Methods to Store and Transport Hydrogen

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FOREGROUND

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1 Introduction to H2 Storage and transportation

Hydrogen is a gas that can be stored and transported in many different ways. It can be stored for short-, medium- and long-term periods. It can be stored in compressed, liquid, under-ground, in metal absorbing material, etc. It is, therefore, important to understand the different types of storage mechanisms available and the different terminology used to define a given storage medium. Understanding these is a critical pre-requirement for anyone who is developing a hydrogen project, whether being in maritime or another sector. This is due to the fact that choosing a hydrogen mechanism depends on many competing factors including but not restricted to:

- The quantity of hydrogen to be stored.
- The application in which hydrogen fuel is to be used.
- The distance hydrogen has to be transported from the point of production to the point of use.

A good storage system can be defined as being able to store a large quantity of energy, with little or no energy used to store the energy (almost impossible) and the storage must not have a high rate of self-discharge. In addition to this, any storage mechanism must not have a fast degradation rate in performance through time. Hydrogen, used as a chemical energy storage (either as gas or liquid) is potentially able to meet most of these criteria all at once. However, hydrogen has another strong characteristic when used as an energy storage medium. It can also be mixed with many different gases and as such it can be directly injected in today's existing natural gas grids – and that in large quantities, though only a small percentage of H2 can be blended with natural (this depends on country's legislation and type of pipes used to transport the natural gas).

As aforementioned, there are many different methods that can be used to store H2. Each method has a number of advantages and disadvantages. Understanding these allow an easy storage selection process. At present, and in addition to the cost of a storage system, the most critical factor to take into account when selecting a storage system is safety. The second factor is related to how easy it is to use a given hydrogen storage system for the chosen application and where the hydrogen is to be used (environment – indoor, outdoor, small confine space, etc. and the location, city, rural, transport, stationary). The below sections provide an overview of the different most common methods used to store and transport hydrogen:

- Compressed hydrogen gas.
- Liquified hydrogen.
- Organic Chemical (MCH).
- Ammonia (NH3) as a fuel.
- Hydrogen absorbing materials.
- Salt caverns.
- Pipelines.

2 Compressed H2 gas storage systems

Pressurising hydrogen into metal cylinder gas storage systems is a well understood field. However, with the increasing demand for hydrogen storage for lighter storing solution, new types of storage have emerged.

H2 gas is usually compressed in two main formats; (a) long-term seasonal storage (months); and (b) short-term storage (hours, and days). In order to store a substantial amount of hydrogen in a confine space, there is a need for compressing it (or pressurising it). The pressurising process needs some input energy to compress the gas, either being electricity or heat (or a combination of both). The devices that perform the compression are known as compressors and these can compress gas to fairly large pressures reaching 1000 bar.

As hydrogen is the smallest molecule, it is difficult to store a substantial quantity (in terms of volumetric density). When compared to petrol, which has a density of 8825 kWh/m^3, hydrogen pressurised at 700 bar (fairly high pressure) can only achieve a density of 1332kWh/m^3. This is substantially lower than petrol. The space needed for hydrogen is almost 6.6 times larger than its petrol equivalent (in terms of energy stored per m^3).

This is also the case when compared to Compressed Natural Gas (CNG). CNG stored at 250 bar achieves a density of 2500 kWh/m^3. Hydrogen requires about 1.8 times the CNG equivalent in space. And this takes into account that hydrogen is stored at 700 bar (again a fairly high pressure). Hydrogen would need much more space if stored at a lower pressure (say, 170 bar, or 200 bar).

In general terms, space for storing hydrogen is not a substantial factor when the application is stationary - unless hydrogen is used in a confine stationary space or if the value of the real estate is high at a particular location (say in a city centre). However, it is usually agreed that the size of cylinders and their associated weight is not a serious problem. In these types of stationary applications, where weight and space are not an issue, it is most likely that standard steel cylinders are selected.

On the other hand, when considering transport applications such as cars, buses, vans, trucks, etc., it is critical to have lightweight and as small a cylinder as possible, with as much energy stored as possible. In the transport sector, weight and space are very important factors used at design stage. The heavier the vehicle, the more fuel consumed. The more space used for a given equipment (i.e., in the case hydrogen storage), the less space available for passengers, for carrying things, or the larger the vehicle to be. The same logic applies to the mobile applications sector. Mobile gensets, remote applications, etc., all require fuel to be transported with the device or fuel to be delivered to the device at regular intervals.

From the above, it is clear that for both transport and mobile applications, the allowed weight and available space of a cylinder(s) for storing hydrogen will be limited. It is for these applications that “light” composite technology has been developed. As a rule of thumb:

- Where space is not an issue, and weight is not an issue, then use metal cylinders.
- Where space is limited (and as such is an issue), and/or weight is issue, then use composite cylinders.

Substantial research and development programs have been launched since the beginning of the 21st century for developing high pressure, light weight hydrogen storage based on what is known as "composite materials".

These programs have led to the development of several types of composite cylinders. The cylinders use as one of their main components carbon fibre technology/material, which provide the well needed lightness and the strength to withhold high pressure, but also promote the desired low permeability to ensure hydrogen does not evacuate the tank.

Nowadays, it is possible to purchase tanks with pressures reaching 900 bar for stationary applications. It is also possible to store hydrogen at 700 bar for transport solutions such as cars and vans. The different composite cylinders available on the market have undertaken fairly stringent tests including drop down, fire tests, etc., to comply and attain accreditation under recognised national and international codes and standard certification.

2.1 Types of compressed hydrogen gas storage cylinders

If cost is of premium, then pressurised gaseous form of storage is the solution to be used, being the most cost-effective mechanism employed to store and move hydrogen (in small quantities). There are mainly five different types of pressurised gas cylinders. The below table summarises these with their associated standard pressure of operation.

There are two main criteria that can be used to differentiate pressurised hydrogen tanks:

- The maximum pressure of a vessel.
- The material used to manufacture the tank (steel, carbon fibre).

The higher the operating pressure of a tank, the more hydrogen that can be stored in a tank. In other words, the higher the pressure, the higher the storage density.

Tank Type	Main Liner Material Used	Types of Composite material used	Max Operating Pressure
Type I	Steel Metal Liner	- No composite used – only steel	200 bar (2900 psi)
Type II	Steel or Aluminium Metal Liner cylinder	- Fibre wrap typically comprises either glass- fibre or carbon- fibre - Hoop fibre wrap only	Steel/carbon - 299bar (4336psi) Al/Glass 263 bar (3814psi)
Type III	Aluminium Metal Liner cylinders	- Complete Hoop and helical fibre overwrapping of liner - Fibre wrap typically comprises either glass-fibre or carbon-fibre - Aramid-fibre has also been used although less commonly - Hybrid fibre wraps have also been used (comprising a mix of glass-fibre and carbon-fibre)	Al/Glass 305bar (3814psi) Al/Aramid 438bar (6352psi) Al/carbon 700bar (10153psi)
Type IV	Plastic - commonly HDPE is used	- Fibre wrap typically comprises either glass-fibre or carbon-fibre	661bar (9586psi) and greater

		- Hybrid fibre wraps have also been used (comprising a mix of glass-fibre and carbon-fibre) - Complete Hoop and helical fibre overwrapping of liner - Aramid-fibre has also been used although less commonly	
Type V	No Liner Required	- Under Research and Development	Under Development

Table 2-1 - Overview of the most common types of gaseous cylinder

Type I steel cylinders have been used for decades and the industry have a long history of operating the tanks. There are the most common cylinders amongst the different storage technologies and they are still by far the cheapest to manufacture. The main downside of these tanks is that they are very heavy. As such, they are not suitable for automotive applications. Type I cylinders are mainly used to store and transport hydrogen for short distances. For instance, from a main gas depot to a close-range distance end user.

Steel hydrogen cylinders come in different shape and sizes. In the case that hydrogen needs to be transported in larger volumes, then a Multi-Cylinder Pack, also referred to by the industry as MCP is used. An MCP is simply a pack of cylinders all interconnected together. These MCPs are used when medium quantities of hydrogen need to be distributed to a local customer.

In case that even larger quantities of hydrogen need to be transported over long distances, then tube trailers are commonly the accepted method. In summary, and as a rule of thumb;

- For small users, it is accepted that single cylinders are delivered.
- For medium size users, MCPs are used.
- For larger users, tube trailers are favoured.

The below figure illustrates the MCP and tube trailer.

Figure 2.1 – Compressed gas storage – Composite (left), MCP (right)[1]

Type II tanks are known to be lighter than their counterpart type I. The reason is simple, manufacture tends to reduce the amount of steel by combining some steel and aluminium or just using aluminium. To strengthen the cylinder (as the quantity of steel is low or non-existent – replaced by aluminium), several layers of filament windings is added (on top of the aluminium). The filament material can include glass fibre, aramid or carbon fibre. Type II cylinders are much lighter than type I, but still considered by the industry are being too heavy to be included as an option for automotive applications.

Type III and IV cylinders are lighter than type I and II. However, they are more expensive as their manufacture require more advance technologies. These are mainly used in automotive applications.

Type V compressed cylinders are still under research waiting for a major breakthrough. The overall idea is to have a tank with no liner, meaning no heavy materials being used. This would substantially reduce the overall weight of the cylinder.

High-pressure carbon composite cylinders have been widely used in the CNG automotive sectors. They have been really successful, but they have also been associated with a multitude number of failures due to human errors, with many casualties. The main common failure is the lack of maintenance of the cylinder, which requires visual checks (for cracks), but also periodic replacements of valves used within the supply system. As such, it is highly advisable to develop a periodic maintenance schedule for all of the

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[1] Courtesy of Pure Energy Centre www.pureenergycentre.com

cylinders being used, especially including the appropriate replacement of the valves etc. at the end of their lifetime.

3 Liquefied H2 storage

Liquifying hydrogen is the process of cooling hydrogen with the aim of turning it from a gaseous state into a liquid form. The cooling process requires a lot of energy as hydrogen only becomes liquid at minus 253°C. There are a number of applications for liquid hydrogen, the most notorious of them being the space industry to launch space rockets.

As hydrogen is extremely cold in its liquid state, storing it requires highly specialised equipment. The most common equipment used is a heavily insulated Dewar tank. The aim is to reduce the ambient heat to reach the liquid hydrogen. By doing so, the difference in temperature between the outer shell of the tank and the inner shell is kept to its minimal, thus reducing the potential for hydrogen to change back from its liquid to gaseous form.

Any liquid H2 cylinder must be manufactured with very strong reinforcement so that it can store liquid hydrogen under pressure. In essence, these types of tanks require maintaining both the integrity of the cylinder under pressure and ensuring that hydrogen does not heat up.

Using liquid hydrogen is complex and most hydrogen application manufacturers would try to avoid using this storage technology if at all possible. The issue is that hydrogen has a tendency to “evaporate” as soon as it heats up. This means that substantial amount of stored hydrogen (in liquid form) could be lost as the hydrogen slowly heats up. As such, a complex set of equipment is needed to manage the evaporation process.

Evaporation will occur if some heat reaches the stored hydrogen. This can happen in a number of ways, through convection, conduction, or radiation. In any of these heating up event, hydrogen will start heating up and deliquefy. This process is known as hydrogen reaching its boiling point where it changes from its liquid state into a gaseous state. An example of a liquified hydrogen tank is shown on the below figure.

Figure 3.1 – NASA liquefied hydrogen tank[2]

The major downside of liquid hydrogen storage is the amount of energy needed to liquify hydrogen. As a rule of thumb, 30kWh of energy is required to convert 100kWh of gaseous hydrogen into liquid H2. The amount of energy required to convert H2 from gas to liquid is about 30% of the total energy transformed in liquid.

This clearly reduces the attractiveness of liquid hydrogen (LH2). It is especially so when considering hydrogen fuel for land transport – too much losses in converting hydrogen to liquid for a small hydrogen tank.

However, for long distances, and for shipping hydrogen from country to country, liquid hydrogen is seen as one of the main potential solutions as it has a high energy density (when compared to gaseous state).

LH2 is also seen as one of the main contenders used as a fuel for marine vessels, though other liquid solutions are being considered (i.e., ammonia, etc.). Many projects are currently being developed for shipping hydrogen using marine vessels, and one of the first of such vessel has been built in Japan by Kawasaki. The below figure illustrates the liquid hydrogen boat.

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[2] https://www.nasa.gov/sites/default/files/thumbnails/image/0-43485369735_45b9ffa8b6_1.jpg

Figure 3.2 – Kawasaki vessel to transport liquid H2[3]

4 Liquid organic storage solutions

For decades, gaseous and liquified hydrogen have been the main two options for storing and transporting hydrogen. However, there are nowadays many more options. One of these options is the Liquid Organic Hydrogen Carrier (LCOH) storage solution. In this option, hydrogen is converted from gaseous into a liquid form. However, this process does not involve cooling off the hydrogen to -253°C, but to bound the hydrogen molecule to another chemical. The other chemical is known as a carrier, because it allows to carry hydrogen from one point to another one.

There are two main reasons for developing this technology; (a) using LCOH, it is possible to easily transport large quantities of hydrogen. This is true even for long distances, while it was not the case for pressurised (density issue) or liquified gas (boiling issue). Liquid organic storage systems are therefore a potential contender for transporting hydrogen from continent to continent, from country to country or from cities to cities.

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[3] https://newatlas.com/marine/kawasaki-worlds-first-liquid-hydrogen-transport-ship/

The second reason is highly critical as it deals with the safety of transporting the H2 fuel. When transporting hydrogen in gaseous or liquified state, there is a highly flammable risks associated with the transport. There is also a pressure risk with the gaseous system and a freezing risk if liquified hydrogen escape its storage. All of these risks do not exist if hydrogen gas is bonded to an appropriate carrier. Bonding H2 to another chemical creates, in many cases, a non-hazardous and non-flammable compound. The new chemical can be stored at ambient pressure, again substantially reducing the cost of safety.

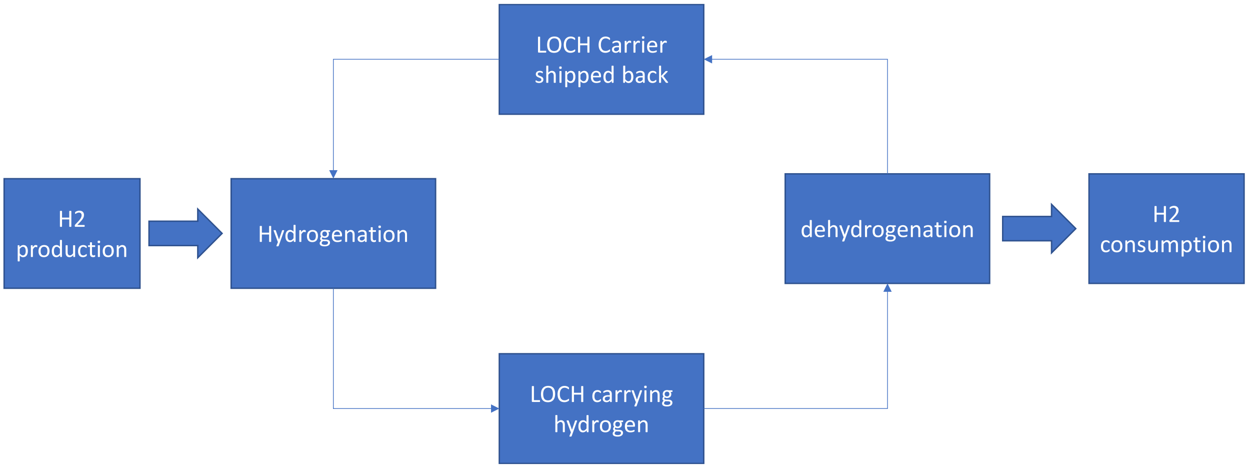
Liquid Organic Hydrogen Carriers (LOHC) is a process that can be used to store H2. LOHCs uses a reversible hydrogenation process. In its simplest form, hydrogen gas is injected into a reactor. In this reactor, hydrogen is hydrogenated with a carrier, the end result being the liquid LOCH.

The LOCH, in its liquid state, can be easily transported from the production site to another site, where H2 will be used and consumed. At the consumption site, H2 is dissociated from the carrier via a dehydrogenation process. The dissociated hydrogen is now ready to be used.

The advantage of this method is that the carrier can be collected during the dehydrogenation. It can be shipped back to the hydrogenation site for reuse. The process is therefore optimised to avoiding waste, and a full hydrogenation / dehydrogenation can start again.

Many different hydrogen carriers have been developed since the beginning of the year 2000. Toluene, Naphthalene, benzyl toluene, dibenzyl toluene, N-ethyl carbazole, phenazine, 1-methyl indole, 2-methyl indole, 1,2-dimethyl indole amongst many others which are at commercialization/demonstration stage[4,5]. The main difference between the carriers is found in the quantity of hydrogen they can bond. In other words, how much hydrogen can be absorbed by the carrier. The higher the quantity absorbed; the more hydrogen can be transported.

Technically, the difference between the different hydrogenation and dehydrogenation processes is found in the operating pressure of the process and the temperature at which the bonding phenomenon occurs. The below figure illustrates the overall high-level process used within an LOCH system.



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[4] https://www.mdpi.com/1996-1073/13/22/6040/pdf

[5] https://www.energy.gov/sites/prod/files/2018/10/f56/fcto-infrastructure-workshop-2018-32-kurosaki.pdf

Figure 4.1 – An LCOH hydrogen overall process

The first stage of a dibenzyltoluene LCOH system is to bond the dibenzyltoluene with H2. In this stage, there is a need to pressurise hydrogen gas to up to 50 bar (this is the usual upper end pressurisation and lower end pressurisation systems exists). The second phase is to feed the pressurised H2 to a reactor. Both H2 and dibenzyltoluene will react chemically inside the reactor where the hydrogen is bonded dibenzyltoluene. When this is achieved, hydrogenation process is deemed to be completed.

The hydrogenation process is exothermic (heat is generated during the process). As such, heat must be controlled, collected, evacuated using radiators or cooling systems. The heat generated in a dibenzyltoluene hydrogenation process has temperatures surrounding 250 degree Celsius.

At the end of the hydrogenation process, a liquid product called Perhydro-dibenzyltoluene is stored for later transportation (by truck or ship). The Perhydro-dibenzyltoluene is packed full with hydrogen. This substance can now be called LOHC carrier.

Hydrogen is easily transportable when converted into an LOCH carrier. Consider that the Perhydro-dibenzyltoluene LOCH has been shipped to where H2 will be consumed. A dehydrogenation unit will now be used to detach the H2 from the dibenzyltoluene.

Simply put, a dehydrogenation unit works in the same way as the hydrogenation one but in reverse. The main difference is in that the dehydrogenation process is endothermic (there is a need for heat to be supplied to the process for it to separate the hydrogen from the dibenzyltoluene). Heat temperature surrounding 300°C is required for H2 gas to be detached from dibenzyltoluene.

The other difference in the process is found in the pressure needed for the chemical reaction to occur. The process only needs 1 to 3 bar pressure to detach the H2. The figure below illustrates the dibenzyltoluene LOCH process.

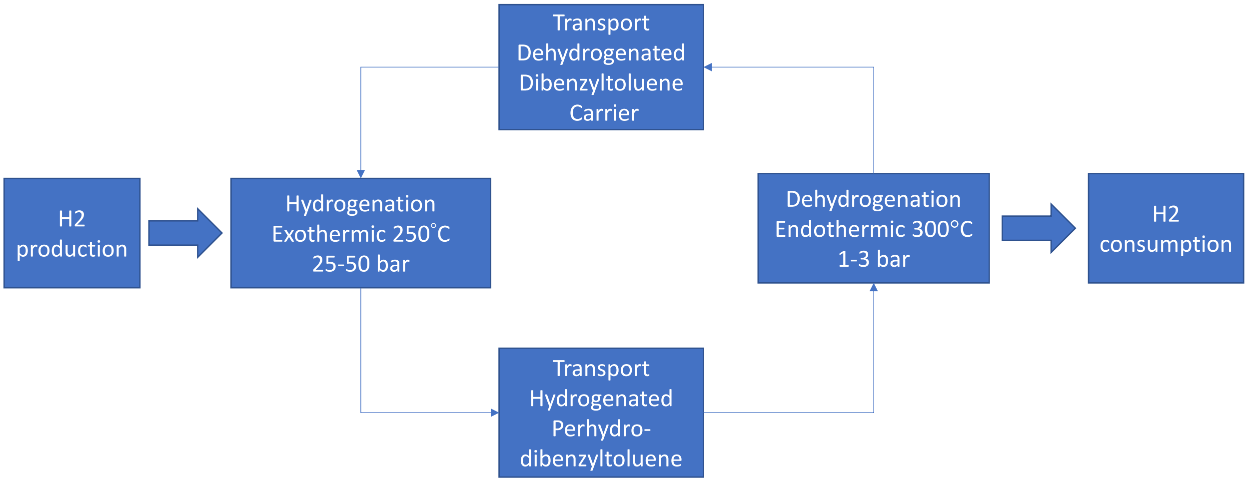

Figure 4.2 – Round cycle of the Dibenzyltoluene LOHC process[6]

There are a number of advantages in using LOCH. The LOCH can store hydrogen for long period of time with very minor evaporation losses. The liquid can be easily transported for long distances carrying substantial amount of hydrogen in a much more-dense medium. As a good example, the above Perhydro-dibenzyltoluene LOCH can store around 630 Nm^3 of H2 in one m^3 LOHC. This is equivalent to transporting 57kg of hydrogen in a 1 m3 container. The percentage by weight has a good ratio of 6.23 (wt%) of LOHC.

It is easy to handle the liquid as it can be used under ambient temperature and pressure, reducing the risks associated with liquified hydrogen and pressurised vessels. The safety associated with the pressurised and flammability aspects with hydrogen is an important one to consider. When considering transporting hydrogen, Perhydro-dibenzyltoluene LOCH may the upper hand in that it is a substance that is non-explosive. It is also classified as not dangerous, though some environmental aspects must be considered such as what is the pollution potential if spillage on land or water occurs. Because the LOCH is not pressurised, neither flammable, it does not require difficult to obtain and highly expensive certification. For instance, it does not need the ADR certification.

Furthermore, the LOCH process can reuse the carrier with minimal losses. This leads to a low OPEX. However, heat must be applied and sourced (or generated) for the de-hydrogenation to occur), which can increase the OPEX if no free heat is available. On the logistical side of this process, any LOCH liquid can be transported in simple and standard vessels on truck trailers, trains, boats, or even in pipelines.

Of interest, some of the infrastructure that is currently used within the oil and gas industry can be easily converted into an LOCH system (storage systems). Also, most of the technologies used in an LCOH system have been demonstrated, though new reactors with higher efficiency and new materials are being investigated.

Overall, a standard LOCH truck trailer can carry around 2500kg of H2 (in a single Perhydro-dibenzyltoluene trip). If this is compared to a pressurised gaseous tube trailed, then it is clear that the LCHO will carry more H2. A tube trailer transporting gaseous H2 at 250 bar can only carry 350 kg of hydrogen.

Currently, liquefied hydrogen trailers transport more hydrogen than a Perhydro-dibenzyltoluene LOCH trailer. A liquefied H2 trailer transport about 3,300 kg of hydrogen per trip. Though a liquefied trailer outperforms an LOCH one, it is important that LOCH does not experience from boil-off conditions. Any liquified system has a 1 to 3% of hydrogen “evaporating” due to the boil-off effect.

5 Ammonia (NH3) as a carrier and fuel

Ammonia is a product that plays a critical part in human wellbeing. It is a chemical substance that is widely used as a fertiliser and as such supports the overall food supply chain. Ammonia only needs two gases to be produced, hydrogen (H2) and nitrogen (N2). N2 is widely available in the atmosphere and can be easily captured and stored. Combined with H2, it will form NH3.

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[6] Courtesy of Pure Energy Centre – www.pureenergycentre.com

NH3 has a very strong advantage in that it can be produced from a variety of feedstocks. This ranges from natural gas (H2 produced using SMR), coal (H2 produced using gasification), biomass, electrolysis of water, etc.

Though NH3 is an important commodity because it is used as a fertiliser, it is also a liquid product that can be used as a fuel. Though currently not used as fuel, NH3 has been widely tested and demonstrated in various sectors. In the transport sector, NH3 has been demonstrated as fuel for cars, trucks, tractors, buses, and boats. In the stationary sector, it has been used for electricity generation and can be applied anywhere there is an internal combustion engine.

NH3 fuel has also been used in fuel cells and turbines. NH3 is therefore a potential important hydrogen carrier with a wide variety of applications in mainly the stationary and transport (marine and land) sectors.

Figure 5.1 - Ammonia fuelled tractor (top)[7] and ammonia fuelled car (bottom)[8]

As mentioned above, NH3 can be produced from hydrocarbon hydrogen feedstocks (gas, coal, etc.). However, and in order to reduce GHG emissions, H2 from renewable or CCUS H2 are the preferred route to chemically producing the commodity (i.e., NH3). The aim in using GH2 (Green hydrogen) is to reduce the emissions related to gas SMR and coal gasification.

Green Nitrogen (GN2) can also be produced using green electricity. To produce NH3, nitrogen available in the air is extracted using a Pressure Swing Adsorption (PSA) system (or other process system) and fed to a storage system. At the same time, green hydrogen is produced. N2 and H2 gas are then injected into a pressurised reactor, when they end up forming Green NH3 (GNH3).

In the case that CCUS produced hydrogen is used with GN2, then Blue NH3 is produced. The process that is the most commonly used to produce ammonia is the Haber-Bosch, as shown below.

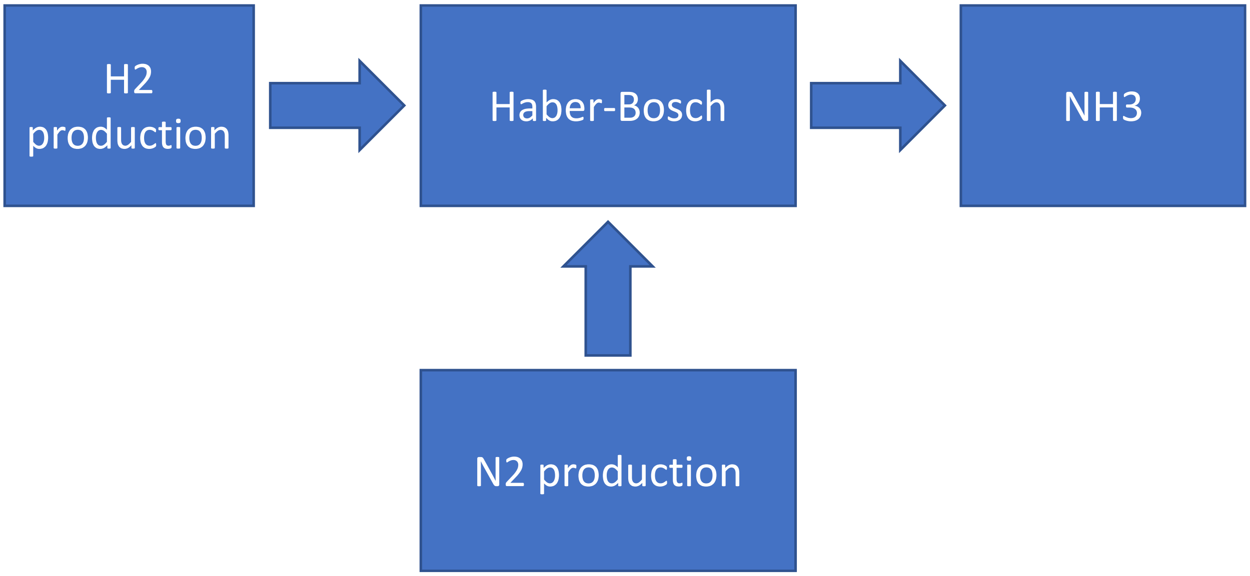

Figure 5.2 - Basic ammonia production process[9]

Ammonia is a fuel that is currently being described as the fuel to be used by the maritime sector. Ammonia, being a liquid fuel, is easily stored. It can, therefore, be easily transported in vessels by train, tankers, shipping, but also via pipelines, etc.

The main reason why NH3 is the fuel being considered for the maritime sector is that it has a fairly high energy density. There is another reason behind promoting NH3 as a fuel in that it already has a global transportation and storage infrastructure that can be used and customers ready to purchase the commodity. In addition, NH3 is a well understood fuel.

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[7] http://solarhydrogensystem.com/the-system/image-gallery/

[8] http://www.nh3car.com/how.htm

[9] Courtesy Pure Energy Centre www.pureenergycentre.com

The bellow figure provides a quick visual snapshot as to the cost of transporting ammonia. This cost is compared to compressed and liquefied hydrogen transport.

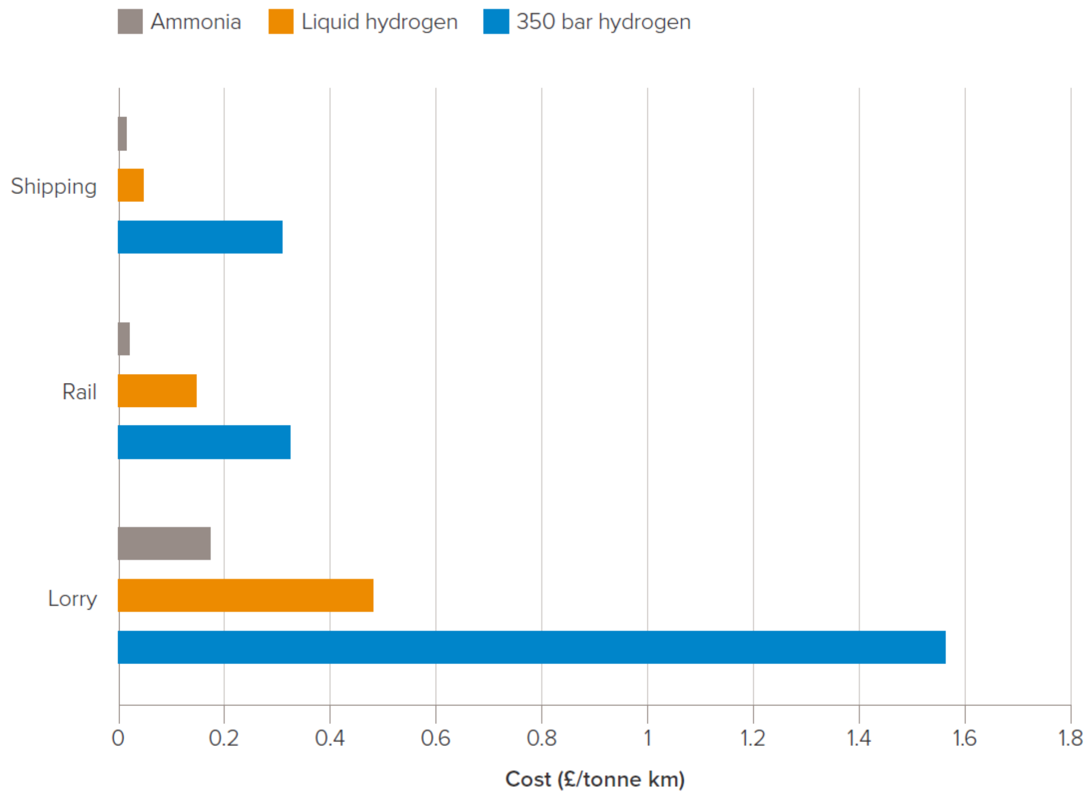

Figure 5.3 - Cost comparison between transporting NH3, liquid H2 and compressed H2[10]

6 Summary comparison between LH2, LOCH and NH3

There are many different solutions being developed for LOHC hydrogen storage carriers. However, the one solution that is being the most used at large scale is the methylcyclohexane (MCH). In fact, Japan has already invested into an MCH plant in Brunei to ship hydrogen from Brunei to Japan. Japan has also invested in a vessel for country-to-country shipment of LOCH.

In addition to this, Japan has developed a liquid hydrogen (H2) vessel for shipping LH2 from Australia to Japan (the hydrogen is to be produced through coal gasification (in Australia) away from the shore line, transported in to a harbour via truck trailers (about 150 km distance), transferred in liquid form onto the Japanese liquid hydrogen storage vessel and then the ship will sail to Japan where the hydrogen fuel will be used. The three different liquid solutions being methylcyclohexane (MCH), liquefied H2 (LH2) and

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[10] https://royalsociety.org/-/media/policy/projects/green-ammonia/green-ammonia-policy-briefing.pdf - Ammonia: zero-carbon fertiliser, fuel and energy store, Policy Briefing, The Royal Society, ISBN: 978-1-78252-448-9, February 2020

ammonia (NH3) are the solutions being considered for intercontinental and intercountry shipment of hydrogen.

Each of the medium used for storing hydrogen have advantages and disadvantages (none being perfect). MCH LOHC requires energy for the dehydrogenation process to take place. If no free heat is available, then there is a need to factor in the cost for producing the heat. There are concerns that MCH may be harmful to the environment if spillage occurs.

In terms of NH3, there is a need for input energy in order to produce ammonia for both synthesis and decomposition (if decomposition is required). In addition, NH3 is toxic and therefore must be manipulated with caution. Furthermore, if NH3 is used in an internal combustion engine, this engine will need special equipment to avoid NOx emissions which are highly harmful to the environment.

On the other hand, H2 needs a significant of energy to convert from gaseous to liquefied state (this is the worse of the three-liquid H2 solution in terms of energy needs). LH2 comes with many safety challenges in addition to having to manage by the evaporation of H2 through boil-off when being stored.

NH3 has the highest overall energy efficiency (production and utilisation). This is followed by liquid H2, and finally MCH. NH3 used directly as a fuel (without the need to extract hydrogen through cracking) is believed to have the lowest price per m^3 stored of energy.

In the case that high purity H2 is a must, such as in the application of PEM fuel cell for the transport sector, transporting hydrogen for long distances is best achieved with liquid H2. The rational is that it would take substantial amount of energy to dissociate hydrogen from liquid NH3/MCH and then purify the H2 to the level accepted by fuel cell manufacturers[11]. The below picture illustrates that transporting NH3 is much cheaper than doing so using LH2. That is true for both short and long distances.

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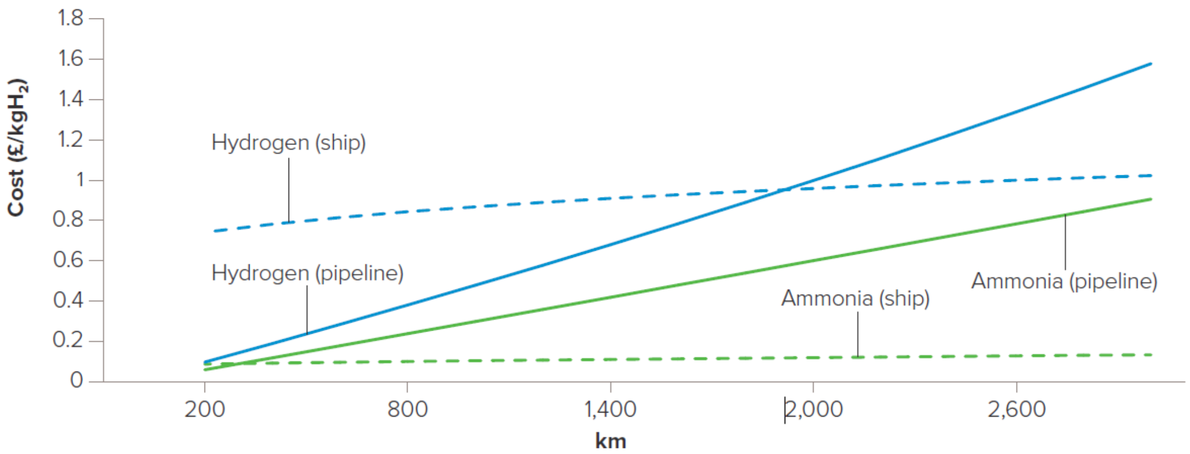
[11] Agung Tri Wijayanta, Takuya Odab, Chandra Wahyu Purnomoc, Takao Kashiwagi, et-all. “Liquid hydrogen, methylcyclohexane, and ammonia as potential hydrogen storage: Comparison review”, International Journal of Hydrogen Energy, Volume 44, Issue 29, 7 June 2019, Pages 15026-15044

Cost estimates for transport of energy as hydrogen or ammonia by ship and pipeline[35].



Note: Hydrogen transported via pipeline is gaseous and liquefied for shipping. Costs include both the transport and storage required; not the conversion, distribution or reconversion.

Figure 6.1 – Cost comparison for transporting H2 and NH3 in ships and pipeline[10]

7 H2 absorbing and desorbing storage

Metal hydride materials can be used to store hydrogen. They are a mixture of metal alloy that are able to absorb and desorb hydrogen under certain conditions. The different metal alloy used within a hydride cylinder dictates how much H2 can be stored. The capacity to store the hydrogen varies substantially from one alloy to another. On average values surrounding 1% to 2% of a cylinder's weight is what is available commercially.

There are, however, a number of organisations that states to have achieved absorbing rates of around 7%. Latest advancements in research and development shows that some complex mixture of metals and hydrides materials are able to absorb and desorb a high amount of hydrogen. The current theoretical quantities of hydrogen that can be stored in a hydride is 18%wt. This is the case for a fairly complex metal borohydrides LiBH4 hydride system[12, 13, 14, 15, 16].

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[12] Hirsher M. "Hand book of hydrogen storage: new materials for future energy storage". Wiley-VCH; 2010. http://eu.wiley.com/WileyCDA/WileyTitle/productCd-3527322736.html ISBN: 978-3-527-32273-2.

[13] Ley MB, Jepsen LH, Lee Y, Cho YW, Bellosta von Colbe JM, Dornheim M, et al. "Complex hydrides for hydrogen storage e new perspectives". Mater Today 2014;17(3):122-8

[14] Zuttel A, Borgschulte A, Schlapbach L. "Hydrogen as future energy carrier". Germany: WILEY-VCH; 2008.

[15] Walker GS. "Solid-state hydrogen storage: mateials and chemcistry" Woodhead publishing Ltd.; 2008.

[16] Eberle U, von Helmolt R. 2Sustainable transportation based on electric vehicle concepts: a brief overview". Energy Environ Sci 2010;3(6):689.

Most manufactures for hydride systems insists on the safety advantage that this technology brings compared to liquefied and pressurised options. They argue that the proposed hydride cylinders have a high safety margins because they operate at fairly low pressure.

The downside of metal hydride storage is that they can be contaminated in the presence of impurities. And these are metal compounds, water is, at time, considered as one of the contaminants that can lead to corrosion. This is why manufacturers take great care in selecting materials that do no corrode easily. It is during the cycle of adsorbing and desorbing that hydrides are contaminated.

In other words, when charging the cylinders with hydrogen, any impurity brought in with the H2 gas may stay in the cylinder. During the discharging sequence of the cylinder, hydrogen will be liberated and allowed to exit the cylinder. However, the impurity will sit inside the cylinder. The effect is that the more hydrogen charging and discharging cycles, the more impurities inside the cylinder. This will lead to the reduced storage capability of hydrogen within the cylinder. To avoid such issues, manufacturers have started to produce reactivation procedures.

The process of reactivating a hydride compound aims at promoting the extraction of impurities from the hydride structure. This means that, at the end of a reactivation process, a hydride cylinder should be able to absorb the quantities of hydrogen it was designed for. It is important to understand that a hydride cylinder lifetime vary from supplier to supplier. Much research has been conducting on this matter, and this demonstrated that it is possible to achieve around 4300 cycles without having the reduction downside effect in storage capacity[17]. As the number of cycles (charging and discharging) increases, the speed of absorption and desorption do slow down.

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[17] Friedlmeier G, Manthey A, Wanner M, Grollm M. Cyclic stability of various application-relevant metal hydrides. J Alloys Compds 1995;231(1–2):880–7.

Figure 7.1 - Hydrogen metal hydride cylinders[18]

The downside of the metal hydride technology is that it requires an overall heat management system to allow a safe charging and discharging process to take place. As a rule of thumb, heat is produced during the hydrogen charging process. On the other hand, the tank cools off during the discharging process. As such, managing the heat is important for both filling and discharging. The faster the filling, the more heat is generated. The faster the discharging, the cooler the tank.

Of importance, if the tank gets too cold, then the release of hydrogen gas from the hydride will stop. This is why promoters of the technology defines that hydride are safer than other hydrogen storage technologies. The promoters describe that if a tank is punctured, then the hydrogen release will decrease through time as no heat is applied to the tank. The view is that hydrogen will be released slowly, allowing it evacuate the scene / area with minimal risks to the surroundings.

From the above, it is clear that there is a need for a heat management system that is developed to specifically optimise and speed up the filling and discharging process of a hydride. When charging a cylinder, a cooling system is used to dissipate the heat. The cooling system can be air cooled, or water cooled. If the user requires a lot of hydrogen to be discharged, then heat will be applied to the hydride.

Fuel cells generates heat when they produce electricity. This heat can be supplied to the hydride cylinder, allowing hydrogen to be released in sufficient quantities for the fuel cell to operate.

7.1 Summary

Hydride cylinders are mostly used by universities for teaching purposes, though some larger systems are currently being commercialised. This technology has an embedded safety factor built into them. They are associated with low pressure operation (though some operates at high pressure) and they require heat to release hydrogen gas from the hydride. This simply means that if there is no heat applied to the hydride cylinder, then the hydrogen will not discharge. In reality, there will always be a little amount of hydrogen desorbed in the tank is left opened. However, the quantities of hydrogen released will be smaller than if a pressurised and liquid tank are left opened.

Overall, if a hydride cylinder is fractured or punctured, then it is believed that hydrogen will only leak from the hydride material for a short period of time. The rational is that no heat is actively applied to the hydride. Because there is no heat, the hydride does not discharge hydrogen gas in large quantities. As fuel cells release heat when the generate electricity, and that hydride requires heat to discharge hydrogen, then hydride technology may provide a good and potential safe solution to the automotive sector as a means to store hydrogen.

There is, however, another point that needs to be taken into consideration in the charging process. For fast charging a hydride cylinder, high pressure gaseous hydrogen gas must be injected into the cylinder. The faster the charging, the higher the inlet pressure to the cylinder, the more heat generated. To put this into perspective, in the case that a cylinder is charged with 6 bar inlet hydrogen gas, then a ventilator may be sufficient to cool off the tank. In the case that a hydride tank is charged with a 100-bar inlet H_2 gas,

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[18] https://commons.wikimedia.org/wiki/File:Metal_Hydride_for_Hydrogen_Storage-Ovonic.jpg

then a bath full of ice-cold water may be needed to extract the heat at a speed that is sufficient to avoid the tank to overheat. This is why, a good heating management system is required, with preference to include a fast-water-cooling system attached to the hydrogen tank.

8 Salt caverns

Salt caverns have been used for decades to store hydrogen gas and other type of gases such as natural gas. Nowadays, depleted oil and gas fields as well as aquifers are being investigated to store large quantities of hydrogen. The overall aim in using these types of underground storage is to store hydrogen over the summer, and used it over the winter season when the demand is high. Worldwide, there is substantial amount of expertise and experience in operating storage caverns. Most of the expertise is currently available around Europe and North America. The below figure shows an example of a salt cavern.

Figure 8.1 - An example of a salt cavern[19]

Underground soils are different from one location to another one. This is why there many different types of underground caverns that can be suitable for storing large quantities of h2 gas. The main difference between the underground caverns is based on their associated geological characteristics. The most typical caverns can be summarised as being:

- Salt cavern.
- Mined caverns.
- Natural caves also known as empty cavities.

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[19] https://www.edie.net/news/6/Work-to-being-on-pioneering-salt-cavern-hydrogen-storage-scheme/

- Empty reservoirs (e.g., oil and gas).
- Aquifer structures.

Salt caverns are probably the first choice for any hydrogen storage site. These have excellent containment properties with extremely low permeability factor. As such hydrogen can be safely stored in such a cavity, with minor leakage. Most of the salt caverns are man created. An underground salt saturated area is first located. Then an empty reservoir is made by dissolving the salt using water. There are times where cement is added on top of the salt to increase containment and reduce permeability. When the cavern is ready, H2 gas is injected downhole for future use.

Aquifers have also been used for a long time to store both hydrocarbons and hydrogen gas. In this type of underground storage, gas (H2, natural gas, or other) is pressurised into porous geological layers. As the gas is being injected, the water that filled the pores is pushed out and replaced with the gas. Special geological conditions are needed when using aquifers to store hydrogen. There are usually only found in restricted numbers and salt caverns are the most common available underground storage systems.

Storing energy as gas in a salt cavern is a cheap solution if compared to storing electricity in a battery. It is usually 100 times cheaper to store energy in a cavern than in an electrical storage medium such as battery.

The advantage that H2 has over battery is that it can be stored in a salt cavern at medium pressures. Most of the hydrogen caverns currently operate between 80 to 200 bar. A likely good storage size is between 6,000 to 8,000 tons of H2 in a single cavern. In energy terms, this is 200 GWh to 266 GWH of stored H2 energy. As mentioned above, the permeability factor for hydrogen gas in caverns is pretty low. So even in a seasonal storage scenario (H2 stored over the summer for winter use), the risk of significant H2 energy losses is highly unlikely. The budget for storing 6,000 tons of H2 in salt cavern is around €100 million euros.

On the other hand, it is also possible to store s 200 GWh of electricity in a large-scale battery. But the cost for storing so much energy is staggering. Such battery would require an investment in the order of €20 billion with a standard battery storage cost at 100 €/kWh. The logistics of constructing such battery and the size would also be problematic. The potential negative environment effect of a battery leakage or catching fire would be disastrous. However, and this is where hydrogen works best (though the round cycle for hydrogen is low compared to battery), battery have no ability to store energy on a seasonal cycle, all due to energy losses[20].

Overall, where electrical efficiency is critical and the round cycle is short (time between electricity stored back to electricity discharged), then batteries are best. This is true for MW size batteries. However, when GW figures are discussed, then the cost of battery installation is difficult to justify and hydrogen underground storage should be investigated.

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9 Pipeline

Large quantities of hydrogen can be easily transported using ships and truck trailers. However, gas pipelines are the preferred route for in-country and inter-country transport of bulk hydrogen gas (if at all possible). The different technologies used to transport H2 gas in pipelines is the same as the technologies used for natural gas. The only difference is the type of materials used for hydrogen pipes compared to natural gas pipelines (though this is currently changing – more on this below).

There is a long history of hydrogen pipelines around the world. There also is a large network of hydrogen pipelines globally. In fact, and in the USA, there is around 1600 miles of operational H2 pipelines. The pipelines have been built at locations where this is a need to transport/distribute large quantities of hydrogen between different organisations and/or within a large site. Good examples of such sites are chemical industries and refineries.

As aforementioned, storing hydrogen gas underground and in large quantities is a far more cost-effective method of storing energy than batteries. The same applies with transporting bulk hydrogen. The cost of transporting hydrogen in a pipeline is cheaper than to transporting electricity via high-voltage power lines.

Hydrogen transported in pipelines is between 10 to 20 times cheaper than transporting electricity via a subsea electrical power cable. Hydrogen transported using a pipeline is also a more efficient solution in terms of volume of energy transferred from one location to another location. As an example, there is a need to invest nearly €500 million for a subsea of 1GW capacity. A €500 million hydrogen pipeline will provide 15GW capacity (equivalent). Usually, a 1GW electrical cable would be able to transport 8 TWh of power a year. If the same amount of money were to be invested in a hydrogen gas pipeline, about 120 TWh of energy a year could be transported[21].

A wide variety of materials are used in the process of manufacturing pipelines. The most common for small pipes is Stainless Steel., while for all other size pipes microalloyed steels, carbon steels, Carbon-Molybdenum (C-Mo) and Carbon-Molybdenum-Chrome (C-Mo-Cr) low alloy steels, copper, cobalt alloys and nickel alloys. Going forward, many countries are investigating the used of cheaper materials, mainly focused on polyethylene[22].

The research is aimed at defining if pipelines made out of polyethylene P80 and P100 can hold hydrogen with a very low permeability factor and that the pipeline do not deteriorate through time. The reason for this research is related to the fact that countries around the world are nowadays replacing their old natural gas pipeline networks with polyethylene P80 and P100 pipelines. New natural gas pipelines are also being installed using this type of material, polyethylene being cheaper to manufacture and cheaper to install.

The research confirmed that using H2 has no side effect on the material and the integrity of the pipe. Both the mechanical and chemical properties of a number of PE80 and PE100 pipes where examined. To be thorough, both old (pipelines dedicated to natural gas extracted for the investigation) and new P80 and

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[21] Ulco Vermeulen, Turning a hydrogen economy into reality, 28th Meeting Steering Committee IPHE, The Hague, 21 November 2017

[22] https://h2tools.org/sites/default/files/Doc121_04%20H2TransportationPipelines.pdf

P100 were inspected with 100% pure hydrogen. When hydrogen was used in the pipes, no adverse material reaction or degradation were discovered. This is true for the pipe's mechanical and chemical properties. The overall research study established that hydrogen gas can be used safely in the pipes[23]. Below is a figure illustrating a natural gas pipeline made of polyethylene material.

Figure 9.1 - Polyethylene pipelines used to distribute natural gas[24]

Even though the above P80 and P100 pipelines are suitable to transport hydrogen, there are still not being used for such purpose due to the lack of hydrogen production systems and applications. To support the deployment of large-scale hydrogen production systems, the industry is currently considering the use of the existing natural gas pipeline network where H2 would be injected. Obviously, the network is old and based on steel type materials. As such, many countries are taking a precautious slow deployment of hydrogen systems that can inject H2 in natural gas pipelines. The aim is to reduce, and at the same time study any potential side effects. However, to date, only a small percentage of hydrogen can be injected in old pipelines without having an adverse effect on the pipeline and the end user applications.

Currently, end use applications (home or industrial appliances) operate on 100% natural gas. Injecting too much hydrogen in the gas pipeline will lead to modifying the properties of the natural gas. This will, in turn, lead to the appliances ending-up not operate correctly. This could create a potential hazard and safety risks to end users. That is why substantial investment went into researching and investigating the percentage level that is safe for co-mingling hydrogen with natural gas. This research focused on the properties of the pipelines and taking into account the end user applications.

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[23] http://plasticpipesconference.com/content/235/272/5c866611afe7f.pdf

[24] Eugen Avrigean, Laszlo Joszef Hunyadi, Comparative study on the temperatures of welding the polyethylene fittings – sockets – high density polyethylene pipe, 2014

Having different countries, means having different legislations, different pipeline materials, different valves, different compressors, different pressure of operation and even different properties of natural gas (gas coming from different wells have different properties). As such, considering all of these factors, each country (each region) may allow a different percentage of hydrogen into the pipeline. From a very small percentage to larger percentages.

Even the smallest percentage of hydrogen injected into the pipeline may need a large-scale hydrogen production system installed for supplying the demand. A comparison between the United states, the United Kingdom, and Germany may provide a good example in the percentage level that is allowed to be injected into pipelines.

In the United Kingdom, it is only feasible to inject 1 vol% of hydrogen into the gas pipeline. This means that for each and every 100m^3 of natural gas, only 1 m^3 of hydrogen can be injected. There are parts of the UK gas network that can handle up to 5 vol%[25] and other parts of the network with up to 75%.

In Germany, the system can handle higher quantities of hydrogen, with up to 12 vol%. The USA has a much higher tolerance to hydrogen, with a potential for blending starting at 5 vol% to up to 15 vol%. This shows that even if countries wish to shift to a green hydrogen economy, there is a substantial requirement for large scale investment into the gas infrastructure to make the shift become a reality. Overall, the limit percentage amount of H2 permissible in a natural gas pipeline is based on the hypothetical likelihood of damage and risk to the existing natural gas system. This includes the transport, distribution and utilisation infrastructure.

10 Conclusion

Depending on storage size and application, several types of hydrogen storage has been considered:

1. Stationary large storage systems: These are typically storage devices at the production site or at the start or end of pipelines and other transportation pathways.

2. Stationary small storage systems: These are typically at the distribution or inal user level, for example, a storage system to meet the demand of an industrial plant.

3. Mobile storage systems for transport and distribution: These include both large-capacity devices, such as a liquid hydrogen tanker–bulk carrier, and small systems, such as a gaseous or liquid hydrogen truck trailer, pipelines.

4. Vehicle tanks: These are typically used to store hydrogen used as fuel for road vehicles. Because of hydrogen’s low density, its storage always requires relatively large volumes and is associated with either high pressures (thus requiring heavy vessels) or extremely low temperatures and/or a combination with other materials (much heavier than hydrogen itself).

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[25] https://www.fch.europa.eu/sites/default/files/FCH%20Docs/171121_FCH2JU_Application-Package_WG5_P2H_Hydrogen%20into%20gas%20grid%20%28ID%202910558%29%20%28ID%202911642%29.pdf

Future hydrogen supply systems will have a structure similar to today's natural gas supply systems. Underground storage of hydrogen in caverns, aquifers, depleted petroleum and natural gas fields, and man-made caverns resulting from mining and other activities is likely to be technologically and economically feasible. The development of ultralight but strong new composite materials has enabled storage of hydrogen in automobiles. Pressure vessels that allow hydrogen storage at pressures greater than 600 bar have been developed and used in automobiles. A storage density higher than 0.1 kg of hydrogen per 1 kg of total weight is easily achievable, which permit very low weight storage for cars and other transportation systems requiring low weight.

There are many storage systems and it can be chosen depending on the specific characteristics of production and usage to fit at best requirements.