Storage and refuelling of Liquid vs gaseous hydrogen

Contents

Box 310 • 631 04 Eskilstuna
Telefon 016-544 20 00 • Telefax 016-544 20 99
registrator@energimyndigheten.se
www.energimyndigheten.se
Org.nr 202100-5000

Storage on the large-scale

For hydrogen storage there are many different technology options, the type and function vary mostly between those for smaller storage, e.g. in vehicles and those for large-scale storage such as seasonal. Here focus is placed on centralized large-scale storage solutions as the vehicle type is treated in work package 4. To narrow down the field further the technologies described in detail were limited to physical storage alternatives and chosen based on maturity.

As gas

For storing hydrogen as pressurized gas there are alternatives already available on the market. Most commercial solutions are for smaller volumes, below 1000 kg. For large-scale applications much of the technology today is still being developed. Development is often based on the knowhow of natural gas storage. Still, the differences between hydrogen and natural gas are rarely discussed and there is little knowledge on hydrogen leakage for the same systems [1]. For 100% large-scale hydrogen storage there are less than 10 facilities in use today [2].

The technologies expected to be used for large-scale hydrogen storage have quite low energy density as the pressure rarely exceeds 200 bar. However, there are long-term storages at higher pressure being developed on the research stage. In this report five technologies for large-scale gas storage are discussed: lined rock caverns (LRC), salt caverns, pipe storage, gas spheres and future type IV high pressure vessels. The selection was based on the types more commonly discussed and applicable in Europe.

Lined rock caverns

The technology is as describe a cavern in a rock-base that is lined with stainless steel. The lining provides an impermeable barrier when used for natural gas, for which the technology was originally developed. Currently there are no facilities for 100% hydrogen in use. The LRC technology is dependent on a stable bed rock and is a good option in countries like Sweden. However, in different countries it is less applicable depending on the local geology. The LRCs come with an above ground facility where compressors and pumps inject/extract the gas. Not all of the injected gas can be extracted as the storage needs to maintain a certain pressure, this non-recoverable volume is called cushion gas. The part of the hydrogen in the storage that can be extracted is called working gas, in LRCs the relative amount of working gas is high around 83% of the storage volume. To calculate the useable energy density in the storage only the working gas is considered. LRCs have one of the higher storage pressures compared to other large-scale alternatives, approx. 200 bar. This results in a potential energy density of 533 kWh/m^3 for hydrogen.

An well-known example of LRC is the storage for natural gas in Skallen, Sweden [2]. Furthermore, one of the first LRCs for pure hydrogen is being built in the Hybrit initiative in the north of Sweden, where parts of an old mine are utilized. From international studies a capital cost for construction of the storage of around 55 €/kg hydrogen to be stored is estimated when starting from unbroken ground. This is a high construction cost compared to other below ground options, but if natural caves or old mine can be utilized it could be reduced. For the price of hydrogen there will also be an operation and maintenance cost added of approx. 0.9 €/kg and year [3]. In this operation and maintenance cost primarily the above ground facility and structural maintenance is included, the values are based on location in the US.

Salt caverns

Salt caverns are applied today for hydrogen storage. The technology creates caverns in salt deposits deep below ground. The salt is leached from a salt deposit to form a hollow with a gas tight layer of salt usually around 0.5-1 m thick. Same as for LRCs this type of geological storage requires cushion gas, and here there is only about 70% working gas. The amount of working gas decreases slightly with how far below the surface the storage is placed. This is counteracted as a deeper cavern allows higher storage pressures, up to 150 bar at 1000 m below ground[4]. Again there is an above ground facility with compressors/pumps for injection/extraction. Additionally, for gas stored in salt caverns there is often a purification facility as there is a risk of impurities in the gas from the geology[5].

One difficulty with salt caverns is that they need an existing salt deposit, which means they are more geologically limited than the LRCs. However, this is the only large scale technique that has been tested for hydrogen storage. Today the technique is used primarily in the USA, but there are possible salt deposits also in Europe [4]. Installing one of these facilities for hydrogen has been estimated to cost around 31-33 €/kg hydrogen to be stored [3]. Mainly because the leaching process is time demanding and expensive. The operational cost of storing hydrogen in salt caverns is estimated to be approx. 1.41 €/kg y and thereby the most expensive to operate [6]. The higher operation and maintenance cost could be related to the large depth of the caverns and the need for gas purification.

Pipe storage,

To construct pipe storages is relatively uncomplicated as it is welded pipes buried a little over a meter below ground. The pipes are produced with a 3-layer polymer coating for corrosion resistance in set lengths of around 12 m and a diameter of 0.45-0.9 m. This technique’s main perk is that it does not put any special demands on the areas geological conditions. The downside is that the land above the storage facility, for example a field, cannot be utilized for activities such as agriculture at the risk of damaging the storage pipes. It therefore needs to be bought and reserved for the use of the below ground storage.

Most pipe storages that are available today are for natural gas and the pressure is limited to around 100 bar. This contributes to quite extensive areas being needed for the large-scale storage. Still, one positive is that about 90% of the storage volume is working gas [3], [6]. Installing one of these facilities for hydrogen has been estimated to around 8 €/kg hydrogen, which is the cheapest below ground alternative. Furthermore, the operation and maintenance cost is expected to be approx. 1 €/kg y [3]. In this operation and maintenance cost the price points were estimated for the US with regard to electricity price, maintenance, labour, insurance and taxes costs.

Pressurized gas spheres/cylinders

Gas spheres have the lowest storage pressure of the studied alternatives and is the only above ground alternative. The gas sphere's are similar in appearance to the vessels for liquid hydrogen. The main difference is that a gas sphere has thin walls around 10 cm, while a liquid hydrogen sphere has walls over a meter thick [3].

Traditionally gas spheres are used for heavier gases such as propane or butane. For the application with hydrogen, they have a very low pressure of around 20 bar. The low pressure results in low energy densities for the storage around 26 kWh/m^3. This means that even if large storages up to 32 000 m3 are built they will only contain around 25 000 kg of hydrogen [3]. This amount of hydrogen is on par with the use during 10 days at a larger HRS meaning it is not a large storage in comparison to the other technologies. There are currently no cases stating costs for these types of hydrogen facilities, but the relatively simple construction and low pressure of a gas sphere indicates that it could be a lower cost option.

Comparison of the existing technologies

The 4 above technologies are all considered options for large-scale storage of hydrogen in gas phase. In Table 1 the data from the text above is summarized and compared side by side. There are downsides and advantages to each of the different technologies. The LRC type has the highest energy density, but has not yet been tested for hydrogen and is expensive to construct. Salt caverns are the only technology that have been tested for hydrogen but are known to affect the gas purity and have a lower part working gas. Pipe storage is the cheapest to build but have a larger land demand and have not been tested for hydrogen. Gas spheres are probably low cost, but the energy density is only a 1/20:th of the one for LRCs. Notably there are no reported values for hydrogen loss/leakage overtime for any of the solutions. This can be attributed to the fact that there are no facilities that have been used for storing hydrogen over long periods of time.

Table 1 - A comparison of the 4 types of large-scale storage presented above. Data is from reference [3]**. Energy density was calculated based on other values and using the LHV for hydrogen.**

	Lined rock cavern	Salt cavern	Pipe storage	Gas spheres
Storage pressure [bar]	200	50-150	up to 100	Up to 20
Storage volume [m^3]	40 000	566 000	6 100	32 000

Kg H2 usable	640 000	3 720 000	~45 000	25 000
Energy density [kWh/m3]	533	219	246	26
Applicability	Below ground, requires stable rock foundation	Below ground, but highly dependent geological conditions	Below ground, close to surface i.e. no agricultural work or other allowed over large areas	Above ground, bulky and more safety risks than below ground.
Usable storage volume	83%	70%	90%	93%
Advantages	Can be constructed in old mines	Have been applied for H2	Useful in most countries Low installation cost	Well tested technique
Challenges	No data for H2 High installation cost	Can only be built in salt deposits Gas purity	No data for H2 Large land use	Low energy density Space demanding No H2 data

Future type IV high pressure vessels

A Type IV pressure vessel is made mostly of polymer fibre composites with some minor details or elements in metal and designed for pressures up to 1000 bar. This is a relatively standardized solution for smaller tanks with 6-10 kg of hydrogen such as the those found in vehicles. Ongoing studies aim to create type IV tanks storing >1000 kg of hydrogen at 500 bar [6], [7]. Using the hydrogen weight and pressure to calculate storage volume give ~25 m^3. This results in an estimated energy density of 1300 kWh/m^3, which is significantly higher than for the long-term alternatives considered today. Furthermore, type IV tank technology is similar to gas spheres and pipe storage, so a high fraction of working gas around 90% is probable. All of the data is defined per vessel and a number of vessels are expected to be used at the same site ton increase storage volume.

As liquid

Storage of liquid hydrogen at 20 K (-253 °C) has been done since the 60s when liquid hydrogen was frequently used in the space programs. For large-scale storage there is only one technology implemented today; large spherical vessels. For smaller storage solutions, for example at industrial sites or refuelling stations, the cylindrical vessels are most common and fully commercialized. Regardless of the size the storages are designed to limit boil-off.

Boil-off

Liquid hydrogen storage vessels have excellent thermal insulation to keep the hydrogen cold but despite this some heat will always seep through into the tank. Over time this causes the liquid hydrogen to warm up and vaporize. To prevent excessive pressure-build up inside the vessels some of the vaporized hydrogen must be released. The hydrogen that vaporizes is known as boil-off. The boil-off is often vented into the surrounding environment, resulting in a direct loss of hydrogen and posing a potential safety hazard if in an enclosed space. There are also active solutions to prevent or utilize boil-off which will be explored in later sections of the report.

Losses due to boil-off are measured as a percentage of the vessel's current contents, e.g. x % of the hydrogen in the vessel needs to be vented each day due to boil-off. Typical values for boil-off losses in stationary storage solutions are 1 – 5 %/day for small storages [8], but as low as 0.1 %/day for larger vessels [9].

For storage solutions one way to reduce boil-off is through the usage of large spherical containers. The sphere has the most optimal shape for minimizing surface area in relation to its volume and this minimizes the passive heat transfer through the walls. It is also beneficial with larger containers as they have more volume of cold liquid in relation to surface area.

Active cooling is another technique to reduce boil-off losses that is being evaluated for large storage facilities. Active cooling uses cryocooling equipment to continuously cool the liquid hydrogen thus preventing vaporization/ boil-off. The trade-off is additional investment costs for the equipment and energy costs to run the equipment. In a NASA report it was found that 12 – 19 cents worth of electricity could save a dollar worth of hydrogen with this type of solution [10].

Temperature gradients in cryogenic storage vessels

As the cryogenic storage vessels cannot be completely isolated, the contents are rarely in thermodynamic equilibrium and constantly undergoing change. It is common that the fluid inside the vessel has both a liquid and vapor phase. Therefore, the pressure and temperature are not even through-out the liquid hydrogen tank. In contrast gaseous hydrogen will have homogenous the pressure and temperature through for example a 200 bar LRC.

The distribution of temperature, pressure and phases through a liquid hydrogen storage vessel depend on its usage and time. In Figure 1 an example of heat distribution inside a tank over time is illustrated using the NASA developed

MATLAB software LH2Sim [11]. It shows a storage vessel with an initial temperature of 20 K and 60 000 kg of LH2. The tank is emptied at a pace of 1 kg H2/s, there is a constant heat transfer from the environment of 20 kW into the tank and no venting of boil-off occurs. The result of the simulation shows a separate liquid phase that develops inside the bottom of the tank and a vapor phase above, the interface between the phases is marked by the dashed line. A temperature gradient also appears inside the tank, most notably in the vapor phase where the warmer hydrogen rises to the top of the tank.

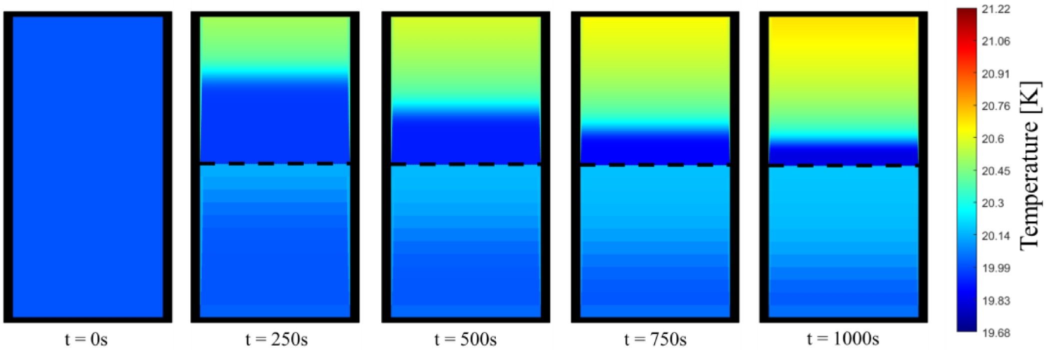

Figure 1: Simulation of thermal stratification inside a LH2 storage vessel.

Key-features of cryogenic storage vessels

The special properties of cryogenic gases mean they cannot be stored in traditional pressure vessels. The structure of liquid hydrogen tanks is designed to limit heats transfer by consisting of multi-layered walls. One of the layers is always a vacuum layer, as this is one of the most efficient ways to limit heat transfer and has long been used for thermoses. The vacuum layer may at times contain a solid porous substance with very low heat conductivity, such as perlite. These layers have varying thickness depending om the size of storage. For large-scale storage the full multilayer-wall becomes > 1m. For smaller vessels they are thinner, which could explain their higher boil-off losses.

Furthermore, the storage vessels require additional features for safe and functional usage [12].The exact design depends on application, some examples are pressure build circuit, differential pressure gauge, economizer circuit and so on as illustrated in Figure 2. These features also introduce additional functionality. For instance, a "pressure build circuit" can increase the pressure inside the vessel. This is accomplished by a heat exchanger fed with the liquid phase that vaporizes and expands by increasing the heat transfer from the environment. Resulting in an increased pressure inside the vessel which is useful for applications that require a minimum pressure to be maintained. Another common feature is a "differential pressure gauge" which measures the pressure difference between the top and bottom of the tank. These values are used to calculate the liquid height inside the tank and letting an operator plan a refill.

Many tanks have the option to provide its contents in either liquid or vapor phase or both, this is possible as the two phases are separate inside. When vapor is needed it is possible to use an "economizer circuit" which access the vapor phase at the top of the vessel if the pressure is high enough. Otherwise, liquid is taken from the bottom and vaporized in a heat exchanger.

One feature that is not optional and should always be included on all cryogenic vessels is the "pressure relief mechanism". Passive heat transfer or usage of the pressure build circuits may cause the pressure inside the tank to rise to unsafe levels. Therefor this valve is necessary to release, pressure/boil-off. There may also be additional safety mechanisms such as a rupture disc [13].

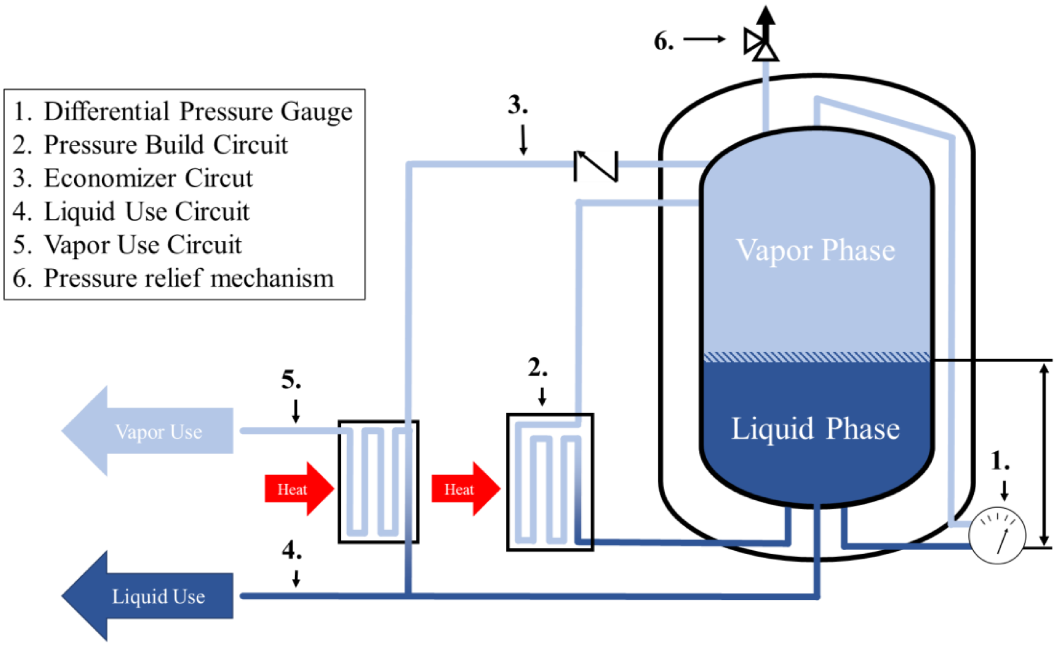

Figure 2: Schematic illustration of cryogenic vessel. Not pictured: Most valves & gates

Costs for LH2 storage

The up-to-date information on cost of liquid hydrogen storage is very limited, most likely as it has been a very specialized application until recently. There was more focus on the technology in the mid 90's. Using their cost estimates and translating them to euros in 2021s value, the installation cost for a large facility (above 200 ton) can be estimated to 28 €/kg. As today the cost of the vessels become more expensive for smaller scale (below 1000 kg) they estimate 22 times the cost around 616 €/kg. This indicates that these values were probably uncertain back when reported and that the cost of the storage vessel will depend highly on storage size [9].

For the operation and maintenance cost there is also an estimate of around 1.76 €/kg y. This includes the power demand for the liquefier as well as other costs surrounding the storage facility [9]. Still, the values are uncertain and more precise costs for the modern technology should be expected in coming years.

Example of Liquid hydrogen storage facilities

The largest in-use facility for storing liquid hydrogen is at NASA. It can store around 460 tons in two spheres with a water volume of 3 400 m^3. This storage has an energy density of around 2 200 kWh/m^3 which is significantly higher than any of the alternatives using compressed gas. As mentioned above a known issue with the storage of liquid hydrogen is losses due to boil-off. In this facility that has been used for a long time the boil-off is now reported to be quite low 0.04 %/day. This is on par with new techniques that estimate around 0.04 %/day. Unless the boil-off is recondensed or utilized some other way this would mean a loss of 276 €/day of hydrogen for a large sphere, assuming a hydrogen production price of 3 €/kg. If the facility is actively cooled and the boil-off reliquefied the cost will instead be 15 €/day an estimate based on the energy needed to liquefy the boil-off.

There are also smaller storage units in use today. Some examples are those produced and sold by Linde for commercial use in industrial facilities. These have a storage capacity of 400 - 4600 kg liquid hydrogen with a boil-off of 0.5-1%/day. For these solutions there is an offer to in-cooperate them in a refuelling station system. Additionally, Linde have developed larger solutions for shipping of liquid hydrogen, one cylindrical and on spherical tank. The cylindrical version can store ~19 tons with 0.3% boil-off and the spherical one can store ~70 tons with 0.1% boil-off [14]. Similar products are of course being offered by other large gas cylinder companies such as Air liquide, Chart or Praxair.

Comparison different storage alternatives

As is obvious from Table 2 below the main advantage of liquid hydrogen storage is the significantly higher energy density. It is more than 5 times higher than the currently most effective gas technology. From the table it is also shown that the cost does not vary significantly. However, the main downside of LH2 is difficult to compare quantitatively to the gas alternatives, i.e. losses over time. For the gas storage alternatives there will probably be some losses during handling and storage, but how much is not clear. For LH2 the losses are know and can be present either as vented gas, high economic loss or as energy for active cooling, lower economic loss. One practicality that also needs to be considered for all technologies discussed is the placement, both geologically and geographically as it can affect the end costs for the value chain. On the overall it is difficult to say one type is preferable as in the end it will most like vary between countries and value chain designs.

Table 2 - A comparison of the 5 types of large-scale storage available today. Gas data is from reference [3] and LH2 data from [9] in the O&M costs the cost of electricity for surrounding equipment such as compressors/liquefier is included. Energy density was calculated based on other values and using the LHV for hydrogen. All values adjusted to 2021 years costs when estimating inflation.

	GAS				LH2
Storage type	LRC	Salt cavern	Pipe	Sphere	Sphere
Energy density [kWh/m3]	533	219	246	26	2192
Construction cost [€/kg H2]	55	31-33	8	No data	28
O&M Cost [€/kg H2 and year]	0.9	1.41	1	No data	1.76

Hydrogen Refueling Stations (HRS)

This section aims to illustrate and investigate the advantages and disadvantages of using liquid or cryo-compressed hydrogen at Hydrogen Refuelling Stations (HRS). There are several ways which LH2 or CcH2 can be used at the HRS. For instance, LH2 can be used both as the bulk supply to the station and/or for fuelling vehicles at the HRS. It is for example possible to have a HRS with a LH2 bulk supply but that refills vehicles with gaseous hydrogen.

In this study the usage of gaseous, cryo-compressed or liquid hydrogen at the refuelling station is categorized as either for supply or refilling. The combinations of supply and refilling which are investigated in this report are listed in **Error! Reference source not found.** below. Depending on the configuration their main-components can vary, the components for five configurations are illustrated in Figures 3 – 7.

Table 3: Station configurations compared in this report

Configuration	1	2	3	4	5
Supply	Gaseous	Liquid	Liquid	Liquid	Gaseous
Refill	CGH2	CGH2	LH2/sLH2	CGH2 & CcH2	CGH2 & CcH2

Configurations - Illustrations

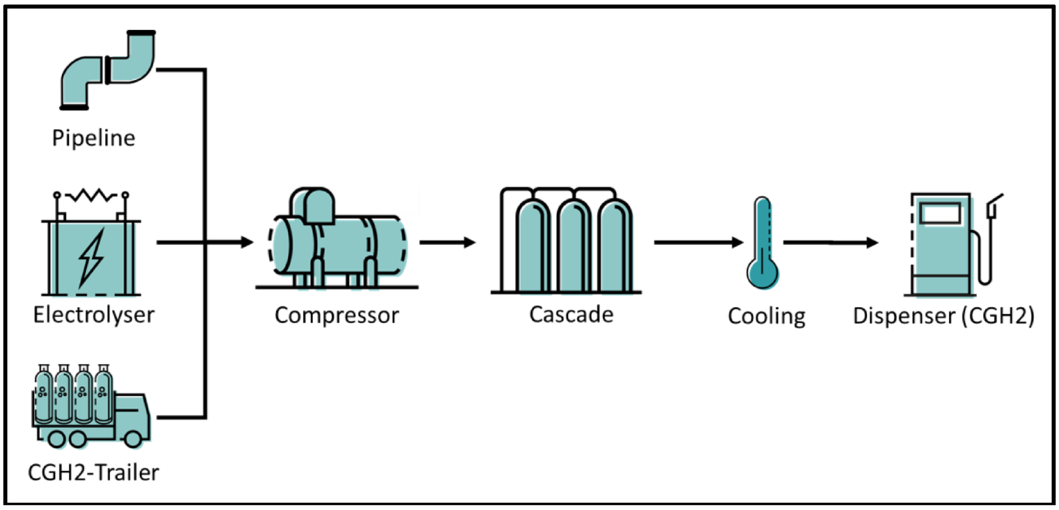

Figure 3: Configuration 1. Gaseous supplied station with CGH2 refills

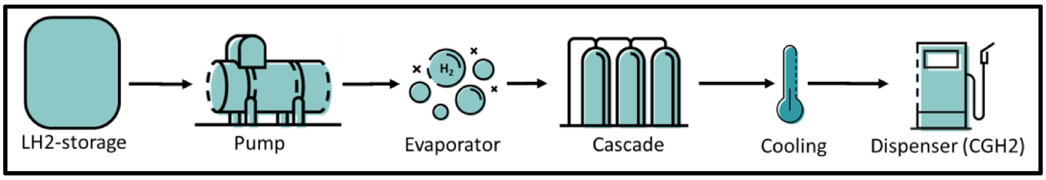

Figure 4: Configuration 2. Liquid supplied station with CGH2 refills

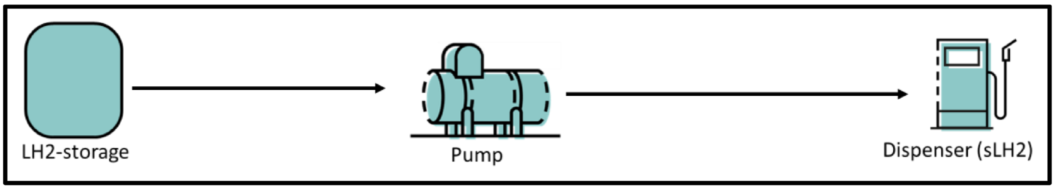

Figure 5: Configuration 3. Liquid supplied station with sLH2/LH2 refills. A more detailed drawing as presented by Daimler and Linde at NOW CEP 21 can be found at [15]**.**

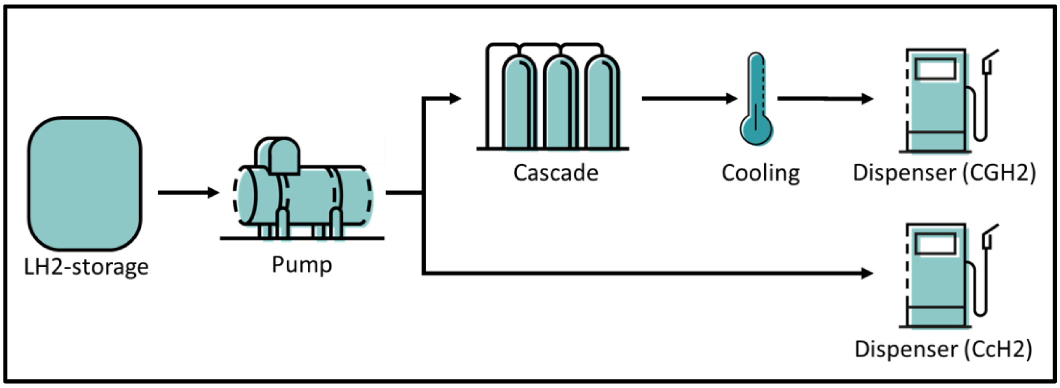

Figure 6: Configuration 4. Liquid supplied station with CcH2 and CGH2 refills. A more detailed drawing as presented by Cryomotive at NOW CEP21 can be found at [16]**.**

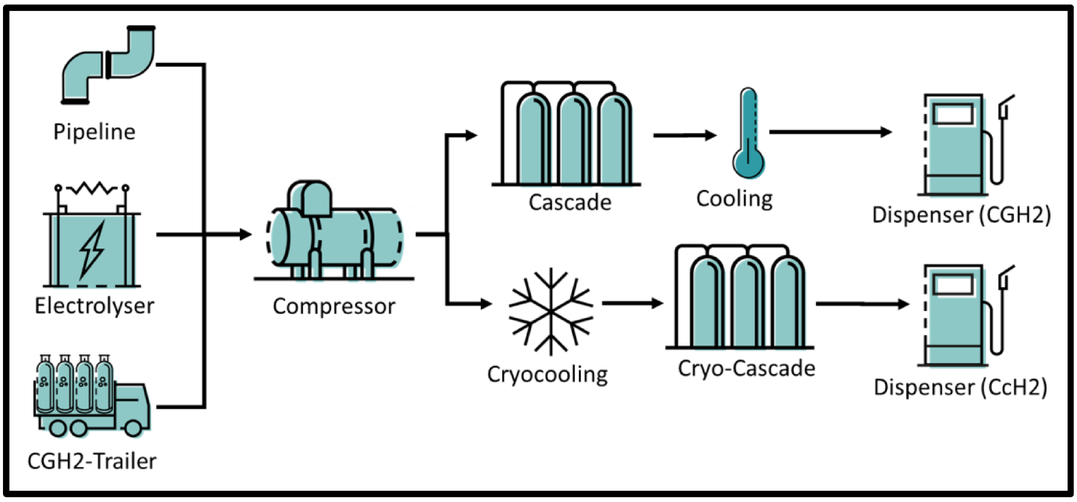

Figure 7: Configuration 5. Gaseous supplied station with CcH2 and CGH2 refills. A more detailed drawing as presented by Cryomotive at NOW CEP21 can be found at [16]**.**

Supply

Gaseous supply

Gaseous hydrogen can be delivered to the station in one of three ways. By pipeline, by truck delivery with a CGH2-trailer or by producing it locally with an electrolyzer. For stations with electrolyzers an additional vessel for more long-term storage of hydrogen may be needed. At HRSs where cheap and reliable renewable electricity can be easily accessed electrolysis becomes a strong option, as producing hydrogen locally eliminates the cost of distribution. . A pipeline is mainly an option if the production site is relatively close the refueling station and if the pipeline can supply other users. One example of this is in Sandvik, Sweden where hydrogen is produced and then a pipeline supply both a nearby industrial site and the Sandvik HRS [17]. The most versatile delivery option is to use specially built CGH2-trailers for the storage of hydrogen. These trailers can be filled with hydrogen at a production site and then be swapped for empty ones at the HRS. CGH2-trailers provide great flexibility of when and from where hydrogen is delivered to the station but results in an additional hydrogen distribution cost.

Liquid supply

Another option is to supply the stations with liquid hydrogen. LH2 can be handled more efficiently at the a HRS, decreasing station footprint and station cost [18]. Currently liquid-supplied stations are less common, only one has been built worldwide [19], but more are planned [20].

Today liquid hydrogen is delivered by truck from centralized production. Either as a trailer swap in a similar manner to the previous CGH2-trailer option or the HRS has a permanent LH2-storage container which is filled from the truck trailer. It is not possible to transport LH2 via pipeline and local small-scale liquefaction at the HRS is considered impractical.

Refilling

CGH2 refills

Today (2022), all public and operational hydrogen refueling stations provide hydrogen to their customer vehicles as a compressed gas at working pressures of either 350 or 700 bar (CGH2). For compressed gas refills there are established standards for refueling (such as SAE J2601) [21]. These standards dictate the refueling procedure and equipment to enable universal refueling of vehicles.However, they are still incomplete, for instance the standard for 700 bar refills for heavy-duty vehicles is still under development [22]. Compared to HRS with liquid (LH2/sLH2) or cryo-compressed (CcH2) refills the CGH2-type stations are well established and understood. Worldwide more than 490 CHG2-type refueling stations already exist [23] and companies such as Nel, Linde, and others already offer turn-key solutions.

The cost of CGH2-stations are still relatively high, but costs are declining with increased experience, cheaper components and larger, more cost-efficient stations being built [20]. The cost of the refueling station is also largely dependent on the choice of hydrogen supply route where LH2-supplied stations have been found to be the cheaper option [24].

Most CGH2-refill HRS use so called "cascade filling" (Figure 8). This uses a cascade storage, a series of high-pressure hydrogen storage that operate between different pressure intervals, one for high-high pressure, one for high -medium pressure and one for high to low pressure. These containers inside the station are used to achieve rapid refills. When a vehicle connects to the HRS hydrogen will flow from the high pressure in the cascade storage to the lower pressure in the vehicle tank. How it is filled from the three cascade steps will depend partly on the current storage levels.

The cascade storage is constantly being refilled by the specially designed compressors or pumps at the refueling station to maintain pressure. These multi-stage compressors, made for gaseous supplied HRSs, compress the hydrogen from 30 – 500 bar up to the cascade storage pressure of max 1000 bar. At liquid supplied stations a pump can be used instead, it vaporizes and compresses the hydrogen up to the required pressure. A vaporizer may be used in combination with the pump [24]. The pumping option tends to be cheaper and more energy efficient than compression. One important aspect of cascade refilling is that after a refill is completed the amount of hydrogen and pressure inside of the cascade storage will have decreased. It will take time for the pressure and hydrogen level to recover and if it is too low inside proper refills will not be possible. Therefor every HRS has a limited number of "back-to-back" refills it can complete before the cascade storage is too low. To achieve more back-to-back refills the size of the cascade or the rate at which the cascade can be refilled can be increased. Large fuel tanks (such as for in heavy-duty vehicles) require larger cascade storages.

There are some less popular alternatives and compliments to the cascade storage such as refills by direct compression (bypassing the cascade entirely) or to use a "booster compressor" connect in between the cascade and the vehicle. Regardless of technology the refilling must always take place under controlled circumstances as defined by the refueling protocol. These protocols are in place to ensure a safe refueling and puts demands on the stations. First of the station needs equipment to control the temperature and flow of hydrogen. Secondly the vehicle and HRS are equipped with sensors to monitor pressures and temperatures simultaneously on both sides. The sensor information is then communicated between the vehicle and HRS via IR-sensors located on the fueling receptacle and nozzle. The information is used by the HRS to govern the refueling process correctly and in if required interrupt it.

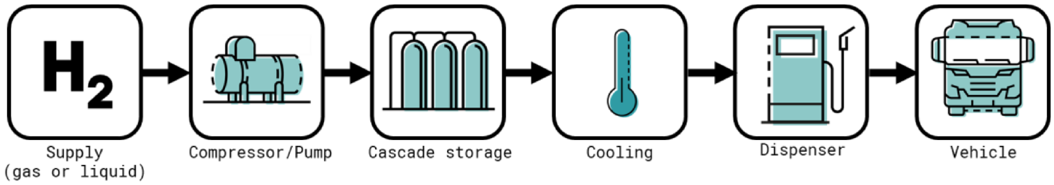

Figure 8: The cascade filling principle

sLH2/LH2 refills

No land vehicles with LH2 onboard storage exist except for prototypes. Therefore, there is no widespread usage of LH2 refilling. There are some promising advantages of LH2 refilling and usage in vehicles. One manufacturer that has announced the development of LH2 fueled trucks is Daimler [25]. They have also stated that LH2 HRSs and refueling protocols will be developed in collaboration with companies Linde and Air Liquide [26]. Daimler and Linde have presented conceptual designs for LH2 HRSs, but only with a limited amount of information. The companies claim that the station design can have a low physical footprint, low total cost of ownership and that no communication is required between station and vehicle during refilling. Daimler and Linde use the terminology "subcooled liquid hydrogen (sLH2)" for their solution.

In principle the refilling of LH2 is simpler than a CGH2-refill. The key component of the refill process is the sLH2 pump. The LH2 is pumped from storage via the dispenser into the vehicle tank at a pressure of 3 – 3.5 bar up to a maximum pressure of 20 bar [15]. An LH2 pump is distinctly different from the pumps used in liquid supplied CGH2 refill stations as the LH2 is only pumped and not vaporized. Neither Linde or Daimler have announced any specific information about this pump other than an estimated low energy consumption (0.05 kWh/kg H2 dispensed) and high flow rates (400 - 500 kg H2/h). Pumps with similar capabilities are manufactured by companies Barber-Nichols and Cryostar [27],[28]. Also, refueling stations for Liquid natural gas has some similar properties and are already established in several locations [29].

So far, few companies other than Daimler and Linde have presented concrete plans for liquid-refill HRS and no prototypes have been built nor test-results publicized. However, Daimler and Linde have announced that they want sLH2 to be an open standard that others can use, probably to promote development.

CcH2 refills

"Cryo-compressed hydrogen" (CcH2) was defined by the company Cryomotive as hydrogen stored at elevated pressures (<350 bar) and very low temperatures (>60 K). CcH2 offers the advantage that it has a high energy density, equal to that of liquid hydrogen, but less risk of boil-off [16]. Similar to the case of Daimler & Linde and their liquid refill stations Cryomotive is the only company known to actively work on this type of solution. They have presented a design for a vehicle fuel tank and information on the workings of this technology. Still, the information available is limited and one-sided.

Additionally, Cryomotive has presented two types of hydrogen refueling stations that are capable of CcH2-refills (at 350 bar), one type is liquid supplied and the other gaseous. The liquid supplied CcH2-refill station has a main storage of liquid hydrogen, either by a permanent container or by LH2-trailers left by the station, just the same as the other liquid supplied stations. The liquid hydrogen is compressed and vaporized by the cryopump. The compressed and low temperature now gaseous hydrogen can either be fed to the CcH2 dispenser or to a cascade storage system which then connects to a dispenser for regular CGH2 refills at 350 bar. Little is publicly known about the gaseous supplied CcH2-refill station design. In principle its function should be similar to the one of a regular gaseous supplied CGH2 station, but with the addition of a cryocooler which can cool the hydrogen down to temperatures of around 80 K [16]. Other than the addition of a cryocooler the cascade storage of the station must also be able to handle the low temperatures which current commonplace cascade storages are not able to.

Handling of Cryogenic Hydrogen at Refuelling Stations

Cryogenic hydrogen (either sLH2/LH2 or CcH2) introduces some new challenges for the HRS to handle. In this section of the report some of these aspects are explored.

Cryocooler functionality at the station

There could be several advantages of having refueling stations equipped with cooling systems for cryogenic temperatures as it would enable the delivery of CcH2-fills without LH2 supply. Despite this, cryocoolers (sometimes also called cryogenic refrigerators) have some technical challenges that must be addressed such as special demands of the HRS, the efficiency, cost and size.

Like liquefaction technologies, cryocoolers have higher cost and energy efficiency as they increase in size [30], this could present a challenge for the size of HRSs. There are many examples of cryocoolers to reach very low temperatures for various gases [30], but no known commercial solutions suitable to the demands of a HRS. It is estimated that a cryocooler suitable for a refueling station should have a capacity of 1000 kg H2/day. This requires a cryocooler capable of cooling down hydrogen to a temperature of 80K at a pressure of at least 350 bar and minimum rate of 42 kg H2/h. The cooling rate is dependent on the station design, a rate of up to 480 kg H2/h could be needed if filling rates of 8 kg H2/min are to be achieved through a direct feed from the cryocooler. For the calculations in the example presented below, a rate of 100 kg H2/h is assumed. It is also assumed that the station has a cascade storage which is able to handle cryogenic temperatures. As mentioned previously, there are uncertainties surrounding this type of cryogenic cascade storage, and it is not known if such storages are practical. The example system is illustrated in **Error! Reference source not found.**.

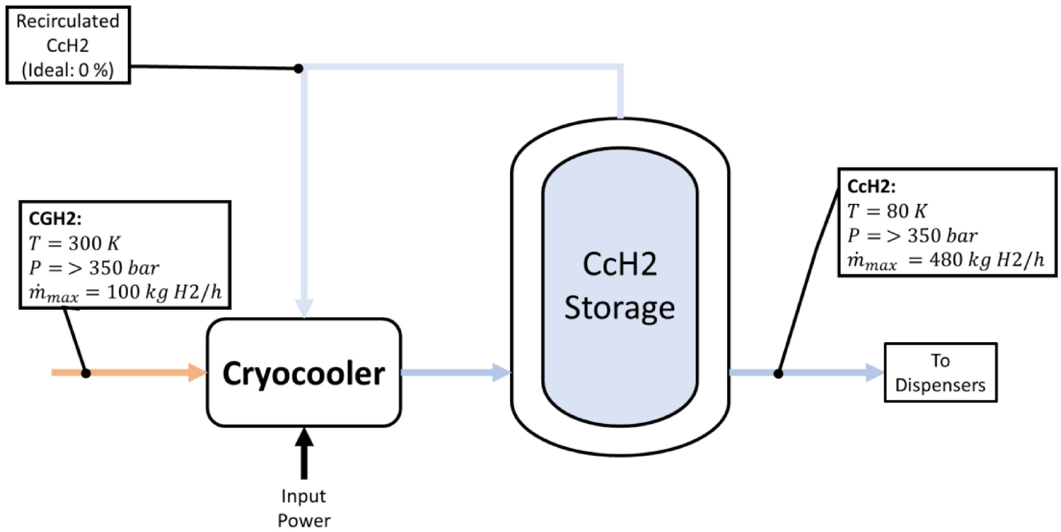

Figure 9: A Cryocooler system capable of fast refills

One commercial product close to meeting the demands of an HRS is the Turbo-Brayton cryogenic system by Air Liquide [31]. The product uses a reversed Tubro-Brayton cycle and can achieve temperatures down to 80 K at the required rates but is only rated for a pressure of 70 bar. The full cooling cycle is illustrated in **Error! Reference source not found.**. There are cooling cycles other than the reversed Turbo-Brayton cycle which also could be viable options, such as Gifford-McMahon or Stirling cycles. However, no such commercial products were found that could meet the requirements.

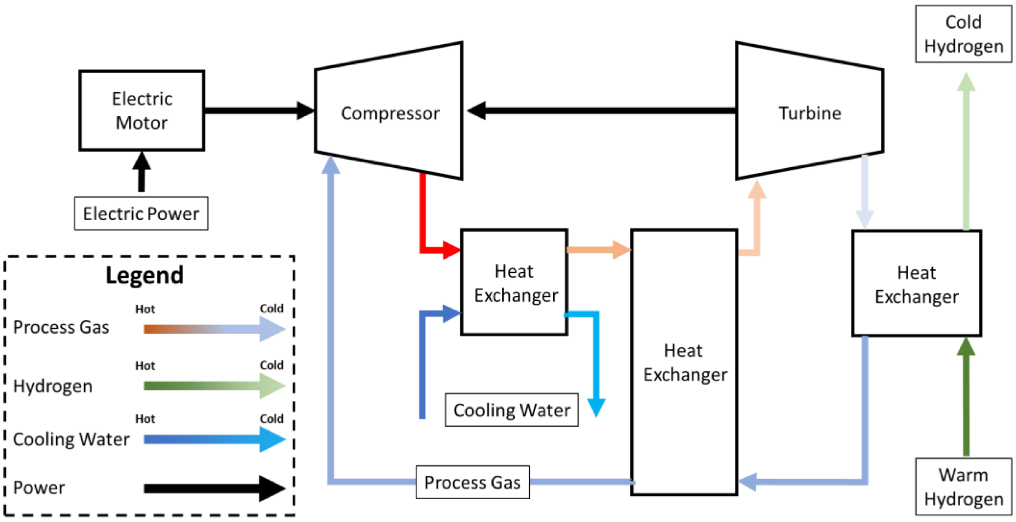

Figure 10: Cryocooler process with the reversed Brayton cycle

The power consumption of the cryocooling system can be estimated based of the data available about the product. Ideally the power required to cool hydrogen from 300 K to 80 K at a pressure of 350 bar and at a rate of 100 kg H2/h is 65,6 kW (see calculations in appendix). However, cooling cycles never operate ideally in reality and at temperatures around 80 K inefficiencies and losses tend to be large. As explained previously, typical FOM (figures of merit) for cryocoolers and liquefiers in general tend to be around 20 – 30 % in the very best case. This means that the actual input power required is closer to 220 - 330 kW or 2.2 – 3.3 kWh/kg H2. Based on the performance presented on the product data sheets for the Turbo-Brayton Cryogenic system the FOM is estimated to 15 – 20 % [31], [32]. With a of FOM 15 % the required input power is 440 kW or 4.4 kWh/kg H2. For this required input the “TBF-700” version of the Turbo-Brayton Cryogenic system could be chosen (the system is available in multiple sizes). The TBF-700 is quite large and measures 12 x 3.5 x 3.5 m (L x W x H). [32]

To summarize, the power consumption of the cryocooler is comparable to the consumption of compressors at CGH2-stations (around 2 – 6 kWh/kg H2) [33]. Additionally, the cryocooler requires a flow of cooling water at temperatures of 15 – 34 °C [31]. The size of the cryocooler presents a challenge at HRSs as the TBF-700 is larger than a 40ft ISO-container. Even the smaller model TBF-350 is at a size of 11 x 1.7 x 3 m. However, the TBF series products are not made to be space-efficient, and future more compact designs adapted for refueling stations could be a possibility. Still, they are only intended for 70 bar at most, modifications or other alternatives are required to handle pressures of 350 bar and higher. Thereby, in theory a HRS equipped with a cryocooler is not unreasonable, but practical demonstrations are still needed.

Boil-off at the refuelling station

At a HRS some activities take place which will cause additional boil-off other than from the storage vessels. The active handling of the LH2, such as pumping, and transfer between vessels is expected to be the main cause of boil-off loss rather than passive heat transfer [34]. For instance a LH2 cryo-pump used for refueling is estimated to cause boil-off losses of 7 %/day for small stations (200 kg H2/day) down to 2 %/day for large stations (2000 kg H2/day) [34].

Strategies can be applied to utilize the boil-off at the refueling station. For example the boiled-off gas can be fed to a fuel cell to generate electricity, to a compressor for storage or to re-cooling and/or re-liquefaction with the use of a cryocooler [34]. In G. Petitpas, 2018 [34] four such solutions for boil-off utilization were compared: fuel cell, mechanical compressor to 290 psi (20 bar), electrochemical compressor to 1000 psi (70 bar) and a Gifford-McMahon type cryocooler. It was shown that all solutions have the potential to be economically beneficial over ventilation of the boil-off, but that the economics were dependent on factors such as the configuration of the HRS (350 & 700 bar were compared), the price of electricity, and the value of the hydrogen. Overall, the mechanical compressor presented the greatest potential for overall cost reduction whilst the fuel cell presented the least.

Warm tank refills

A challenge to overcome for stations with CcH2 or LH2 refills is how to handle refills when the vehicle tank is significantly warmer than the supplied fuel. For instance, if a room-temperature vehicle tank was to be filled with LH2 the temperature difference of more than 250 K would cause large amounts of hydrogen boil-off and possible loss. Stations and vehicles must develop strategies to deal with this issue, solutions have been suggested, but there are no standardized methods yet.

A practice that is common for LNG vehicles[1] is to only fill the tank partially if the tank is warm [35]. The cool fuel will cause the tank to cool down while too high pressure build-up is prevented. Since the tank is now cooler than previously it will be possible to refill larger amounts of fuel on the next refills, until a full refill is possible. The consequence of this strategy is that the vehicle will have reduced range per refill until a low enough temperature is reached to enable full refills.

Another method for CcH2 refills is to use the cryogenic hydrogen as a cooling medium to precool the vehicle tank down to the desired temperature as suggested in Ming He et al., 2020 [36]. The hydrogen used for cooling of the vehicle tank is recirculated to the station and reutilized with the use of a cooling system. A simplified flow-diagram of the process is illustrated in Figure 11.

[1] Liquid Natural Gas vehicles

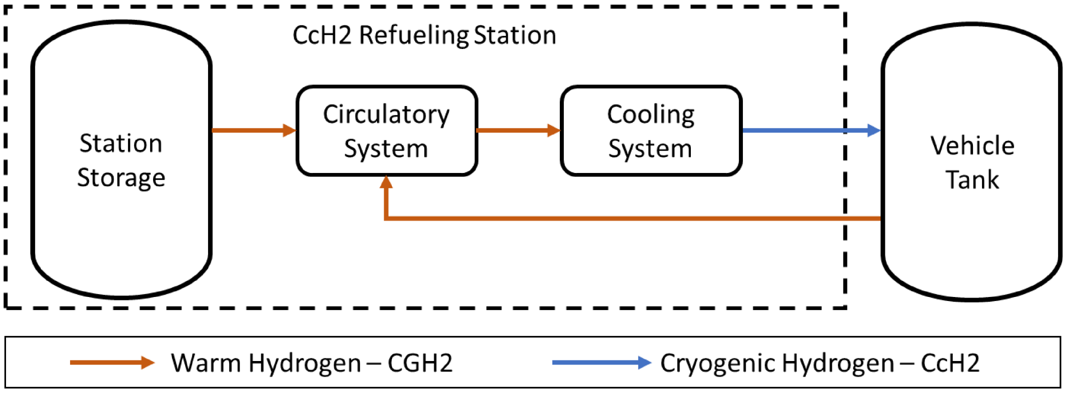

Figure 11: Simplified flow-diagram of the precooling method with CcH2

For this method it was calculated that precooling of a 101 L tank from 300 K, 10 MPa to 80 K, 10 MPa would require 2.25 kg of hydrogen and would take about 2 minutes to complete [36]. For context a 101 L tank would hold about 3 kg of hydrogen at 80 K and 10 MPa. Since the filling speed in the example is 1 kg H2/min it can be concluded that it takes almost as much time and hydrogen to precool the tank as it takes to fill it.

For CcH2-refill stations the re-cooling and re-use of the hydrogen used for cooling of the tank is simplified if they are equipped with a cryocooler. The precooling through hydrogen circulation method is also technically possible for refueling stations with LH2-refills (or CcH2-refill stations without cryocoolers). However, without a cryocooler the hydrogen used for cooling the tank cannot be reutilized and would be wasted. For the 101 L tank example this would mean only 57 % of the total amount of dispensed hydrogen ends up in the vehicle tank and 2.25 kg H2 would be wasted. Therefore, this precooling method is not practical for LH2-refill stations.

Comparison of cost aspects between refueling station configurations

The exact cost situation is case-specific for each station based of its configuration as described in Table 3. Stations with gaseous refills have been studied previously by the U.S. Department of Energy and its National Renewable Energies Laboratory, NREL. NREL has developed analysis tools such as the Hydrogen Refueling Stations Analysis Model (HRSAM) [37]. For stations with LH2 or CcH2 refills no such tools are available the required information for cost estimates is unavailable.

Cost of refueling with gaseous refills

The main difference in cost is between gaseous and liquid supplied stations, this arises from the compressor, cryopump and mode of hydrogen delivery. A cryopump will have a lower energy consumption than a compressor [38], yielding in a lower energy cost. From WP3 it is shown that a LH2-trailer will be significantly cheaper than a CGH2-trailer of the same capacity, contributing to a lower cost of hydrogen delivery. Hence, a LH2 supplied stations will overall be cheaper as the cryopump and storage are more cost-efficient options. The cost-efficiency of refueling stations also tends to improve with increased station size

[20] , [24] which may further favor liquid supplied stations since the physical space required for a liquid supplied station is smaller [18].

NREL with its analysis tool has previously estimated that the future cost of refueling contributed by the refueling stations could be about 2 $/kg H2 for a liquid supplied station and 3 $/kg H2 for a gaseous supplied station [24]. This under the assumptions of a 1000 kg H2/day station and cost reductions for much of the equipment compared to current costs.

Effect of Heavy-duty refills on cost

For stations with gaseous refills the high-pressure cascade storage must be configured to accommodate the desired refueling characteristics. As explained earlier, vehicles with large fuel tanks require larger cascades. Because of this, stations equipped for heavy-duty gaseous refills will have a higher cost.

For stations with LH2 or CcH2 refills a cascade storage[2] is not required, this means that they could be more cost and space-efficient, especially when intended for heavy-duty usage. However, even though the arguments for this are strong, today there is a lack of empirical and publicly available information to quantify and substantiate the claims.

Comparative cost estimates

Although the information required to make a full comparison between the different station types is lack a qualitative assessment can be made. For instance, information about energy use is known for all station types, and cost estimates for CGH2-refill type stations can be made with the tool HRSAM [37]. The CGH2-refill type stations (1 & 2) in Table 4 have a capacity of 1200 kg H2/day and the costs are representative of a future scenario where some cost reductions have taken place (more information about this is found in appendix). It can further be seen that the energy demand per station configuration is 5>1>2>4>3 in decreasing order.

Table 4: Station comparison - 1200 kg H2/day

Configuration	1	2	3	4	5
Supply	Gaseous	Liquid	Liquid	Liquid	Gaseous
Refill	CGH2	CGH2	LH2/sLH2	CGH2 & CcH2	CGH2 & CcH2
CAPEX	2.48 M€	1.75 M€	*No Data*	*No Data*	*No Data*
Average Energy use	1.8 kWh/kg H2	0.54 kWh/kg H2	0.05 kWh/kg H2 [39]	0.5 kWh/kg H2 [16]	6.2 kWh/kg H2[3]
Station cost	2.44 €/kg H2	1.98 €/kg H2	*No Data*	*No Data*	*No Data*

[2] For CcH2 this depends, see later sections of the report

[3] Estimate based of average energy use for station 1 (1.8 kWh/kg H2) for compression and an additional 4.4 kWh/kg H2 for cryocooling.

References

[1] J. O. Abe, A. P. I. Popoola, E. Ajenifuja, and O. M. Popoola, "Hydrogen energy, economy and storage: Review and recommendation," *Int. J. Hydrogen Energy*, vol. 44, no. 29, pp. 15072–15086, 2019, doi: 10.1016/j.ijhydene.2019.04.068.

[2] J. Andersson and S. Grönkvist, "Large-scale storage of hydrogen," *International Journal of Hydrogen Energy*, vol. 44, no. 23. Elsevier Ltd, pp. 11901–11919, May 03, 2019, doi: 10.1016/j.ijhydene.2019.03.063.

[3] D. D. Papadias and R. K. Ahluwalia, "Bulk storage of hydrogen," *Int. J. Hydrogen Energy*, vol. 46, no. 70, pp. 34527–34541, Oct. 2021, doi: 10.1016/J.IJHYDENE.2021.08.028.

[4] D. G. Caglayan *et al.*, "Technical potential of salt caverns for hydrogen storage in Europe," *Int. J. Hydrogen Energy*, vol. 45, no. 11, pp. 6793–6805, Feb. 2020, doi: 10.1016/J.IJHYDENE.2019.12.161.

[5] R. Tarkowski, "Underground hydrogen storage: Characteristics and prospects," *Renew. Sustain. Energy Rev.*, vol. 105, pp. 86–94, May 2019, doi: 10.1016/J.RSER.2019.01.051.

[6] A. M. Elberry, J. Thakur, A. Santasalo-Aarnio, and M. Larmi, "Large-scale compressed hydrogen storage as part of renewable electricity storage systems," *Int. J. Hydrogen Energy*, vol. 46, no. 29, pp. 15671–15690, 2021, doi: 10.1016/j.ijhydene.2021.02.080.

[7] NPROXX, "Stationary Hydrogen Storage Applications - NPROXX." https://www.nproxx.com/hydrogen-storage-transport/stationary-applications/ (accessed Nov. 17, 2021).

[8] H. Derking, L. Van Der Togt, M. Keezer, and C. Bv, "Liquid Hydrogen Storage: Status and Future Perspectives."

[9] W. A. Amos, "Costs of Storing and Transporting Hydrogen." [Online]. Available: http://www.doe.gov/bridge/home.html.

[10] W. U. Notardonato, A. M. Swanger, J. E. Fesmire, K. M. Jumper, W. L. Johnson, and T. M. Tomsik, "Zero boil-off methods for large-scale liquid hydrogen tanks using integrated refrigeration and storage," *IOP Conf. Ser. Mater. Sci. Eng.*, vol. 278, no. 1, pp. 0–9, 2017, doi: 10.1088/1757-899X/278/1/012012.

[11] J. B. M. Daigle, M. Foygel, V. Smelyanskiy, "LH2Sim." 2017, [Online]. Available: https://github.com/nasa/LH2Sim.

[12] CHART Industries, "Intro to Cryogenics," 2016. https://www.youtube.com/watch?v=T-6R5exBUCo (accessed Jan. 05, 2022).

[13] CHART Industries, "Liquid Cylinder Operation," 2016. https://www.youtube.com/watch?v=Ha3_MFZ_MaM (accessed Jan. 05,

2021).

[14] L. Decker Brussels, "Liquid Hydrogen Distribution Technology HYPER Closing Seminar," 2019.

[15] "Heavy-Duty-Event-Subcooled-Liquid-Hydrogen-sLH2-Schaefer-Linde-Maus-Daimler."

[16] Cryomotive, "Heavy-Duty-Event-CRYOGAS-Technology_BrunnerForstner-Cryomotive," 2021. https://www.now-gmbh.de/wp-content/uploads/2021/05/Heavy-Duty-Event-CRYOGAS-Technology_BrunnerForstner-Cryomotive.pdf.

[17] Sandvik, "Nordisk vätgaskonferens I Sandviken," Oct. 2016.

[18] H2Mobility, "Overview Hydrogen Refuelling For Heavy Duty Vehicles." [Online]. Available: https://h2-mobility.de/wp-content/uploads/sites/2/2021/08/H2-MOBILITY_Overview-Hydrogen-Refuelling-For-Heavy-Duty-Vehicles_2021-08-10.pdf.

[19] FuelCellsWorks, "California: Oakland Hydrogen Station Opens," 2019.

[20] M. M. Mariya Koleva, "Title: Hydrogen Fueling Stations Cost," 2021. [Online]. Available: https://www.hydrogen.energy.gov/pdfs/21002-hydrogen-fueling-station-cost.pdf.

[21] SAE, "SAE J2601," *Fueling Protocols for Light Duty Gaseous Hydrogen Surface Vehicles J2601_202005*, May 29, 2021. .

[22] wwwPRHYDEeu Prhyde, "PRHYDE-Protocol for heavy-duty hydrogen refuelling Call Identifier FCH-04-2-2019: Refuelling Protocols for Medium and Heavy-Duty Vehicles." [Online]. Available: www.PRHYDE.eu.

[23] Hydrogen Tools, "International Hydrogen Fueling Stations - FY21Q4," *International Hydrogen Fueling Stations - FY21Q4*, 2021. https://h2tools.org/hyarc/hydrogen-data/international-hydrogen-fueling-stations.

[24] K. Reddi, A. Elgowainy, N. Rustagi, and E. Gupta, "Impact of hydrogen refueling configurations and market parameters on the refueling cost of hydrogen," *Int. J. Hydrogen Energy*, vol. 42, no. 34, pp. 21855–21865, Aug. 2017, doi: 10.1016/j.ijhydene.2017.05.122.

[25] J. Zerhusen, "Imported hydrogen fuels for long distance trucking in Germany (70 MPa, LH 2 , CcH 2) NOW/CEP Heavy Duty Event." [Online]. Available: https://www.daimler-truck.com/innovation-sustainability/efficient-emission-.

[26] N. | Monday, "Air Liquide supports Daimler Truck AG with Liquid Hydrogen for heavy-duty long-haul fuel-cell Truck prototype tests Clean transportation Energies Logistics," 2021.

[27] Barber-Nichols, "Liquid Hydrogen Pumps," 2021. https://www.barber-

nichols.com/products/pumps/cryogenic-pumps/liquid-hydrogen-pumps/ (accessed Nov. 30, 2021).

[28] Cryostar, "LIQUID HYDROGEN TRANSFER PUMPS," 2021. https://cryostar-hydrogen-solutions.com/liquid-hydrogen-transfer-pumps/ (accessed Nov. 30, 2021).

[29] Linde Engineering, "LNG fueling stations," 2021. https://www.linde-engineering.com/en/process-plants/lng-and-natural-gas-processing-plants/lng-fueling-stations/index.html (accessed Nov. 30, 2021).

[30] Ray Radebaugh, "Cryogenic Technology Resources." https://trc.nist.gov/cryogenics/cryocoolers.html (accessed Dec. 08, 2021).

[31] Air Liquide, "Turbo-Brayton cryogenic systems," 2021. https://advancedtech.airliquide.com/turbo-brayton-cryogenic-systems (accessed Dec. 08, 2021).

[32] Air Liquide, "Turbo-Brayton subcooler for Liquefied Natural Gas (LNG) boil-off reliquefaction." https://advancedtech.airliquide.com/sites/abt_at/files/2019/03/27/turbo-brayton_lng_boiloff_reliquefaction_en_09.19_sd_0.pdf (accessed Dec. 08, 2021).

[33] DOE, "Energy requirements for hydrogen gas compression and liquefaction as related to vehicle storage needs," 2009. [Online]. Available: http://www.hydrogen.energy.gov/storage.html.

[34] G. Petitpas, "Boil-off losses along LH2 pathway," 2018.

[35] CHART Industries, "First Fill/Hot Fill and Warm Fill Fueling Procedure for LNG Vehicle Tanks," 2015. https://files.chartindustries.com/VT-0013_ws.pdf (accessed Dec. 08, 2021).

[36] M. He *et al.*, "The design and optimization of a cryogenic compressed hydrogen refueling process," *Int. J. Hydrogen Energy*, vol. 46, no. 57, pp. 29391–29399, Aug. 2021, doi: 10.1016/j.ijhydene.2020.11.061.

[37] NREL, "HRSAM," 2014. https://hdsam.es.anl.gov/index.php?content=hrsam (accessed Dec. 10, 2021).

[38] NREL, "HYDROGEN DELIVERY SCENARIO ANALYSIS MODEL (HDSAM)," 2014. https://hdsam.es.anl.gov/index.php?content=hdsam (accessed Oct. 21, 2021).

[39] D. S. S. (Linde); D. S. M. (Daimler), "Heavy-Duty-Event-Subcooled-Liquid-Hydrogen-sLH2-Schaefer-Linde-Maus-Daimler," 2021. https://www.now-gmbh.de/wp-content/uploads/2021/05/Heavy-Duty-Event-Subcooled-Liquid-Hydrogen-sLH2-Schaefer-Linde-Maus-Daimler.pdf.

[40] J. M. Pfotenhauer, "Refrigeration & Liquefaction," [Online]. Available:

https://uspas.fnal.gov/materials/10MIT/Lecture_2.1.pdf.

[41] National Institute of Standards and Technology, “Thermophysical Properties of Fluid Systems.” .

Appendix

HRSAM inputs

HRSAM – Hydrogen Refuelling Station Analysis Model - is a tool developed by the National Renewable Energies Laboratory of the U.S. Department of Energy. The tool lets the user compare costs of alternative hydrogen refuelling options and to identify cost drivers for various station configurations and more. The tool calculates the cost of refuelling based of current costs for the key components of the refuelling station such as compressors and storage units. The tool is also able to provide cost estimates for future scenarios where due to increased production volumes the costs of refuelling stations has decreased from current levels. In Table 4 the costs presented are assuming a "mid-sized" production volume which results in costs 40.7 % and 32.5 % lower for configuration 1 and 2 (from Table 4) respectively than if a "low-sized" production volume is used. All specific inputs used for the results in Table 5 are presented below in Table 5. All other inputs are left as default.

Table 5: HRSAM specific inputs

Configuration	1	2
Station type	Gaseous H2 Station	Liquid H2 Station
Hydrogen Source	Tube-trailer supply	-
Dispensing	700 bar Cascade dispensing	700 bar via LH2 pump/vaporization
Refueling Station Size	1200 kg H2/day	1200 kg H2/day
Production Volume	Mid	Mid

Download HRSAM from: *https://hdsam.es.anl.gov/index.php?content=hrsam*

Energimyndigheten

Calculation of Ideal Cool Down Work

The ideal cool down work (least possible work) required to cool down a gas from one temperature to another at a constant pressure can be calculated with the formula presented below [40]:

$$\Delta W = \int_{T_c}^{T_h} mc_p(T)\left[\frac{T_h}{T} - 1\right] dT$$

$\Delta W - Ideal\ Cool\ Down\ Work\ [kJ]$	$T - Temperature\ [K]$
$m - Mass\ [kg]$	$T_h - Outside\ \&\ Starting\ Temperature\ [K]$
$c_p(T) - Specific\ Heat\ Capacity\ [kJ/kg\ K]$	$T_c - Target\ Temperature\ [K]$

For 1 kg of hydrogen at a constant pressure of 350 bar, an outside and starting temperature of 300 K and a target cold temperature of 80 K is calculated to be 2469 kJ which equals 0.656 kWh/kg H2. The specific heat capacity for hydrogen at 350 bar (Figure 12) is received from the NIST Thermophysical properties of Fluid Systems database [41].

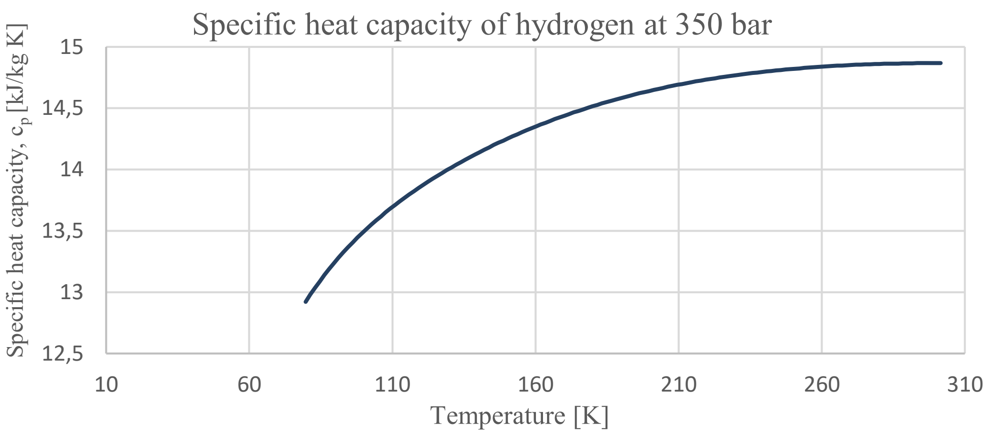

Figure 12: Specific heat capacity for hydrogen at 350 bar. Data source: NIST