of research, and in particular hydrogen storage technologies, specific targets have been set (and are revised, as required) for the on-board hydrogen storage media in order to become competitive with conventional fuels in terms of performance and driving range. As an example, the set targets for on-board vehicles shown in the following table (Table 6) and in Figure 23, considering short and long term goals, are the latest approved targets (soon to be revised) [22].

Table 6 – Short and long term goals for on-board hydrogen storage materials – Reference [22]

On-Board H₂ Storage Alternatives			
<i>Short-term Goal: 3 kg H₂ (215 km)</i>			
Technology	Storage System Volume [l]	Storage System Weight [kg]	Technology Readiness
5,000 psi (~350 bar) Compressed Hydrogen Tanks	145	45	
10,000 psi (~700 bar) Compressed Hydrogen Tanks	100	50	
Low Temperature Metal Hydrides	55	215	
Liquid Hydrogen	90	40	
On-Board H₂ Storage Alternatives			
<i>Long-term Goal: 7 kg H₂ (700 km)</i>			
Technology	Storage System Volume [l]	Storage System Weight [kg]	Technology Readiness
5,000 psi (~350 bar) Compressed Hydrogen Tanks	320	90	
10,000 psi (~700 bar) Compressed Hydrogen Tanks	220	100	
Alanate Hydrides	200	222	
Carbon Nanotubes	~130	~120	

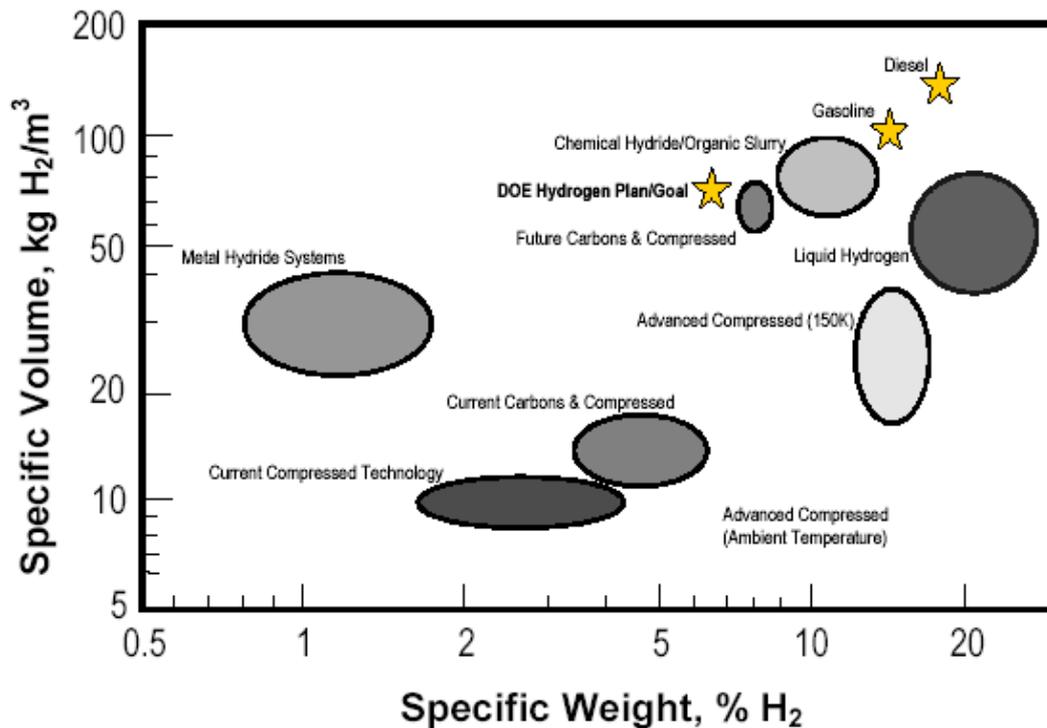


Figure 23 – Specific volume versus weight for a number of hydrogen storage media and US DOE originally set targets [44]

Most recently though, the DoE Hydrogen, Fuel Cells and Infrastructure Program following re-evaluation of the available options, set new targets for on-board hydrogen storage materials that at the moment are required to achieve greater than 480 km driving distance. Summarising the present situation, the on-board hydrogen storage becomes challenging considering issues such as energy efficiency, cost, safety, reversibility at useful temperatures and pressures for chemical storage and size for physical storage. When compared to gasoline, hydrogen has on a weight basis three times the energy content but the situation is reversed when volume is considered [72 - 74].

The US DoE is following two approaches to on-board hydrogen storage: physical storage and chemical storage. Physical storage refers to the development of tanks for either compressed hydrogen gas or liquid hydrogen. Chemical storage covers both reversible and irreversible. Reversible chemical storage is hydrogen storage in solid materials – the hydrogen can be released and refilled without physically removing the storage medium from the vehicle. The case of the irreversible chemical storage systems involves releasing of hydrogen via an on-board chemical reaction with the storage material and replenishing the hydrogen off-board. According to US DoE and taking into consideration this classification, hydrogen storage media should by 2010 demonstrate the following performance characteristics –

Table 7 [72].

Table 7 – Technological requirements of vehicle applications set by DOE for 2010 – Reference [72]

	Units	Target	Status Physical Storage	Status Chemical Storage
Storage Weight Percent	%	6	5.2	3.4
Energy Efficiency	%	97	94	88
Energy Density	Wh/l	1100	800	1300
Specific Energy	Wh/kg	2000	1745	1080
Cost	\$/kWh	5	50	18
Operating Temperature	°C	-40–50°C	-40–50°C	-20–50°C
Start-up Time to Full Flow	s	15	<1	<15
Hydrogen Loss	sc/h/l	1.0	1.0	1.0
Cycle Life	Cycles	500	>500	20-50
Refuelling Time	Min	<5	TBD	TBD
Recoverable Usable Amount	%	90	99.7	>90

Nevertheless, according to General Motors even these DoE targets for energy densities may still be low (see Figure 24) as recently indicated and could soon be revised [49, 74].

GENERAL MOTORS HYDROGEN STORAGE PARAMETERS	
Metric	Goal
Mass Energy Density (MJ/kg)	See Graph
Volumetric Energy Density (MJ/l)	See Graph
Refuelling Time (min)	<5
Durability (total miles maintaining 80% capacity)	150,000
Hydrogen Release Rate [g/(s*kW _{stack})]	.025 (1.5 g/s @ 60 kW)
H ₂ Release Temperature (°C)	<80
Energy Penalty for H ₂ Release (%)	<5
On-board Heat Dissipation During Refuelling (kW)	0

General Motors
Gravimetric Energy Density vs. Volumetric Energy Density
of Fuel Cell Hydrogen Storage Systems

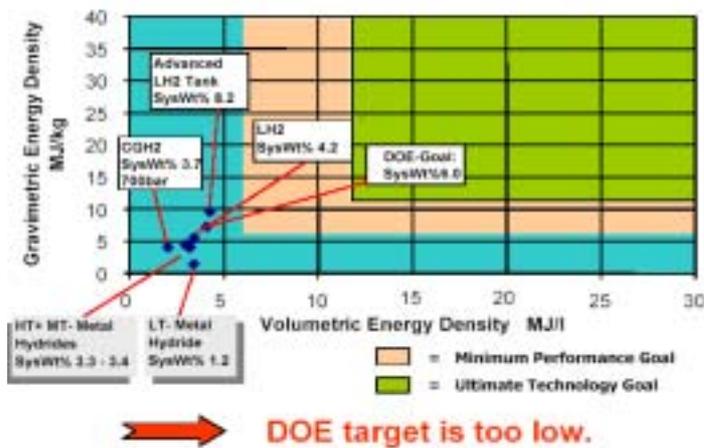


Figure 24 – Extracted from a presentation given by General Motors on new targets for hydrogen storage parameters indicating that originally set DoE targets are rather low [49, 74]

Moving to individual storage options, more specific targets can be identified. For compressed hydrogen storage, type IV all composite tanks are currently available at 350 bar whereas only the prototypes at 700 bar are completed. There have been optimisations on the design of cryogenic tank systems but the “boil-off” issue has not been entirely controlled yet and liquefaction remains an energy intensive process. Reversible metal hydrides, have rather low capacity and slow kinetics for vehicle

applications including the most promising NaAlH_4 , which is limited to about 5.6 wt.% [73]. Fundamental studies may need to continue on NaAlH_4 as model system, whereas other hydrides with a storage capacity above 6wt.% should be identified or new materials could be developed to achieve even higher storage capacities. Engineering analyses should target preliminary cost evaluation, large-scale production and safety/standardisation requirements. With respect to chemical hydrides, (see Borax), higher than in metal hydrides capacities have recently been recorded (10wt.%) [73], but their full potential may not yet be realised. Work could concentrate on the thermodynamic energy requirements including regeneration and on the development of new processes and catalysts. Single-Wall Carbon Nanotubes have a capacity around 4wt.% and doped SWNTs can reach 7wt.%. Issues though such as reproducibility, better understanding of the fundamentals of carbon adsorption and the actual need for validated data and standardised procedures for production and testing still need to be satisfactorily addressed. In general, the case of the hydrogen storage potential of all carbonaceous materials is still open. At the moment there is no consensus on whether they can reversibly store significant quantities (~5wt.%) of hydrogen at room temperature. Previously reported high values of hydrogen storage have been challenged by a number of researchers and attributed to sample contamination or experimental error. Recent work has shown that high surface area carbons do indeed physisorb significant amounts of hydrogen at cryogenic temperatures (up to 7wt.%), and they could be suitable candidates for bulk hydrogen stores but not for mobile applications [24].

There is currently discussion on the so-called “advanced storage concepts” and their potential for hydrogen storage. This classification includes crystalline nanoporous materials, polymer microspheres, boron nitride nanotubes, advanced hydrides, bulk amorphous materials and many others [72, 73]. Research and development priorities for these materials are set as being the maximum storage capacity, the understanding and optimisation of absorption/desorption kinetics, the energy balance versus life cycle analysis, safety and cost effectiveness.

Under the DoE hydrogen related programme, quantitative performance targets have been generally set in line with the so-called “6-10 Law” According to this, hydrogen storage materials need to demonstrate capacities of 6-10wt.%, 6-10 MJ/Kg, 6-10 MJ/L, and at least six to ten times better desorption kinetics, faster filling time and improved heat transfer, as compared to the current situation [72, 73].

The most recent publication concerning new prospective targets set by the US DoE for hydrogen storage is the June 2003 draft of the Hydrogen, Fuel Cells & Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan prepared for public review [75]. This document describes the planned research, development and demonstration activities for hydrogen and fuel cell technologies through 2010 for transportation and stationary applications.

In brief, for 480 km vehicle range, the suggested objectives (not final yet) [75, 76] are to develop and verify

- on-board hydrogen storage systems achieving :
 - by 2005, 1.5 kWh/kg (for 4.5wt.%), 1.2 kWh/L, and \$6/kWh.
 - by 2010, 2 kWh/kg (for 6wt.%), 1.5 kWh/L, and \$4/kWh.
 - by 2015, 3kWh/kg (for 9wt.%), 2.7 kWh/L, and \$2/kWh.
- interface technologies for fuelling on-board hydrogen storage systems, by 2015.

- by 2015, low-cost off-board hydrogen storage systems, as required for hydrogen infrastructure needs to support transportation, stationary and portable power markets.

2.6.2 Stationary applications

Stationary (off-board) hydrogen storage is an important element of the hydrogen infrastructure, required both for transport applications as well as for power generation in the future. Bulk hydrogen storage facilities are necessary elements of hydrogen production plants, regional/local hydrogen distribution centres and end-use sites, such as refuelling stations or fuel cell-based power generation plants. The requirements for storage capacity vary with the application; storage capacities may range from thousands of tonnes in production sites, to 50-100 tonnes in distribution centres, to tens of tonnes in refuelling stations [77].

The requirements for stationary storage are generally less restrictive than those for on-board applications. For example, for most stationary applications the weight requirement is relaxed, although the requirement of volume minimisation for the storage vessel is important. Other requirements related with stationary storage vessels include the ability to manufacture these vessels with a range of storage capacity; tolerance of the vessel to poisoning by trace elements, good long-term cycling behaviour, reasonably fast recharge and delivery flow rates and low hydrogen losses [78, 79]. Finally, the requirement for low cost vessels for stationary applications is not as stringent as for transport applications. However production, operating and maintenance costs have to be minimised to make the hydrogen infrastructure competitive with the conventional fuel infrastructure.

2.6.2.1 *The state-of-the-art*

Currently, stationary hydrogen storage has been demonstrated at hydrogen production plants, hydrogen utilisation sites and demonstration hydrogen refuelling stations. Today's practice is to store hydrogen in large quantities either as compressed gas or as cryogenic liquid. It is envisaged that in the future, hydrogen can be also stored in hydrides or underground (a practice common for natural gas storage). These practises are reviewed next.

Gaseous Storage

The storage of hydrogen in a compressed gaseous form offers the simplest storage solution in terms of infrastructure requirements and has become the most popular and most highly developed method. However, the volumetric storage density is low, depending on the gas pressure, as was already discussed.

Compressed hydrogen is stored mainly in cylinders with hemispherical end domes, similar to those used for storing natural gas and other process gases. The flow of gas in and out of the cylinder is done via valves located at the hemispherical domes. Pressure release valves and pressure and temperature transducers may also be installed in the vessel. Cylinders for stationary applications are mostly of type I (see previous section) made wholly of steel (typically out of austenitic stainless steel, e.g. AISI 316 and 304 [5]) to reduce material and manufacturing costs. Although vessels can also be produced from composite materials (types II, III and IV), their cost is prohibitive, given that the

advantages offered (reduced weight and high strength) are generally not required for bulk stationary applications.

For storage of small amounts of hydrogen, the gas is compressed to about 200 bar and stored in standard 50-litre cylinders [80, 81]. For larger storage capacity, cylindrical tanks with maximum operating pressure of 50 bar and 2.8 m in diameter are available in a range of lengths from 7.3 m to 19 m, with capacities from 1,300 m³ to 4,500 m³. Vessels with capacities of about 2,000 m³, pressurised to about 185 bar (mostly spherical containers) have been the state-of-the-art for many years and have not exhibited any major operating problems [2, 18]. Currently, large pressure vessels that can store hydrogen at 200-300 bar are available; however, according to Ref. [2], vessels of higher volumes (... > 2,000 m³...) and increased pressures (... > 185 bar...) ‘...have not always been trouble free...’. According to Ref. [18], European countries tend to use low pressure cylindrical tanks with a maximum operating pressure of 50 bar and storage capacities of 115-400 kg (approx. 100-350 m³), see Figure 25. Compressed hydrogen storage vessels are typically made available to the users by the gas manufacturer on lease.



Figure 25 – Pressure vessels for stationary hydrogen storage [123]

An issue associated with compressed hydrogen storage is the ‘cushion’ gas that remains in the cylinder at the end of its discharge, which may lead to large hydrogen losses in large vessels. In addition, the safety of compressed hydrogen storage vessels is a major issue, given that they are installed in populated areas (e.g. refuelling stations). Construction is based on standards and each cylinder is subjected to hydrostatic and leak tests during manufacturing; furthermore selected cylinders from each lot are subjected to cyclic and burst tests.

Liquid Storage

Liquid hydrogen is stored in cryogenic containers at -253°C and at ambient pressure in thermally insulated vessels. Hydrogen can be delivered from the storage vessel either as liquid or gas. Significant experience has been gained over the years on the storage of liquid hydrogen, especially due to its extensive use in the space industry.

The design of liquid storage vessels is dictated by the requirement to minimise the loss of hydrogen due to evaporation (boil-off) caused by heat flow from the surroundings to liquid hydrogen. As there is no liquid phase existent above the critical temperature of hydrogen (-240°C), liquid hydrogen is stored in vented systems; otherwise very high pressures can build up in the cryogenic storage vessel by the accumulation of hydrogen vapour. Storage vessels are designed to include sophisticated thermal insulation systems to reduce conductive, convective and radiant heat flow into the liquid hydrogen to minimise evaporation. A cryogenic container is a two-wall construction. The space between the 2 shells is under vacuum to minimise convective and conductive heat transfer. Furthermore, perlite, silica aerogel, diatomaceous earth, fused alumina, phenolic spheres, and multiple layers (30-100) of reflective, low-emittance heat shielding materials, such as Mylar, are also placed between the 2 shells of the container to reduce heat flow. The insulation is supported by materials with a low thermal conductivity such as titanium or Hastelloy [2]. Large vessels have an additional outer wall with the space filled with liquid nitrogen, reducing the heat transfer [18]. The strength requirements are small compared to compressed hydrogen vessels. Nevertheless, large cryogenic vessels need to be robust to withstand their weight as well as stresses caused by the build-up of hydrogen vapour (inner shell) and the pressure difference between the environment and the vacuum insulation (outer shell). The inner shell is designed to be thin for cost and cooling considerations. It is usually manufactured from austenitic or alloy steels, materials that retain their mechanical properties at liquid hydrogen temperatures. The outer shell is thicker than the inner shell (to withstand stresses that may result in collapsing or buckling due to the pressure difference at its opposite surfaces), being manufactured out of conventional steel, containing stiffening rings to support the weight of the inner shell and its contents [19].

Most liquid hydrogen containers are spherical. The spherical shape helps in reducing evaporation losses as it has the lowest surface area per unit volume. With the increase in diameter of the container, and thus its size, the volume increases faster than the surface area, so a large container has lower hydrogen losses per unit volume than a smaller container. For example, the daily losses of 50 m^3 , 100 m^3 and $20,000\text{ m}^3$ containers are about 0.4%, 0.2% and 0.04% respectively [5]. Cylindrical containers are also available (see Figure 26) as they cost less to manufacture.

However, losses of hydrogen due to evaporation (boil-off) are unavoidable. The boil-off rate depends on the size, shape and insulation of the container. These losses are of the order of 2-3% per day in smaller vessels and up to 0.2% in larger containers. Since most storage vessels are designed to withstand pressures up to 5 bar, the evaporated hydrogen (that causes the increase of pressure inside the vessel) can either be vented through a pressure-release valve or consumed as hydrogen gas (or returned to the liquefaction process if the storage vessel supports such a plant). Vented hydrogen is not only a loss of hydrogen but also imposes a safety hazard. The length of time required for the build-up of pressure so that the maximum acceptable pressure is reached and venting starts is called the *lock-up* time. The lock-up time in state-of-the-art storage vessels can be up to 50 hours [82]. Another factor that may cause evaporation is the incomplete transformation of hydrogen from ortho- to para- state during liquefaction. Para-

hydrogen in liquid slowly transforms into ortho- releasing energy into the liquid hydrogen, thus increasing the evaporation rate.

Besides the risk of explosion associated with venting hydrogen, there are dangers associated with the low temperatures. These dangers include severe frostbites to humans, as well as failure of materials used in storing, since they become brittle at low temperature, increasing the risks of vessel failure.

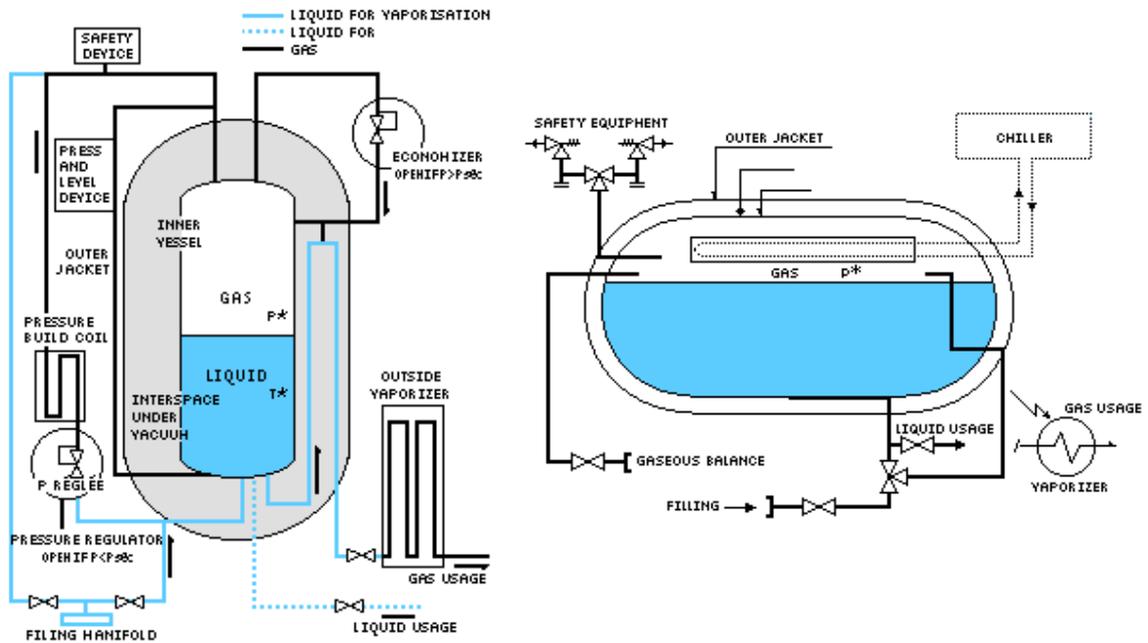


Figure 26 – Generic cryogenic storage vessels for liquid process gases: These vessels come in vertical (left) and horizontal designs (right) [83]

Liquid storage vessels at utilisation sites have a capacity of 110-5,300 kg, while at production plants their capacity is in excess of 100,000 kg. For example, the Linde liquefaction plant in Germany stores the produced hydrogen in a 270 m³ vessel, with a capacity of 19,000 kg [84]. The largest liquid storage tank in the world is spherical with a diameter of 20 m, volume of 3,800 m³ and capacity of about 230,000 kg and is located at the Kennedy Space (KSC) Center of NASA, where it is used to provide liquid hydrogen to the Space Transportation System (Space Shuttle), see Figure 27. Its evaporation rate is 0.1 to 1% per day [81]. It is claimed that there are no technological barriers to construct spherical vessels with a capacity up to 900,000 kg [18]. Liquid hydrogen vessels are typically manufactured by the producers of industrial gases.



Figure 27 – Liquid hydrogen vessel at KSC/NASA [85]

Underground storage

Underground storage emerges as a major option for storing large quantities of hydrogen (of the order of million m^3) for long times. There is significant experience on the storage of natural gas and town gas (a gas with a high concentration of hydrogen in underground reservoirs, such as rock and salt caverns, porous rock and aquifers. Furthermore, gaseous helium is successfully stored underground in the USA, a gas with a higher diffusivity than hydrogen [18]. According to literature [80, 81] seasonal storage of town gas in caverns is being practiced in Kiel, Germany, since 1971; hydrogen-rich gases were stored in a 330 million m^3 aquifer in Beynes, France by Gas de France; and hydrogen is stored in brine compensated salt caverns in Teeside, England by the chemical manufacturer ICI.

A prerequisite for the storage of hydrogen underground is the presence of suitable cap-rock to prohibit hydrogen from being diffusing into the atmosphere. Porous rock saturated with water is a good example of cap-rock [18]. Nevertheless, there is a significant amount of hydrogen sacrificed as cushion gas that occupies the underground storage volume at the end of the discharge cycle, up to 50% of the stored volume, which can be of the order of hundreds of tonnes, depending on the storage capacity of the underground reservoir.

Metal hydrides

The storage of hydrogen in metal hydrides for stationary applications, although it has not yet seen any commercial application or large-scale demonstration because it is still in the research stage, may play an important role in the future. Figure 28 shows a conceptual picture of such a storage facility, where hydrides are stored in cylindrical containers.

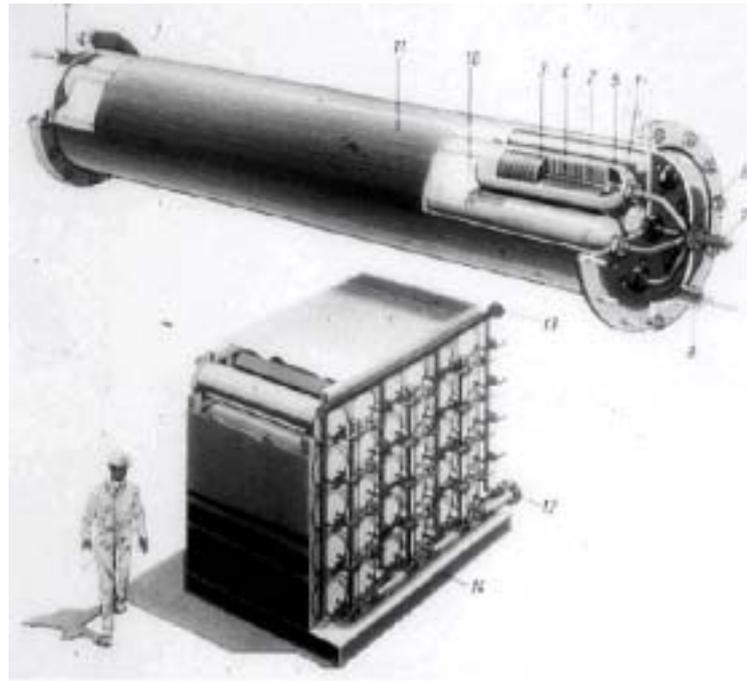


Figure 28 – Future hydrogen storage facility based on metal hydrides [79]

2.6.2.2 R&D challenges

The storage of hydrogen for stationary applications is currently based on mature technologies, however not optimised to reduce costs when large numbers of vessels are manufactured and utilised. Main areas that require additional research and development include the increase of storage capacity, the decrease of vessel volumes, the minimisation of leakage rates and the improvement of safety. According to [77], the areas that require further research include: inexpensive materials for low pressure storage to avoid hydrogen leakage, with superior hydrogen embrittlement resistance; new manufacturing processes for high pressure tanks in large number of units and low cost; development of sensors and odorants to be used for leak detection; development of materials and insulators for cryogenic vessels; development of geologic storage technologies and modelling of the behaviour of hydrogen in underground storage sites. Furthermore, there is a need for the development of tools to optimise storage systems, and codes and standards to address end-use requirements.

The issues associated with stationary storage are not as pressing as for on-board storage. For example, while the US Multi-Year Research, Development and Demonstration Plan of activities for hydrogen for 2003-2010 (Draft 6/3/03), has set firm milestones for on-board storage, compression and liquefaction, there are no specific targets or milestones associated with stationary storage, since targets are scenario and end-use dependent. The target of the US program is stated as ‘...to develop and verify low-cost stationary storage systems as required for hydrogen infrastructure needs to support transport, stationary and power markets...’ [75].

2.6.3 Auxiliary technologies

Compressors, heat exchangers and mechanical expanders are typical equipment required for the conditioning (compression and liquefaction) of hydrogen. The state-of-the-art of these auxiliary technologies is presented in brief next.

2.6.3.1 Compressors

Compressors are indispensable components of the hydrogen infrastructure, being used throughout the chain of hydrogen production and utilisation. Their purpose is to take a fixed quantity of hydrogen and deliver it at an increased pressure. Typically, a compressor is used in combination with a storage facility (stationary or mobile) that requires the supply of pressurised hydrogen.

The selection of the most appropriate type of compressor is based on process variables such as capacity, suction and discharge pressure. Given that the required pressure for hydrogen storage applications exceeds 150 bar, the state-of-the-art in hydrogen compressors is the use of reciprocating piston engines for large applications, such as for pipeline transportation, and piston or diaphragm compressors for smaller applications, such as refuelling stations (see Figure 29). From an engineering point of view, the most appropriate type is the one that accomplishes the required compression with the minimum input of work.

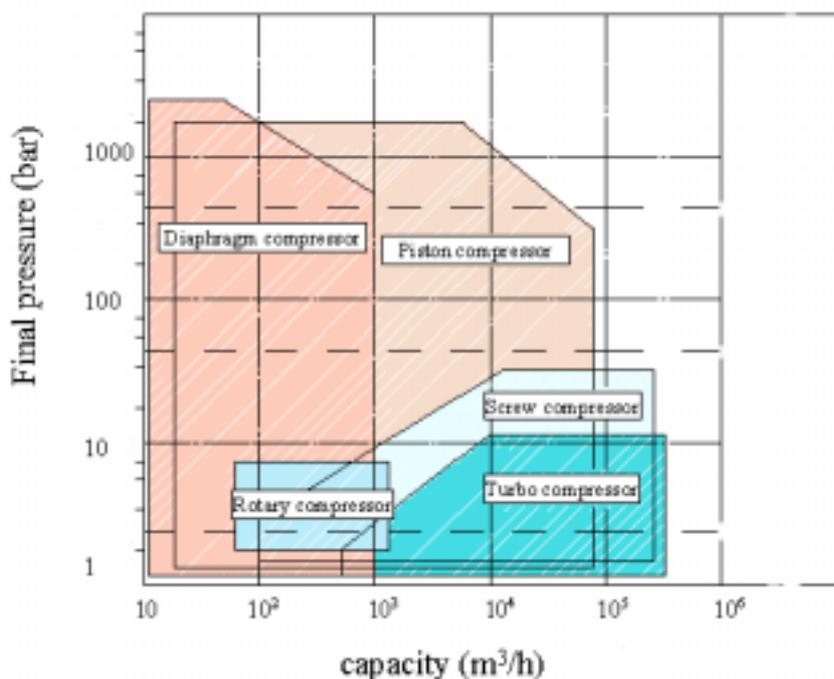


Figure 29 – Operational regimes of various compression types [86]

The reciprocating piston hydrogen compressor

A simple single-stage reciprocating compressor consists of a piston, a connecting rod, a crank and a cylinder (see Figure 30). Compression is achieved by the pulsating action of the piston: after the cylinder is filled with hydrogen, the stroke of the returning piston increases the gas pressure to a threshold value that opens the delivery valve supplying the compressed hydrogen.

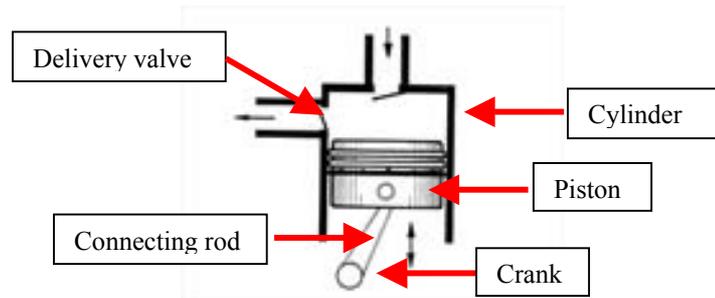


Figure 30 – A schematic of a single-acting reciprocating process gas compressor [87]

Single stage compressors can achieve compression ratios (i.e. the ratio of discharge to suction pressure) of 3:1 to 4:1; however special designs are available that can achieve higher compression ratios, up to 6:1. The limitation in the maximum achievable compression ratio is imposed by the maximum acceptable temperature for the compressed gas (approx. 250°C [88]), given that the increase in the temperature of the gas during compression depends on the compression ratio (see Eq. 13 in chapter 1). Therefore, multi-stage compressors are used to compress hydrogen at high pressures. Furthermore, multi-stage compressors are more energy efficient when compared to single stage-compressors, see chapter 3. A 2-stage hydrogen compressor is shown in Figure 31. Initially, hydrogen fills the larger diameter first-stage cylinder and is pressurised by the stroke of the hydraulic piston, when moving to the left. The pressurised hydrogen is cooled by water either after the compression in an intercooler, or within the compression cylinder by its water-based cooling system. Finally, the cooled hydrogen is directed to the second stage-cylinder of smaller diameter where the compression of hydrogen to the desired pressure is achieved by the motion of the piston to the right.

Given the nature of operation of reciprocating compressors, friction and wear are always present. As such, lubrication of the cylinder is required in order to reduce the wear, improve the overall reliability of the equipment and minimise hydrogen leakage. Manufacturing companies report hydrogen losses up to 5% in used equipment. High hydrogen losses impose difficulties in obtaining high pressures and become a safety concern. A major compressor manufacturer has reported that the cylinder lubrication system is ranked among the most important factors that dictate the reliability of a compressor. Furthermore, it is claimed that while the life of a well-lubricated piston compressor can exceed 3 years of continuous operation, a typical life of a non-lubricated compressor is 6 months [89]. Thus, to ensure the continuity of operations compressors are installed in redundant units (with a concurrent increase in costs). However, the lubricating oil enters the compression chamber contaminating the compressed gas. In order to keep the quality of hydrogen unaltered during compression, the oil has to be separated from hydrogen in a later stage. To overcome this problem, advanced polymeric materials, e.g. teflon, that exhibit heat and chemical resistance and adequate sliding properties are used in non-lubricating type piston compressors. However, wear cannot be avoided and leakage of compressed gas through the seals is increased compared with lubricating-type piston compressors. Furthermore, the compressed gas can still be contaminated by abrasive particles of the seals but to a lesser extent. Lubrication-free compressors can be used for discharge pressures up to 150 bar. For higher discharge pressures, lubricating systems are used. Schematics of lubricated and unlubricated piston compressors are shown in Figure 32.

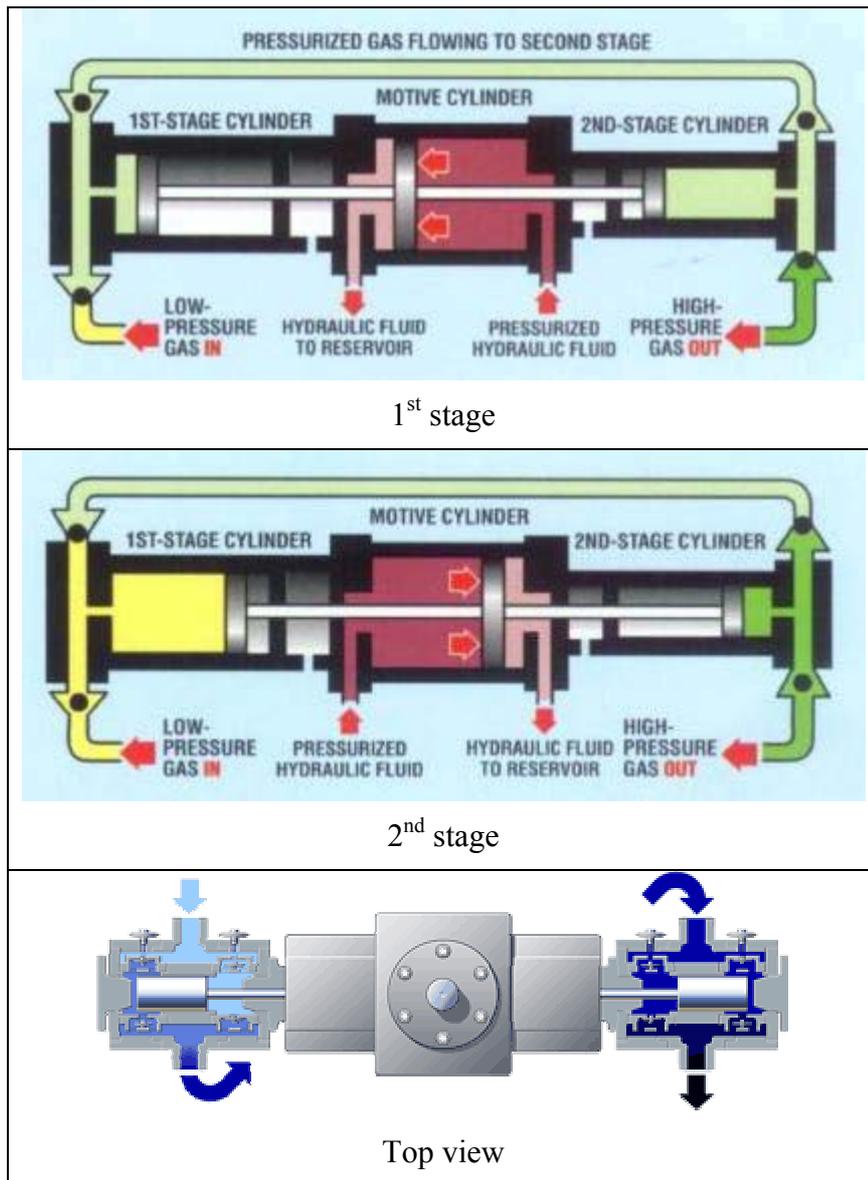


Figure 31 – Operation of a 2-stage hydraulic piston compressor [90, 91]

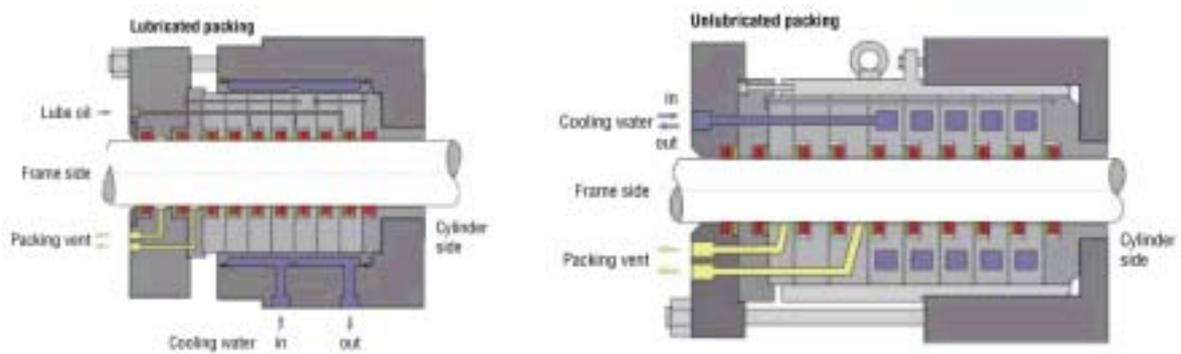


Figure 32 – Lubricated and unlubricated packing for piston compressors [92]

Another issue, common for all types of hydrogen compressors, is the selection of materials to avoid hydrogen-induced damage (see chapter 1). Given that at elevated pressure and temperature hydrogen can diffuse into carbon steels causing decarbonisation with detrimental effects in their mechanical properties, compressors are made of stainless steel, or alloy steels containing chromium and molybdenum.

There is a range of compressor models to meet the requirements in terms of capacity, suction and delivery pressures, for small and large applications. Reciprocating piston compressors are available in vertical and horizontal designs. Compressors delivering hydrogen at pressures up to 500 bar are readily available in the market. Furthermore, special piston compressor models with a discharge pressure of 1000 bar are also available. Compressed hydrogen can be delivered at a wide range of flow rates depending on the model, from 50 to 100,000 Nm³/h; the capacity is limited only by the pulsating speed of the piston. Electric motors for compressors can have a nominal power ranging from a few kW to several thousand. The efficiency of piston compressors depends on the suction pressure and on the presence of a lubricating system. Oil-lubricated compressors have a higher efficiency compared to non-lubricated compressors (the latter have an efficiency of the order of 65-75% [88]). Furthermore, the lower the suction pressure, the lower the efficiency of the compressor is. With suction pressure as low as 7 bar, the adiabatic efficiency of the compressor can be as low as 50%, while for higher suction pressure, the efficiency can reach 80%. Major manufacturing companies include: Sultzer Burckhardt, Dresser-Rand, Ariel, Mannesmann-Demag and Neuman-Esser.

Diaphragm Compressors

Diaphragm compressors are piston-driven reciprocating machines without sliding components in the compression chamber that need lubrication. Compression is achieved by the oscillating deflection of a metallic 3-layer sandwich-type diaphragm within a double concave chamber. The motion of the diaphragm is achieved by varying the pressure of a compression oil positioned behind it, between the diaphragm and the piston, using a reciprocating engine, see Figure 33. At the beginning of the compression cycle, hydrogen is sucked into the enlarged chamber while the piston moves rightwards in Figure 33. At the end of suction, the suction valve closes and the motion of the piston is reversed forcing the diaphragm to move leftwards, increasing the pressure of the hydrogen in the compression chamber. The compressed hydrogen is finally delivered via the discharge valve.

The diaphragm is clamped between the cover of the compressor and the oil flange, thus leakage of compressed hydrogen towards the piston is avoided. The overall leakage rates of diaphragm compressors are significantly lower than these of the piston compressors (of the order of 10⁻⁴ mbar·l/s [88] or 10⁻⁵-10⁻⁷ cm³/s depending on the type of seals used [93]) given that these compressors are hermetically sealed from the outside. Since the cylinder and its lubricating oil are isolated from the compressed gas by the diaphragm, there is no contamination of hydrogen by oil or abrasive particles with the exception of the case of diaphragm rupture. Diaphragm failures are normally attributed to particles or contamination in the gas or lubricating oil systems of the compressor, moisture condensation in the compression chamber, or improper tightening of the compressor cover bolts [94]. A typical life of a diaphragm is about 40,000 h, or 4.5 years of continuous service.

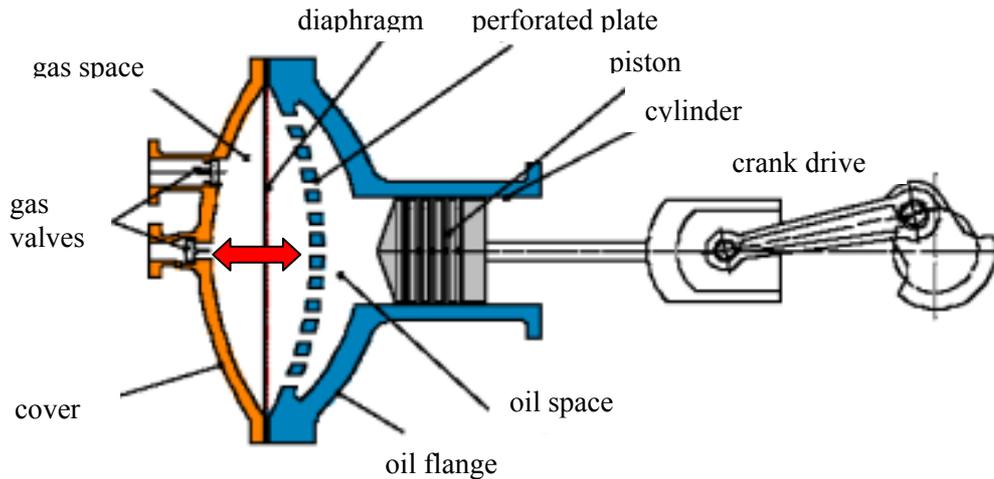


Figure 33 – Schematic of the operating principle of a single-stage diaphragm compressor [88]

Diaphragm compressors remove the heat generated during compression more effectively than piston compressors do, because of the relatively large surface of the compression chamber and the diaphragm, the presence of the cooled compression oil next to the diaphragm and the presence of a cooling system in the cover of the compressor. As a result the increase of the temperature of the compressed hydrogen is significantly lower than the corresponding increase of temperature in piston compressors [94]. From a thermodynamic point of view, diaphragm compressors operate close to isothermal and reversible conditions, thus higher compression ratios can be achieved than in reciprocating compressors, typically 15:1 per stage and up to 20:1 in small compressors, reducing the number of stages required to deliver hydrogen at high pressure.

Multi-stage diaphragm compressors can deliver hydrogen at very high pressure, in excess of 1,000 bar. However, the flow rates are small, no more than 200 m³/h per stage, or 700 m³/h for multi-stage equipment. This limitation is imposed by the size of the diaphragm. Given that the diaphragm is manufactured from precision-rolled stainless steel, the maximum size of a diaphragm that can be manufactured today is limited by the current maximum width of stainless steel roll available, approx. 1 m [93]. The electric motors range in power from 4 kW to 150 kW. The efficiency of diaphragm compressors ranges between 80 and 85%.

Future developments

The main issues nowadays associated with hydrogen compression are the improvement of energy efficiency and reliability and the issue of cost (discussed in a subsequent section). New approaches are being considered such as the use of guided rotor and linear compressors, the development of electrically driven membranes and hydride compressors. According to the US Multi-Year Research, Development and Demonstration Plan for hydrogen for 2003-2010 (Draft 6/3/03) one of the objectives of the *Hydrogen Delivery* program element is to improve the energy efficiency of hydrogen compression from ambient pressure to 200 bars to 92% in 2005 and to 95% in 2010 [75].

2.6.3.2 Heat Exchangers

Heat exchangers are used in liquefaction plants to transfer heat from the stream of hydrogen to be throttled or expanded to the stream of cooler gas returning from the liquid hydrogen separation process (see chapter 1). Heat exchange is accomplished by convection from the gaseous hydrogen over the surface of the heat exchanger and by conduction through the construction of the heat exchanger. As a result of heat transfer, the temperature of the gas to be liquefied drops as it passes through the heat exchanger. Typically, heat exchangers used in refrigeration applications are of the *countercurrent-flow* type, i.e. the fluids flow in opposite directions. Types of cryogenic heat exchangers are tubular exchangers, switching regenerators and compact units; their difference being the spatial configuration of the fluid streams. In tubular heat exchangers the gas to be cooled flows through the middle tube of an array of tubes, while the cooler gas that returns to the compressor flows in the surrounding tubes (Figure 34). In the switching regenerator the fluids occupy the same space in turn or are in contact with the same matrix in turn (Figure 35) [16]. The compact units comprise a matrix of flat plates and corrugated fins, studs or ribs in a sandwich construction, in order to increase the cooling effect for a given volume, also called *extended surface* heat exchangers (Figure 36).

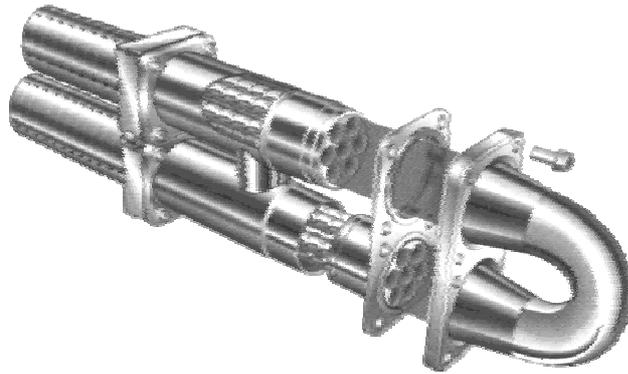


Figure 34 – A schematic of a tubular heat exchanger [95]

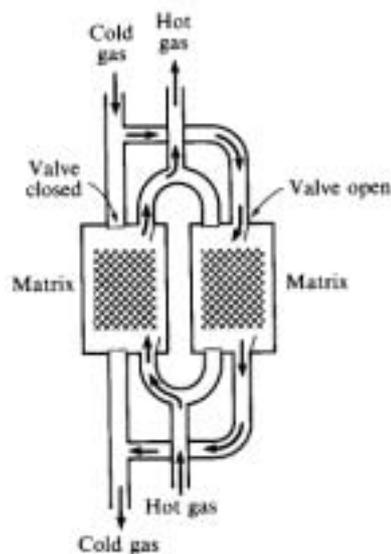


Figure 35 – A schematic of the regenerative exchanger [16]

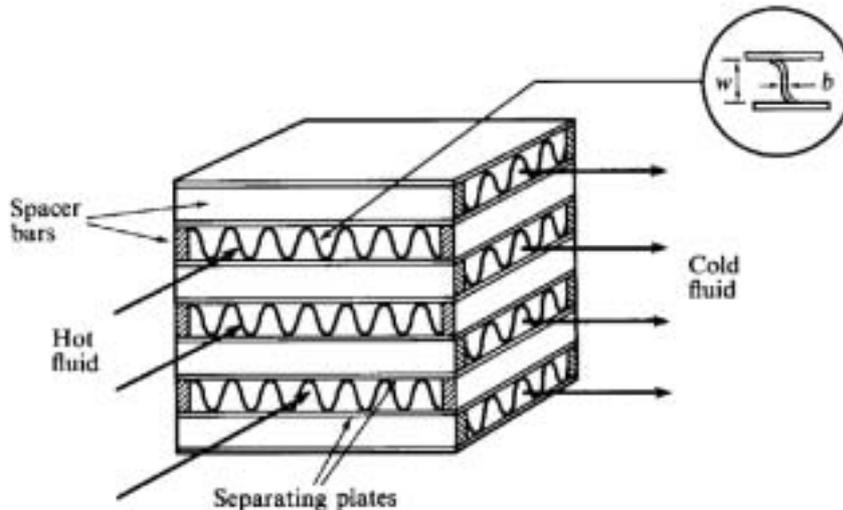


Figure 36 – A schematic of the extended surface heat exchanger [16]

Cryogenic heat exchangers are designed to operate at pressures up to 60 bar [96]. They are compact to reduce the amount of heat entering from the environment, well insulated and frequently in vacuum to reduce convection losses. They are manufactured from materials with low thermal expansion coefficients (typically aluminium) to reduce thermal stresses, with appropriate thermal conductivity and high strength with a low ductile-to-brittle transition temperature to retain their ductility at the low operating temperatures. As with compressors, chromium and molybdenum alloy steels are also used for the manufacturing of heat exchangers to resist to hydrogen embrittlement.

The most important characteristic of a heat exchanger is its efficiency to transfer heat. This efficiency is measured by the *effectiveness* of a heat exchanger, defined as the ratio of the actual heat transferred to the maximum possible heat transfer. The effectiveness of tubular heat exchangers is typically of the order of 60%, and the effectiveness of extended surface heat exchangers is in excess of 95%. The use of advanced alloys and manufacturing technologies may improve effectiveness further. It is claimed that the reduction in the efficiency of heat exchangers by 1% can cause a reduction in the overall efficiency of the liquefaction system by 6-7% [19].

2.6.3.3 Mechanical expanders

As was explained in chapter 1, the last step of hydrogen liquefaction involves the cooling of hydrogen from the inversion temperature to its boiling point, by means of isenthalpic expansion, where pressure and temperature, and thus the available energy of hydrogen, are reduced.

In small liquefaction facilities the expansion of hydrogen is achieved by throttling while in larger plants expansion is achieved by mechanical means, either using a reciprocating expansion engine or a turbine expander.

A flow of hydrogen is called to be throttled when the following conditions are fulfilled: (i) there is some restriction to the flow, (ii) the velocities before and after the restriction are either equal or negligibly different, and (iii) there is a negligible heat loss to the surroundings, i.e. the process is adiabatic. The restriction to the flow can be a partially

open valve, an orifice or any other sudden reduction in the cross-section to the flow [16]. Typically, needle-type valves modified for cryogenic operation are used [96].

However, thermal expansion using throttling valves is accompanied by low liquid hydrogen yield and energy losses due to frictional heating. To avoid the dissipation of energy during expansion, mechanical expanders are used and they can increase the liquid hydrogen yield with the concurrent generation of power. In this context, reciprocating piston expanders and turbine expanders are utilised.

The reciprocating piston expander was introduced by the French engineer Georges Claude in 1902. It is a typical piston engine, however working in reverse. The thermal energy of the compressed hydrogen stream is used to create force and motion by the expansion of the gas, which in turn drives a motor generator or other equipment. Unlike the combustion engine, the desired result is not the motion created but the temperature drop caused by the expenditure of energy in the form of heat transmitted by hydrogen during the reduction of temperature [97]. Its operation is shown schematically in Figure 37. Generally, these units are used with inlet pressures of 40 to 200 bar, operating at speeds up to 500 cycles per minute. Their thermal efficiencies range between 75% for small units to 85% for larger machines [96].

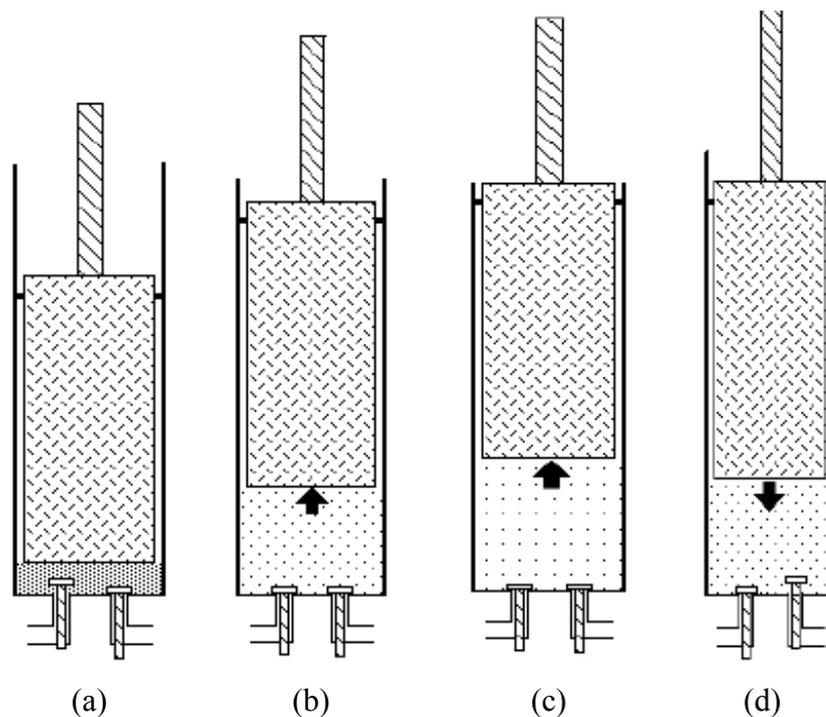


Figure 37 – Description of the operation of the reciprocating piston expander: Initially, the intake valve opens allowing high-pressure hydrogen to enter the cylinder (a). Consequently, the piston moves upwards driven by the expansion of the compressed gas (b) until it reaches the top of the cylinder (c). Finally, the exhaust valve opens and the piston moves downwards, driven by another piston, delivering cooled hydrogen at a reduced pressure [97].

Another type of mechanical expander that is used in modern liquefaction plants is the turbine expander; equipment which is characterised also by high efficiencies of the order of 70-80% [99]. Turbine expanders offer the advantages of higher reliability and

availability than piston expanders, longer component lifetime and lower maintenance requirements. However, they have a higher capital cost. The operating principle is similar to the piston expander: gas is fed through a turbine (or a set of them), which has a braking system incorporated onto a shaft. The braking effect forces the gas to do work and the gas expands, resulting in the reduction of its pressure and temperature [84]. Turbine expanders are used for intermediate cooling before throttling, or for the final expansion. Then, liquid hydrogen is separated on blade surfaces, forming high velocity liquid films. The energy generated is absorbed by electric generators, pumps or compressors, improving the overall energy efficiency of the system. Both axial and radial turbine expanders of impulse and reactive type are used for cryogenic applications, see Figure 38. Sizes for cryogenic applications range from 0.75 to 7500 kW with flow rates of up to 28 million m³/d [96]. However, in medium-sized plants, expanders with refrigeration output of 30 kW are adequate [84]. It is claimed that the use of turbine expanders can double the liquid hydrogen output when compared with throttle valves [98].

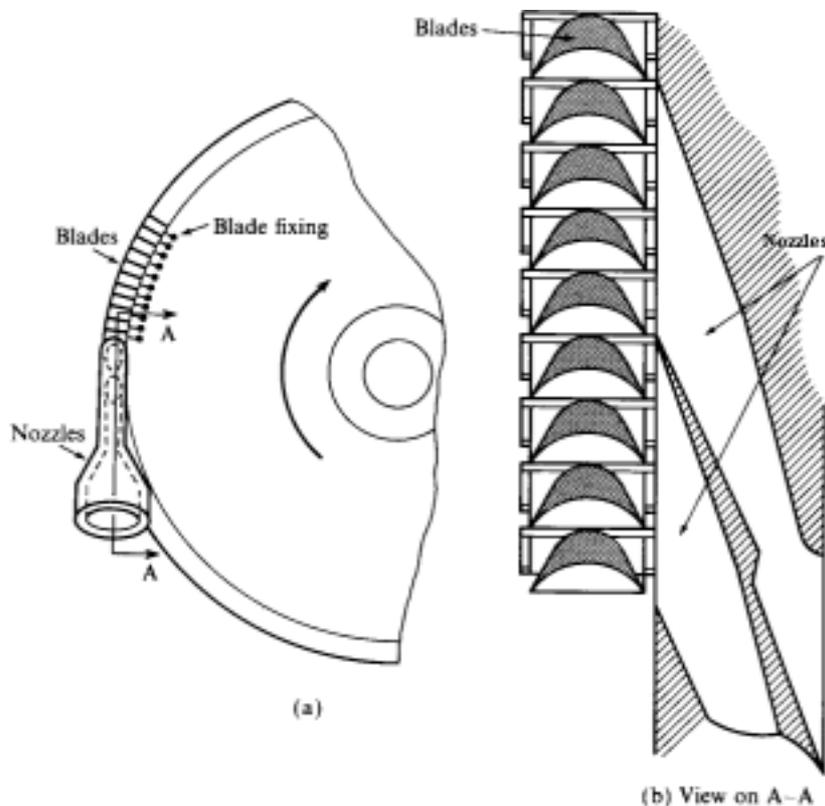


Figure 38 – Simple impulse turbine (a) showing cross-section through blades and nozzles (b) [16]. The blades of the turbine reverse the direction of the fluid flow causing angular momentum of the fluid to be transferred to the rotor. Part of hydrogen liquefies and power is generated.

2.6.3.4 Liquefaction plants

Hydrogen liquefaction plants were first built in the 1960's in the USA mainly to support the space program and to a lesser extent other processing industries. Before that era, hydrogen liquefaction was only performed on a laboratory scale for research purposes in

universities and research centres. Liquefaction plants in Europe were constructed in the 1980's, also in connection with the deployment of the European space program, the Ariane rocket. Nowadays, 3 hydrogen liquefaction plants are operational in Europe and 10 in N. America. The American capacity in 1997 was about 250 tons per day; while the European capacity is 19.9 tons per day, see Figure 39 and Table 8. The first-built plants were designed with capacity rates up to 55 tons per day. Recent plants were built much smaller, with capacities ranging between 2.5 and 11 tons per day [100].

Table 8 – Hydrogen liquefaction plants in Europe [84]

<i>Company</i>	<i>Site</i>	<i>Start-up</i>	<i>Capacity</i>
<i>Air products</i>	Netherlands/Rozenburg	1987	5.0 t/d
<i>L’Air Liquide</i>	France/Wazier	1988	10.5 t/d
<i>Linde</i>	Germany/Ingolstadt	1992	4.4 t/d

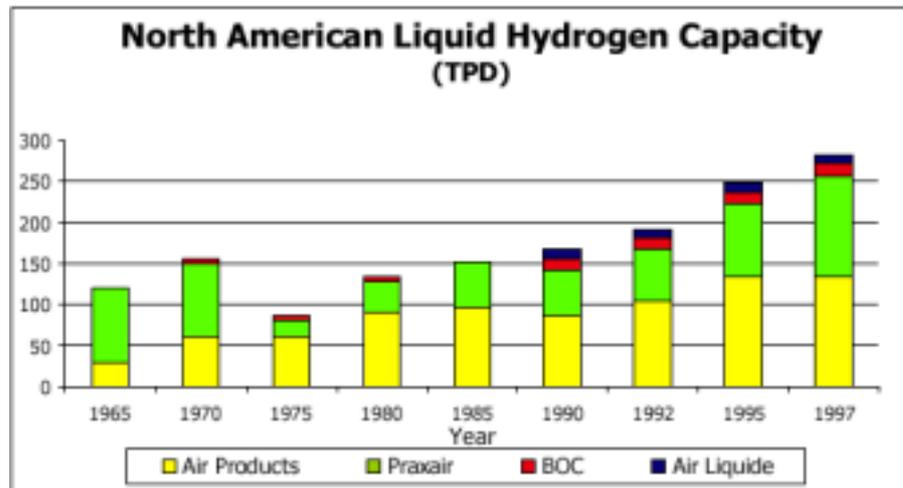


Figure 39 – North American capacity to store liquid hydrogen, in tons per day [14]

Nowadays, the space industry still remains the main customer for liquid hydrogen. However, the demand for hydrogen had always been significantly smaller than the installed capacity, leading plants to operate at partial loads.

The different types of liquefaction plants were discussed in chapter 1. Compressors, heat exchangers and expanders are used to cool hydrogen below its boiling point of -253°C . In brief, hydrogen is initially compressed to pressures up to 60 bar, depending on plant design. The compressed hydrogen is initially pre-cooled in heat exchangers using liquid nitrogen at -193°C . Subsequently, hydrogen is cooled below its inversion temperature using a series of heat exchangers and mechanical expanders, see Figure 13. Ultimately, hydrogen is cooled at its boiling point by expansion in throttle valves or mechanical expanders to produce some liquid, while the gaseous hydrogen that is not liquefied returns to the compressor via the heat exchangers that cool the compressed hydrogen.

The existing liquefaction plants have been built using conventional technology, with the aim to reduce capital costs, while energy efficiency did not play an important role in their design [101]. Their efficiency¹⁶ does not exceed 40%, due to their high energy consumption. Typical power requirements in liquefaction plants vary between 10 and 15 kWh_{el}/kg_{LH₂}, or equivalently 0.89-1.06 kWh_{el}/l_{LH₂} [14, 19, 101]. This energy requirement corresponds to 30% to 45% of the LHV of hydrogen, highlighting the energy intensiveness of the liquefaction process.

Major issues associated with hydrogen liquefaction are the improvement in thermodynamic efficiency and the reduction of capital costs (discussed in the next chapter). The thermodynamic efficiency can be improved by using innovative liquefaction technologies, e.g. by using novel refrigerants for cooling in conventional processes or developing magneto-caloric liquefaction processes. It is expected that in the medium term the energy requirements will decrease to 0.8 kWh_{el}/l_{H₂} and in the long term, to 0.35 kWh_{el}/l_{H₂} [101, 81]. According to the US Multi-Year Research, Development and Demonstration Plan for hydrogen for 2003-2010 (Draft 6/3/03) one of the objectives of the *Hydrogen Delivery* program element is to improve the energy efficiency of hydrogen liquefaction from 65% (state-of-the-art according to the report) to 70% in 2005 and to 87% in 2010 [75]. These target efficiencies correspond to energy consumption of 0.35, 0.33 and 0.26 kWh_{el}/l_{H₂}.

Manufacturers of liquefaction plants include L'Air Liquide, Linde, BOC, Air Products and Praxair.

2.6.4 Safety, regulations and standards

Some of the main barriers for realising the hydrogen economy include lack of infrastructure, of coordination and collaboration among potential operators, and of public acceptance. In addition issues such as unavailability of codes, standards, and other safety information that can enable and ensure the required infrastructure are equally pressing.

Going back to history, in general, hydrogen has an excellent safety record despite its reputation (see “Hindenburg Zeppelin” accident at Lakehurst, 1937), and it is as safe for transport, storage and use as many other fuels. Nevertheless, safety does remain a top priority in all aspects of hydrogen energy. It is addressed through stringent design and testing of storage and transport concepts. Quantitative risk assessment tools are also employed for evaluating the safety level offered by the hydrogen storage systems. The research community is working towards the development of more sophisticated tools incorporating existing experiences from other technical areas, such as aeronautics or nuclear power plants. Such risk assessment tools are based on statistical material properties data, typical load distributions, for different filling procedures and storage systems. Safety components, valves and pressure-relief devices, and the respective requirements for their design, mounting and reliability also constitute a research topic. Similarly, sensors and surveillance electronics for production and operation but also quality standards concerning the requirements on data exchange between the filling stations, the on board computers and the tank sensors/electronics, may also need to be established. As part of design for safety, accident typologies, interaction crash

¹⁶ As was mentioned in chapter 1, the thermodynamic efficiency of a liquefaction plant is defined as the ratio of the work of ideal liquefaction to the actual work required for liquefaction.

behaviour of storage receptacle - chassis, and existing European and international regulations will have to be carefully consulted [24].

The research efforts concentrated on hydrogen and its potential as an energy carrier must be complemented by accompanying measures on the definition and harmonisation of norms and standards related to all segments of the hydrogen economy including storage, to ensure quality and safety for the end-users. In response to this, there have been intensive efforts and there are also currently running initiatives on hydrogen technology standardisation at national, European and international level. These are mainly addressing automotive applications and not yet the stationary power generation domain. In Europe, there already exist some specific legal requirements/directives for stationary applications of hydrogen technologies, with respect to the protection of workers and equipments and legislations on classified installations for the environmental protection. There is also a rather well developed European activity concentrating on safety aspects and on the drafting of codes and standards for hydrogen storage in transport applications. This is the well-known prenormative project called European Integrated Hydrogen Project (EIHP-<http://www.eihp.org>). The EIHP is funded by the European Commission, under the Fifth Framework Programme, and it is currently in its second phase (2001-2003). EIHP is comprising a number of companies, organisations and research institutes that are highly experienced and actively involved in the hydrogen transport applications, infrastructure and safety. This Consortium is actually concentrating the European research and development efforts to enable harmonisation of standards and drawing of regulations for hydrogen fuel vehicles and their components powered by combustion and fuel cell engines. As a result of this activity, the first drafts for new regulations have already been issued (available on line - <http://www.eihp.org/>). They were inspired from the existing regulations and standards for Compressed Natural Gas (CNG) and Liquid Petroleum Gas (LPG). The newly drafted recommendations by the EIHP for the on-board storage system for gaseous and liquid hydrogen, were submitted to the Economic Commission for Europe (ECE), a United Nations organisation in Geneva, and in particular to the ECE WP29 Working Group on Pollution and Energy (GRPE). These draft regulations are expected to be developed to such a level that they can be globally harmonised, initially between the EU and North America. The aim is to apply them to the design and certification of fuel cell vehicles with direct onboard hydrogen storage. These vehicles will be validated by taking into account both hydrogen related vehicle components and systems but also safety requirements, refuelling procedures and periodic inspections (roadworthiness). The EIHP are also targeting their work towards developing a global standard for the relevant refuelling infrastructure, subsystems or components.

Concerning International activities on hydrogen technologies-related standards, there exists the Technical Committee TC 197 on Hydrogen Technologies of the International Standard Organisation (ISO). It was created in 1990 and it is composed of seven Working Groups that aim at developing standards in the field of systems for production, storage, measurement and utilisation of hydrogen. They have specific activities in the field of liquid and compressed hydrogen storage.

The National Hydrogen Association (NHA) [102] in the USA, according to its strategy, supports the development of codes and standards for hydrogen in a variety of organisations (industry, academia, national laboratories). This is done by providing experts, technical reports, data and other information needed by the Code Officials to complete the development of these new codes. The items considered are storage tanks, fuelling nozzles, connectors, safety equipment, and other key components and

integrated systems needed to move hydrogen into the energy sector. A comprehensive list of hydrogen standards and regulations currently available or under development can be found under Reference [103]. This is a continuously updated list provided by the NHA, under the Hydrogen Safety Report.

The US Department of Energy, Energy Efficiency and Renewable Energy, has a five-year plan [104] to accelerate codes drafting and standardisation activities for hydrogen-fuelled systems. In the area of storage and transport applications, there is a small number of key codes currently available (for instance, the NFPA 50A for gaseous hydrogen, NFPA 50B for liquid hydrogen, ASME Boiler-pressure vessel sec VIII) and some others under development.

At the moment there are a number of national and international bodies and specific technical committees involved in the standardisation and the regulatory work for hydrogen within CEN (for instance: TC 23, TC 286, TC 296), ISO (TC 58, 220) and the UNECE.

2.7 International R&D and demonstration programmes

Over the last years there has been an increased activity at international level for the support of hydrogen technologies. Figure 40 gives an illustration of the evolution of some international activities and demonstration projects on hydrogen from 2000 to 2010 [105, 106]. There follows a brief description of the main international and national initiatives on hydrogen research and development.

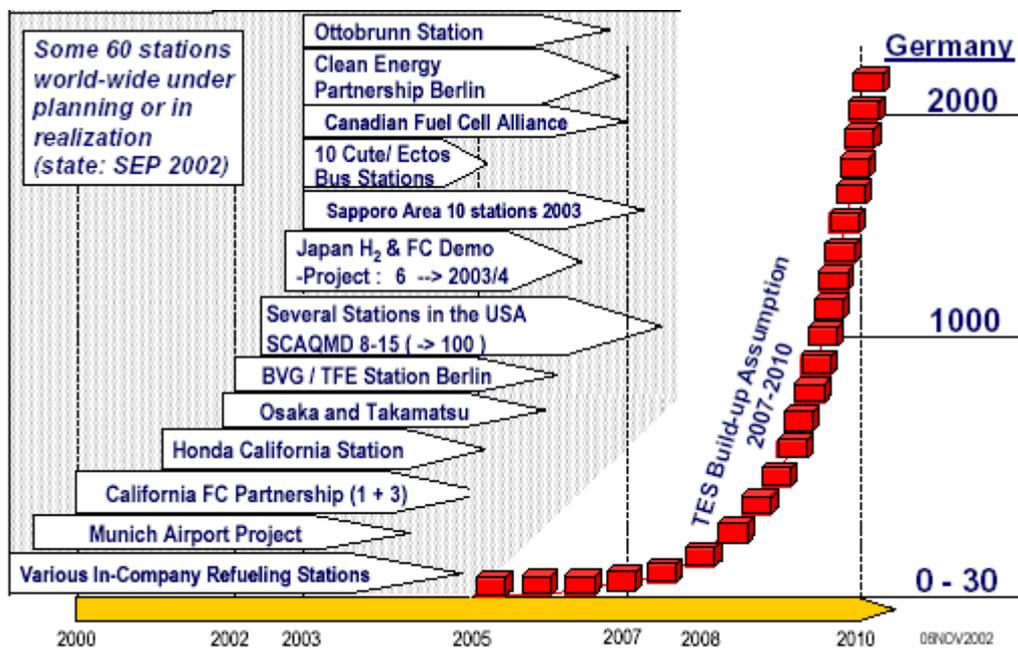


Figure 40 – Important international activities and demonstration projects for the hydrogen infrastructure, as given in Reference [105]

EU funded research

In line with the EU policy actions on Energy¹⁷ where hydrogen is seen as the alternative fuel that will penetrate by 5% the transport sector by 2020, EC has been supporting research (prenormative and strategic projects, thematic networks) and demonstration projects on fuel cells and hydrogen. This was done under the Framework Programme 5 (FP5) - €130 million, representing 50% of European projects in this area and currently under the platform of the FP6. Funded demonstration projects on fuel cell buses and hydrogen infrastructure (from 2001 to 2005 – first phase) include the ECTOS (Ecological City Transport System) and the CUTE (Clean Urban Transport for Europe) projects. Under these projects, demo buses fuelled with hydrogen are being used in Reykjavik-Iceland for ECTOS and in 10 European cities for CUTE. The objective is to test the new technology in terms of performance, and also determine the cost associated with its implementation and the benefits of the transition [107]. These demonstration projects may assist in getting a better insight into the general expectations towards the new technology, to identify possible obstacles that may have to be faced, and even how they may be overcome [108]. This way the researcher community will gain some socio-economic understanding of what is needed to shift energy consumption to renewable and environmentally friendly sources. A well-known prenormative project is the European Integrated Hydrogen Project (EIHP-<http://www.eihp.org>), currently on its second phase (2001-2003). As stated earlier, this project concentrates the European hydrogen technologies related efforts on research and development to enable the harmonisation of standards and drawing of regulations. It addresses the case of hydrogen fuel vehicles and their components powered by combustion and fuel cell engines. More details on the activities of the EIHP can be found under the heading “Safety, regulations and standards” of the present report. Under the umbrella of the Framework Programme 6 (FP6), hydrogen research falls in the thematic priority of sustainable energy systems. The first research proposals under FP6 on various aspects of the hydrogen energy economy have already been submitted and are currently being evaluated.

A rather new but important initiative is the establishment by the European Commission of the High Level Group on Hydrogen and Fuel Cell Technologies [http://europa.eu.int/comm/research/energy/nn/nn_rt_hlg2_en.html]. Details on the terms of reference, mandate and recent and planned activities of this High Level Group can be found under the “Targets” section of the present report.

Other strategic groups with activities related to hydrogen storage are the Alternative Fuels Contact Group established by the European Commission, the HyNet a European Thematic Network on Hydrogen Energy, the FUERO (Fuel cell systems and components general research for vehicle applications) and the TES – Transport Energy Strategy [105].

National EU member states programmes

Most of the EU Member States are developing research programmes on hydrogen technologies, including storage. In these programmes, hydrogen storage is either directly addressed (see the UK example) or treated as a basic research area for strengthening the contribution of renewables and alternative sources (France).

¹⁷ Green Paper on the security of energy supply - COM (2000)769, White Paper on a common EU transport policy - COM(2001)370, and Communication on alternative fuels - COM (2001)547; this list is not exhaustive.

Nevertheless it is recognised that these efforts are rather fragmented and need to be better coordinated and fine-tuned. Hydrogen storage research therefore constitutes an example theme where the European Research Area (ERA) [70] will assist to strengthen the coherence of research activities and policies conducted in the EU and make them more competitive.

Germany has been actively involved in the hydrogen research field and has shown a strong commitment to hydrogen especially for its use in transportation (hydrogen automobiles demonstration projects) with the funding of governmental (German Federal Ministry of Education and Research-BMBF) and industrial bodies. Near future research will be focusing on fuel cells and electrolyzers with emphasis on cost reduction of these technologies. The BMBF has recently cut the funding on the hydrogen research to the absolute necessary for technology conservation. This action was based on the rather pessimistic prediction that hydrogen may play an economically significant role as an energy carrier in 30 to 50 years time. In the state of Bavaria though there is still a strong interest in hydrogen technologies backed up by the car manufacturers present in the region. The most popular demonstration project there is the conversion to hydrogen fuelling of ground vehicles serving aircrafts at Munich airport. There is even discussion for the possible conversion of a spa resort to the use of hydrogen as a demonstration town [109].

Iceland

Iceland recently negotiated to erect new power intensive metal industries that will result in an increase of the CO₂ emissions by more than the 10% (from the 1990 levels) allowed for Iceland by the Kyoto agreement. Since Iceland is relying on non-polluting hydro and geothermal energy, the only way to reduce CO₂ emissions is by reducing fossil fuels consumption and replacing it with hydrogen usage. For this reason a joint venture company named Icelandic New Energy Ltd. has been created by VistOrka hf, Norsk Hydro ASA, Daimler Chrysler AG and Shell Hydrogen BV aiming at a full implementation of the hydrogen economy by 2030. Iceland provides an ideal environment for this 'field' test of hydrogen technologies. The project is fully endorsed by the people and local authorities while the Icelandic climate will test the limits of the new technology under severe conditions. As part of this initiative, there is a fuel cell bus demonstration project (ECTOS) currently running in Reykjavik that will be followed by a gradual introduction of a bus fleet and of a fuel cell passengers vehicle demonstration project. There are also plans, as the last phase of this experiment, for the introduction of fuel cell fishing vessels fleet [108]. Recently, 24 April 2003, there was the inauguration of a hydrogen fuel station that is actually the world's first public commercial filling station for hydrogen-powered vehicles. It was opened in Reykjavik and will be used in the coming months for filling up Iceland's hydrogen-powered buses going into service under the ECTOS project.

IEA Research

The International Energy Agency (IEA) has established a Hydrogen Programme and for more than 20 years has supported collaborative activities focused on the advancement and widespread use of hydrogen technologies. This programme is structured into Tasks that cover production (Task 14, 15, 16), storage (Task 17) and utilisation (Task 13) of hydrogen technologies. Task 17: Solid and Liquid State Hydrogen Storage Materials is a follow-up of the successful five years effort under Task 12, Hydrogen Storage in Metal Hydrides and Carbon. Task 17 investigates fundamental material formulation and treatment techniques, focusing on on-board storage applications. The specific targets of

the task are to develop a reversible hydrogen storage medium with at least 5wt.% H₂ recoverable at < 80°C and 1 atm absolute pressure. Also to gain fundamental and engineering understanding of hydrogen storage by various hydrogen storage media that have the capability of meeting the above storage target. Under this action, a number of advances have already been reported. The international experts undertook sixteen metal hydride and four carbon projects and they developed materials with improved gravimetric capacity (5wt%) and lower temperature (100–150°C) release of hydrogen (see catalysed sodium aluminium hydrides) [110]. An example of these efforts is the construction of very comprehensive hydride materials databases [111, 112], which are available in the web. These databases include extensive listings of alloys reported to hydride, engineering properties of selected hydrogen-storage elements and alloys and a hydride-applications database. Twenty-two new projects have now been launched. They are concentrating on fundamental investigations of new material formulations, on the mechanisms of chemical and physical hydrogen storage, and they are considering engineering solutions for practical on-board storage. Work will also include investigations on chemical hydrides.

United Nations Agency

The governing body of the United Nations Global Environmental Facility has authorised a demonstration project for fuel cell buses to the major cities and capitals of five developing countries with some of the worst air pollution levels, such as Brazil, Mexico, Egypt, India and China [109].

Canada

Canada is also running a national hydrogen programme administered by the federal government, co-funded by the industry. It addresses hydrogen systems for both stationary and transport applications. Canadian technologies but also foreign technologies when meeting the programme objectives are funded. A number of Canadian provinces, such as British Columbia (BC), Quebec, Ontario and Alberta also have regional hydrogen programmes [109].

USA

The most important activities related to hydrogen storage within the USA include the conception and implementation of the National Hydrogen Energy Roadmap by the DoE (Department of Energy), the NHA (National Hydrogen Association) and the industry. There is collaboration of the research bodies with the industrial organisations involved in hydrogen research through also the International Hydrogen Infrastructure Group (IHIG). As an example, the FreedomCAR Partnership is a Federal programme by DoE with the car industry for clean energy-efficient automotive transportation [http://www.ornl.gov/ORNL/Energy_Eff/freedomcar.htm;http://www.ott.doe.gov/freedom_car.shtml] [105, 113]. Its strategy is to develop technologies to enable mass production of affordable hydrogen-powered fuel cell vehicles while retaining the functional characteristics of current vehicles and assuring the hydrogen infrastructure to support the new ones.

Other hydrogen-related actions are the California (CA) Fuel Cell Partnership [<http://www.fuelcellpartnership.org/index.html>] and the CA Stationary Fuel Cell Collaborative. The former is a collaboration (1999) of automotive companies, fuel providers, fuel cell technology companies and government agencies that is placing fuel cell electric vehicles on the Californian roads under real day-to-day driving conditions (claiming 60 vehicles, by the end of 2003). They are also examining fuel infrastructure

issues and how to prepare the California market for this new technology. The CA Stationary Fuel Cell Collaborative is composed of governmental organisations and national research bodies. Their mission is to promote the stationary fuel cell commercialisation via a number of specific actions in a variety of applications (industrial, commercial, residential, premium, remote, backup and base-load power applications). Also under the umbrella of the South Coast AQMD (Air Quality Management District) Programs, efforts are concentrated on R&D and implementation issues of fuel cell and hydrogen-related technologies.

The Department of Energy Hydrogen, Fuel cells and Infrastructure Technologies Programme fosters research and engineering development for making hydrogen a cost-effective energy carrier for utility, buildings, and transportation applications. Its current priorities lie with hydrogen storage, production and fuel cell cost reduction. Safety and standards as well as vehicle infrastructure testing and validation and education are identified as the main focus areas for its near future activities.

In a recent development, the U.S. Secretary of Energy Spencer Abraham called for International Partners for a Hydrogen Economy. This *International Partnership for the Hydrogen Economy (IPHE)* aims to provide a mechanism to organise, evaluate, prioritise and coordinate multinational R&D and deployment programmes that will advance the transition to a global hydrogen economy.

The EU and US have already signed a fuel cells technologies co-operation agreement on the 16 June 2003. Under this agreement research links will be strengthened by joining forces to tackle challenges such as cost reductions, improved performance and durability in order to make fuel cells commercially competitive.

Japan

In Japan, the World Energy-Network WE-NET (Ministry of Economy, Trade and Industry - METI, universities and industry) [http://www.ena.or.jp/WE-NET/contents_e.html] and the Millennium Project¹⁸ with a budget of €250 million for 2003-2007 (METI, universities and industry) are the most known programmes on hydrogen technologies and infrastructure for automotive applications. There is also the Fuel Cell Commercialisation Conference of Japan (FCCJ) a rather important forum on hydrogen technologies attracting many industrial members and national and international researchers. The WE-NET project aims at contributing to the management of global environmental problems by means of large scale and effective utilisation of clean and renewable energies. Its work targets the establishment of technologies (including hydrogen production, conversion, transportation, storage, power generation and distribution) that will enable the design and introduction of an international energy network used in field [109]. The WE-NET started in 1993 and it is currently in its second phase (1999-2005). It concentrates amongst others on the construction of facilities in Japan in order to demonstrate technologies that produce, store and use hydrogen. A number of demonstration projects are planned for Tokyo and Yokohama areas in 2002-2004 while 6 hydrogen filling stations using various fuels (by-product hydrogen, liquid hydrogen, methanol, etc.) are foreseen to be constructed up to end of 2003. Hydrogen storage is a subtask of this project linked to transport. It currently

¹⁸ An international think tank comprising more than 1,000 futurists, scholars, business leaders, scientists and policymakers from more than 50 countries. Its ambition is to work towards securing energy supply safely and efficiently, without adding to the growth of greenhouse gases.

concentrates on the analysis of a large-scale hydrogen liquefaction plant, a tanker transporting liquid hydrogen and on the performance of hydrogen absorbing alloys.

3. Perspectives

3.1 The deployment of hydrogen storage infrastructure

Hydrogen storage, along with distribution, is a key group technology associated with the wide utilisation of hydrogen. Both these two group technologies seem to be the most limiting factors, presently and in the near future, to the penetration of hydrogen in the energy system and the commercialisation of hydrogen vehicles. The deployment of hydrogen infrastructure and thus of hydrogen storage facilities, is scenario and policy dependent, while decisions about broad market introduction of hydrogen are based to a large extent on solutions on technological and economical issues. The requirements for the deployment of the hydrogen infrastructure are currently assessed; therefore the formulation of specific timetables for the deployment of the hydrogen storage infrastructure is currently seen as rather premature by the stakeholders.

The choice between central and on-site production and storage of hydrogen, and of the transport mode between sites depends on the demand of either gaseous or liquid hydrogen. However, which production mode will prevail at the early stages of the hydrogen economy is still an open question. Yet, one could argue that the integration of mobile and stationary applications would support the de-centralised production of hydrogen.

To date, discussions at a European level are limited to the use of hydrogen in the transport sector, while it is generally widely accepted that the use of hydrogen for power generation will lag behind. The rate of hydrogen penetration in the transport sector is reflected in the Commission Communication on alternative fuels [114], where targets of 2% fuel market shares in 2015 and 5% in 2020 are suggested. The 2% target for 2015 would translate to up to 5 million vehicles by that time on the basis of average fuel consumption [115]. This target implies that plans for the deployment of hydrogen infrastructure should start being realised as early as 2010. Furthermore, a refuelling infrastructure must be in place by 2015 to provide full area coverage. It has been calculated that about 15-20% of all European refuelling stations should be equipped with hydrogen supply, a percentage that corresponds to about 15,000 to 20,000 refuelling stations in EU-15 alone. An integral element of this infrastructure is storage. However, the required storage capacities will also be determined by the decisions to be made about the pathways to produce and distribute hydrogen. The type of the plant used to produce hydrogen will dictate the storage capacity and the type of storage vessel installed on the production site. Another issue to be resolved concerns the form in which hydrogen should be distributed, as a compressed gas or liquid. The hydrogen distribution system will shape the demand for regional/local storage facilities. Finally, the storage capacity at each refuelling station will depend on how hydrogen will be delivered to the station (via pipeline, via electrolysis at night where storage of about 70% of the daily hydrogen consumption will be needed, or via continuous electrolysis, where about 30% of the daily consumption of hydrogen will need to be buffered) and how hydrogen will be used in vehicles (compressed gas or liquid). Irrespective of the hydrogen production, distribution and utilisation option(s) that will be followed, tens of thousands of stationary storage vessels and millions of vessels for on-board storage will need to be manufactured and installed in the coming decade, creating a large hydrogen storage market. Furthermore, this demand will increase with time, as the infrastructure develops further and the hydrogen-fuelled fleet expands.

3.2 Performance and cost analysis

3.2.1 Cost assessment of hydrogen storage

Hydrogen as a fuel cannot become an economically viable option unless its costs are comparable to those of conventional fuels. A major element in the cost of hydrogen is the cost of storage. The costs of storage vessels, the cost of hydrogen compression or liquefaction and the overall cost of hydrogen storage (that comprises materials, manufacturing and installation costs) are reviewed next.

3.2.1.1 Cost of hydrogen compression and liquefaction

Hydrogen compression

The cost of hydrogen compression has been reviewed in a number of publications [18, 19, 116]. Compressors are rated based on the work they can perform, which in turn depends on the inlet and the discharge pressure and the flow rate. Figure 41 shows the cost of compressors, as reported by various sources. Sizing exponents¹⁹ range between 0.61 [116] and 0.80 [18].

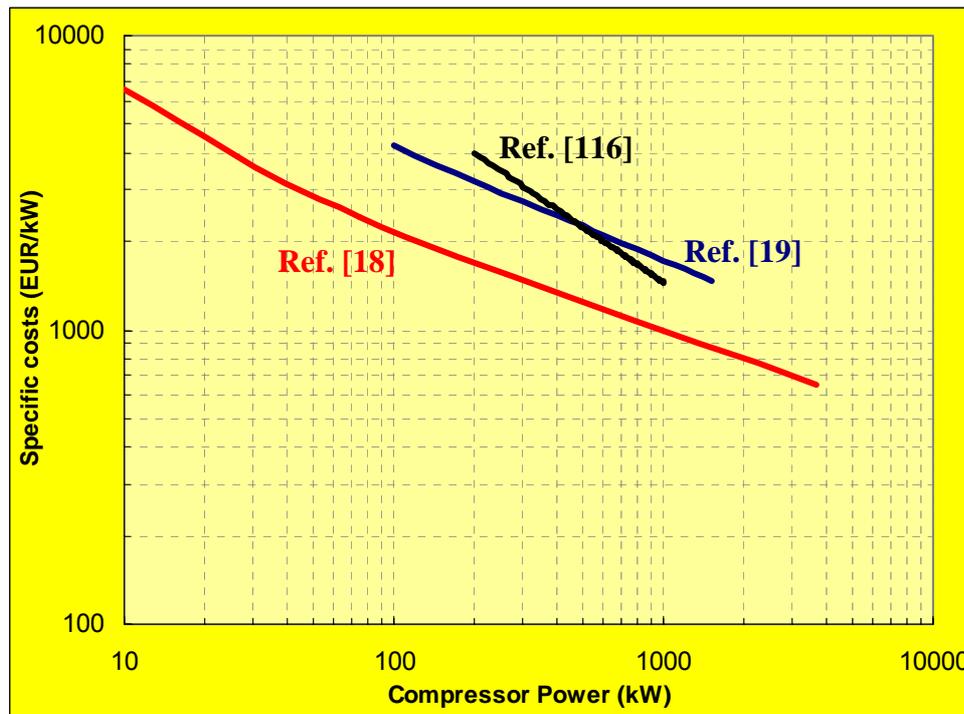


Figure 41 – Cost of compressors as reported by various sources

¹⁹ The cost of specific components typically depends on size or scale and can often be correlated by the approximate relationship:

$$\frac{C}{C_R} = \left(\frac{S}{S_R} \right)^n \text{ or } C = k S^n$$

where, C is the cost of the item at size or scale S; C_R is the cost of the reference item at scale or size S_R, k is a constant and n is the sizing exponent [116].

The discrepancy of the reported costs may be attributed to:

- The reporting year (2000 for [116], 1997 in [19] and 1995 in [18]).
- The exchange rates (original values are reported in British pounds [116] and US dollars [18, 19], and converted into euros based on 1.45 and 1.0 conversion factors respectively).
- Whether the cost of motor and auxiliaries has been accounted for (References [116] and [19] state explicitly that these costs have been included; however, this is not stated in [18]).

Prices for small compressors (e.g. 50 kW) are in the order of €5,000/kW, while the specific prices of larger compressors are lower, being in the order of €1000-1500/kW for a 100-kW piece of equipment. On top of these costs, the installation costs (approx. 35% of the bare cost of a compressor) and the cost of material and labour for its foundation, building, electrical, piping and other works (approx. equal to the bare cost of the compressor) should also be considered. The overall cost of purchasing and installing a compressor is about 2.39 times its bare purchasing cost [19].

As was explained in chapter 2, compressors are prone to failure due to wear. To provide for continuous operation in case of scheduled or unexpected maintenance, compressors are installed in redundant units increasing the total costs. Furthermore, the costs of maintenance and of electricity are major contributors to the variable costs associated with compressors. The electricity consumption is calculated based on the efficiency of the compressor (70-85% based on its type and operating conditions) and the efficiency of the motor (90%), see Figure 12, chapter 1.

Auxiliary equipment

The cost of other auxiliary equipment is given in [19], however based on the work of S.M. Walas: '*Chemical process equipment selection and design, Butterworths Pub. Boston, 1988*'. These costs (in 1998 values) are presented next, assuming that US dollar is in par with the euro. The accompanied comments are also based on [19], in cases being stated verbatim.

- *Heat exchangers*: The estimation of the actual costs of a heat exchanger requires its design optimisation beforehand. The cost, C_{hx} , depends on the surface area of the exchanger, A , and the type of insulation. The cost may be estimated by the following equation: $C_{hx} = C_{unit}A + C_{ins}$, where C_{unit} is the cost per unit surface area, depending on the material and the manufacturing process, and C_{ins} is the cost of insulation. The cost may also be calculated using a formula of the form: $C_{hx} = K A^n$, where K and n depend on the type of heat exchanger. For compact heat exchangers K and n have values of 250 and 0.6 respectively. The cost of installation and bringing the heat exchanger in operation is approx. 1.235 times its bare cost. Nevertheless, it is questionable, whether these generic formulae can be used for heat exchangers used in liquefaction plants, given that these pieces of equipment are not exactly 'out-of-the-shelf', but are manufactured on request, in small quantities, with very high requirements for materials, design and insulation.
- *Expanders*: The cost of turbine expanders is given by the formula:

$$C_{turb.expander} = 421.6 \left(\frac{kW}{0.746} \right)^{0.81}$$

Hydrogen Liquefaction

The cost of hydrogen liquefaction comprises capital costs, the cost of power and operating and maintenance costs (O&M). According to [14], about 62% of the cost of hydrogen liquefaction in large plants is attributed to fixed charges of the capital cost, 30% to power consumption and 8% to O&M costs. However, these costs depend strongly on plant efficiency and capacity.

The capital investment for a liquefaction plant depends on the production rate, the type of cycle utilised, and, the location of the plant [19]. It accounts for the cost of land, equipment (see above), engineering (5-10% of the total capital cost), overhead and administration etc. The cost of a 4.4 t/d plant built in Europe in the early 90's was about €15 million [84], i.e. approx. €3.4 million per tonne-per-day production rate. Cost data presented in [18] show that the specific capital investment decreases with the increase in the production rate with a scaling factor of 0.6-0.7, reporting that the specific capital cost for a 36 t/d plant is about \$1.1 million/(t/d) (1995 price). However, [117] reports capital costs of the order of €1,015-1,125/(kg/h) for a 100 t/d plant, or \$50,000/(t/d). This aforementioned cost excludes the cost of land and working capital. Finally, it is reported that the total capital cost comprises 10% planning costs, 60% equipment costs (mainly the compressors and the heat exchangers), and 30% construction costs [18].

Power consumption in liquefaction plants was discussed in chapter 2. The consumption for current plants is within the range of 0.89-1.06 kWh_{el}/l_{LH2}. According to the US hydrogen program, the average cost of hydrogen liquefaction is about \$1.11/kg_{LH2}. The target of the US program is to reduce these costs to \$1.01/kg in 2005 and to \$0.53/kg in 2010 [75]. Power requirements are rather independent from plant capacity and depend on the efficiency of the process. Finally, O&M costs depend on the process efficiency and the production rate: increased efficiencies and production rates decrease the O&M costs [19]. Ref. [19] has assessed the costs of hydrogen liquefaction in 3 plants: a simple conceptual plant with 17% efficiency; an intermediate plant based on the Claude cycle with a 24% efficiency; and, an optimised large scale liquefier with a 31.5% efficiency. For large and optimised plants, the cost of liquid hydrogen can be as low as \$0.7/kg. The results are summarized in Figure 42.

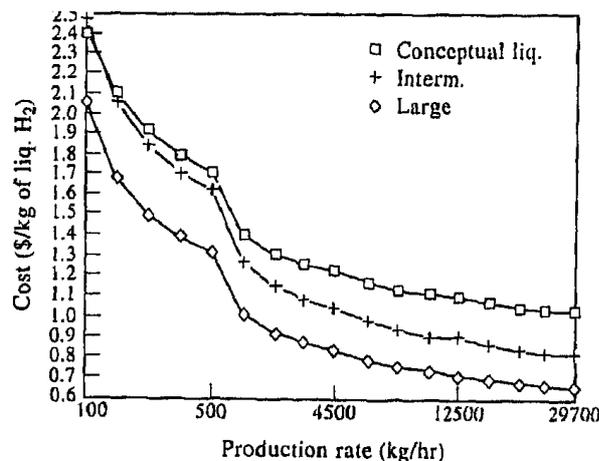


Figure 42 – Cost of hydrogen liquefaction, as calculated in Ref. [19]

3.2.1.2 Cost of hydrogen storage

Compressed gas storage

The cost of compressed gas vessels increases with the operating pressure and their capacity. According to [117], the cost of a vessel operating at 140 bar is about \$400/kg of stored hydrogen and of a vessel operating at 540 bar about \$2100/kg, see Figure 43. Furthermore, according to [118], cylindrical steel tanks with volume of 765 l and operating at about 415 bar may cost about \$13,000, yielding a specific cost of about \$650 per kg of storage capacity. The same source states that the cost of similar tanks for compressed natural gas are of the order of \$500/kg of gas stored. The main difference is attributed to the production volume, given that the costs associated with the production of a small number of vessels is excessive, compared to large scale manufacturing due to the large number of processing steps required for the construction of such vessels. According to the same source, composite pressure vessels may cost about \$350/kg. The low costs, compared with the conventional steel tanks, are attributed to the lower cost of material (HDPE) and reinforcing fiber, despite the higher manufacturing costs. Finally, [88] mentions that a modern full-composite vessel with a volume of 150 l costs about €4,000.

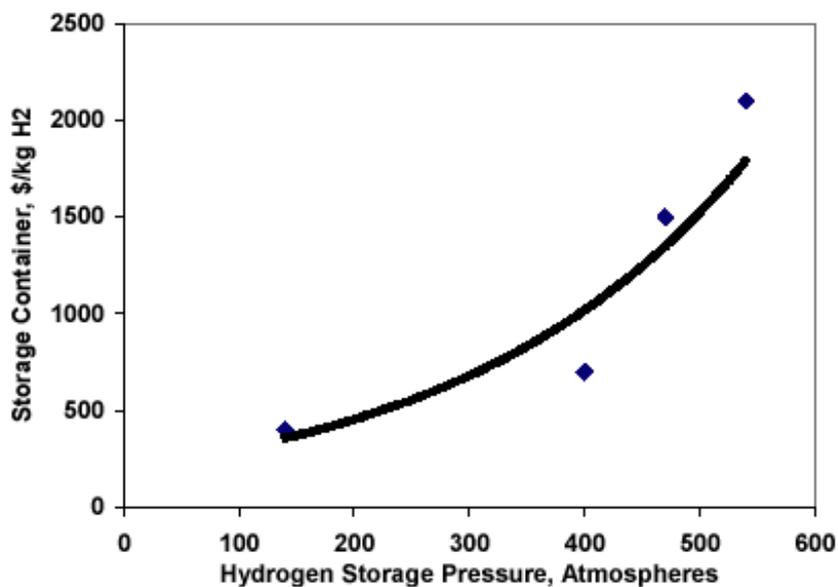


Figure 43 – Costs of compressed hydrogen storage vessels [117]

Ref. [80] reports the *capital cost of pressurised vessels* normalized to storage capacity (in kg of hydrogen) as a function of their storage capacity. This information is being plotted in Figure 44. Clearly, the specific capital investment drops with the increase in storage capacity. The same source also estimates the *overall cost of the storage process*, defined as the sum of capital and O&M costs divided by the annual hydrogen throughput. The operating costs of compressed hydrogen storage account mostly for the energy to compress the hydrogen. The energy consumption depends on the final pressure. The results are plotted in Figure 45. Based on these results, the total capital investment for vessels with capacities up to 1,000 tonnes is \$204-\$1,080/kg of hydrogen stored (or \$1,700-\$9,000/GJ). Furthermore, short-term storage costs varies with storage

capacity between \$1.5-\$4/GJ, while long-term storage costs are increased, varying between \$7-\$13/GJ.

According to today's practice, storage vessels for stationary applications are currently rented and not bought by the utilities. Monthly rentals are of the order of several thousand euros, depending on capacity.

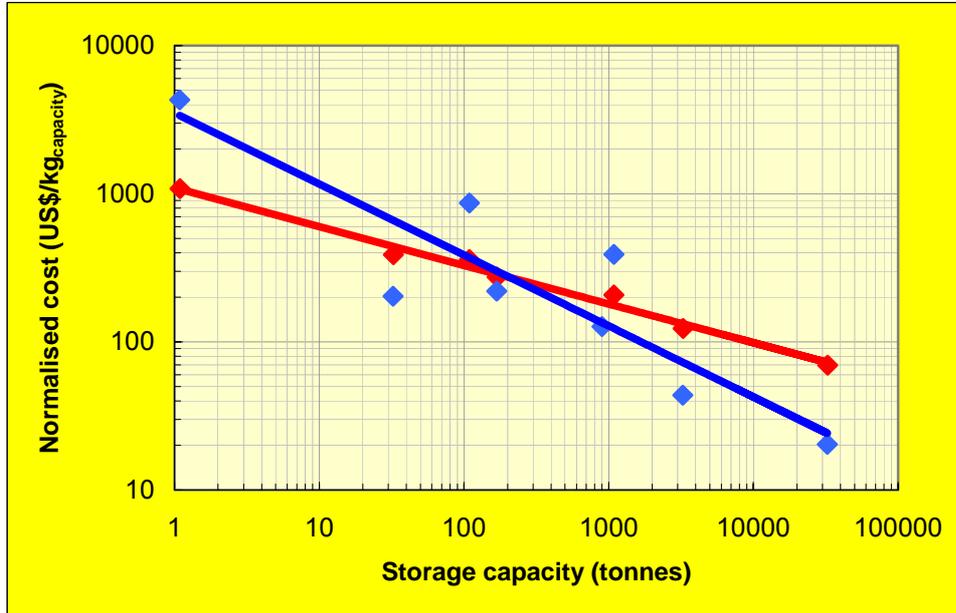


Figure 44 – Capital cost of pressured hydrogen vessels (in red) and of cryogenic liquid storage vessels (in blue) normalized to storage capacity (in tonnes). Data after [80]

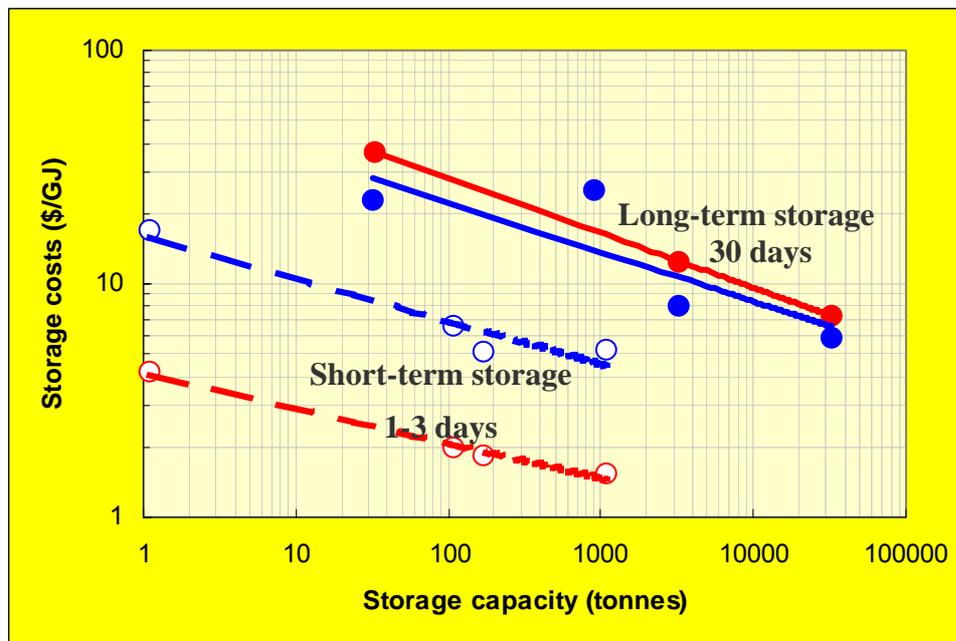


Figure 45 – Compressed (in red) and liquid hydrogen (in blue) costs of the storage process for short-term (1-3 days) and long-term (30 days) storage (Data after [80])

Liquid storage

The cost of liquid hydrogen storage has been reviewed by [80] and [18] and the results have been summarised in Figure 44 and Figure 45. Capital costs for cryogenic storage vessels may vary between \$20 and \$4,500/kg depending on the storage capacity. Based on these data, the capital cost of a cryogenic vessel is lower than that of a compressed gas vessel at capacities in excess of 200 tonnes of hydrogen (or 2,800 m³). The cost of short-term storage using liquid hydrogen is significantly higher than the cost of compressed hydrogen. However, the storage of hydrogen as liquid for long periods of time appears to offer a cost advantage when compared to compressed hydrogen storage. Energy consumption in the liquefaction plant may account for 60% to 80% of the cost of short-term liquid hydrogen storage and between 30 to 60% for long-term storage [80]. It is also reported that the cost of storage is relatively insensitive to capacity for large storage vessels (>13,000 GJ or 1530 m³).

Finally, it is very difficult to estimate the cost of liquid hydrogen vessels for on-board applications, given that the existing vessels are prototypes. It is estimated that the costs will be in the range of \$1,280-\$2,550/GJ [80].

Metal hydride storage

There are many uncertainties surrounding the estimation of costs of hydrogen storage using metal hydrides, given that this storage option depends on a technology that is at its infancy. The overall cost of a metal hydride storage vessel is dictated to a large extent by the cost of the hydride material itself. Furthermore, no economies of scale are applicable to this storage option, i.e. the storage cost increases linearly with capacity [80]. Reported capital costs for metal hydrates range from \$4,200/GJ to \$18,400/GJ, and the cost of storage may vary between \$2.90-\$7.50/GJ. Furthermore, it is reported that on-board storage systems may cost \$4,200-\$7,020/GJ [80]. Another source indicates that the cost for storing 1, 10 and 100 m³ of hydrogen is about €400-€1500, €200-€750, and €150-€550 respectively [81].

Underground storage

Underground storage appears to be the most inexpensive storage option for hydrogen. According to [80], capital costs for underground storage lie within the range of \$16-80/GJ, the cost of daily storage between \$1-5/GJ while the cost of monthly storage is 50% to 80% higher than that of daily storage.

3.2.2 Performance analysis

To evaluate in a harmonised way the storage technologies to be used in the frame of a 'Hydrogen Economy', common tools and assessment methodologies have to be employed. Different storage technologies currently available should be compared in terms of maturity taking into account technical aspects and issues such as commercialisation, environment, industrial/technological risk, and economic and social impact [24]. Such an assessment tool was reported as having already been used for the hydrogen production processes evaluation [119]. This methodology was developed and funded by Ecobilan, CEA and EdF, with an additional financial support of ADEME (French agency for the management of energy and environment); it is the so-called MASIT (Multicriteria Analysis for Sustainable Industrial Technologies) [120]. The developers of this tool claim that it allows a sector to compare new technologies to the referenced one while matching up financial, technical and social criteria to the

environmental criteria. Similar tools or even more comprehensive ones can be developed in the future.

As a general comment and based on currently available techno-economic analyses reports, it may be concluded that, at present, no single hydrogen storage technology satisfies all performance criteria required by manufacturers and end-users for the introduction of hydrogen into the global energy system. Technical advances and cost reductions are needed in hydrogen storage and distribution [121]. All storage options currently available (compressed, liquid, metal hydrides, porous structures) offer advantages and disadvantages with respect to weight, volume, energy efficiency, and cost and safety aspects. Aiming at providing economically and environmentally attractive storage solutions, research efforts should focus on improving existing commercial technologies (compressed gas and liquid hydrogen) but also on the rather higher risk but still promising advanced solid storage technologies.

To recapitulate, possible improvements and topics for further R&D on hydrogen storage can concentrate on the following areas, particularly bearing in mind the prospective applications:

Gaseous form: even though it is currently the most mature technology, improvements may still be needed in weight/volume storage efficiency, and work could be directed towards optimised/versatile/safe tank designs. Also aspects such as system integration and cost reduction for producing the next generation of safe pressurised storage systems with an acceptable filling speed, may have to be carefully addressed. Coming to applications, this type of storage is seen as a competitive option for short storage times and low production rates. Electricity costs of compression at high production rates and pressure vessel cost for long storage times (impetus for higher pressure vessels) are still issues that may need to be carefully considered [121, 122]. With respect to on-board applications, lightweight, cost-effective, high-pressure balance-of-plant components, such as tubing, fittings, regulators, check valves, sensors, may be lacking [75].

Liquid form: it provides a medium with a good volumetric storage efficiency. However issues such as special handling requirements, heat transfer, long-term storage losses, and the energy intensive process of cryogenic liquefaction have to be better understood and resolved. Due to its high energy density this storage solution is appealing to transport applications, may be ideal for high production rate and long storage time whereas it is uneconomical at low production rates and suffers from the energy costs of the liquefaction process [121]. The ‘boil-off’ issue is an energy penalty and a potential safety hazard and needs to be controlled [75].

Metal hydrides: not yet a mature technology, but a rather promising lower pressure hydrogen storage option, with conformable shapes, and reasonable volumetric storage efficiency. Material data validation, weight penalties, thermal management issues and quite importantly development of actual test protocols may still need to be tackled [75]. With respect to the conventional metal hydrides, capacity improvements are rather unlikely, however there is still potential for improving the kinetics, cycle life, tolerance and operating temperature [121]. As far as novel metal hydrides are concerned, most promising in terms of capacity and kinetics appear to be the sodium aluminium and the lithium beryllium hydrides or systems with similar properties but working nearer the ambient temperature. With respect to applications, metal hydride storage is seen as the safest option, however it has reportedly no economy of scale (high capital cost of storage alloy) [121] since it does not compete at high production rate or long storage time. It may be an ideal solution or at least become competitive for low flow rate/short

storage time and therefore a leading candidate for on-board vehicle storage. Improvements in energy density are still though required and dispensing technologies have to be defined [75, 122].

Porous systems: a longer-term storage solution, which has the advantage of being inherently safe, but still the least developed of all. The full understanding of fundamentals issues such as the exact adsorption/desorption mechanisms and its implications on the volumetric capacity of porous structures, is still lacking. There is also an imminent need to compare, replicate, and validate material and sorption data in independent laboratories.

Other media: Challenges include synthesis, processing, thermal/pressure management and better understanding of absorption / desorption.

In general, the optimisation of the storage system to be used depends on a number of variables, such as the production rate (compressor/liquefaction plant size, operating costs), the actual storage time including the overall capacity, the unit size and cost, the availability of the infrastructure and the type of the end-use application. Nevertheless capital costs, maintenance requirements and also safety issues are equally influential parameters for choosing the best-suited storage solution.

3.2.3 Concluding remarks

The applicability of the various storage options will ultimately depend on the application (on-board or stationary), which in turn will dictate parameters like the minimum required energy density, quantity of hydrogen to be stored and the storage period, reliability and availability of the storage system, minimum safety requirements and capital and operating costs. Based on the current state-of-the-art of hydrogen storage technologies, and on short to medium term anticipated developments, as discussed above, the following generalised statements can be made:

- Storage of hydrogen as compressed gas at high pressures (up to 700 bar) can be used to store small quantities of gas.
- Storage of hydrogen in liquid form can be used for storing large quantities of gas for longer times, however at high-energy penalties for liquefaction.
- Metal hydrides may offer an advantage for storing small quantities of gas in the medium to long term.

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Abstract

Hydrogen is seen as a major energy carrier for the future. A key precondition for the realisation of a hydrogen economy is the development of a hydrogen infrastructure, which, by definition includes the system needed to produce hydrogen, store it, and deliver it to its users. Considering the particular issue of hydrogen storage, all systems still need to be analysed in a comprehensive way. Unlike gasoline or diesel, easily handled liquids at ambient conditions, hydrogen is a lightweight gas and has the lowest volumetric energy density of any fuels at normal temperature and pressure. Therefore the most significant problem for hydrogen (in particular for on-board vehicles) is to store sufficient amounts of hydrogen.

This report reviews the current technical and economic status of technologies for hydrogen storage and the likely areas for technical progress. Research efforts devoted to these issues worldwide are highlighted and options under development are discussed along with commercially available hydrogen storage technologies. Although all applications for hydrogen are addressed, emphasis is given more to the use of hydrogen in transport.

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