



Hydrogen liquefaction, storage,
transport and application of liquid
hydrogen



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1

Summary

Hydrogen as an energy vector is currently attracting a great deal of attention – as is its liquid aggregate state, liquid hydrogen (LH₂). At the outset of the project, the topic was relevant only to the stakeholders. As a CO₂-free vector of high gravimetric energy density, LH₂ holds great potential for applications in energy technology, mobility and the supply of hydrogen networks with hydrogen regasified from LH₂ for sustainable energy systems and a supporting hydrogen economy.

For decades, LH₂ has been used as a fuel in space travel and as a source of high-purity process gas in industry. This white paper is primarily intended to highlight the opportunities presented by LH₂ as an energy source in a global hydrogen economy. It also outlines general principles, the current status of the technology, and dispels some of the misunderstandings and prejudices that often dominate the discussion on the topic of hydrogen and, in particular, LH₂. The authors deliberately focus on the fields of application of liquid hydrogen.

The high storage density of LH₂ is the main motivation for current development projects aimed at replacing fossil fuels, not only for the established niche of space travel, but also for everyday mobile applications. In aviation, as well as in the areas of rail and commercial vehicles, sufficient range can currently only be achieved with liquid hydrogen. In shipping, in addition to the use of LH₂, the other liquid hydrogen derivatives (methanol, ammonia) are also conceivable, but these are not strictly "zero-emission".

If fuel cells are used, the extremely high purity (99.9999% and better) of the gas extracted from the liquid phase is another advantage with regard to their lifespan. For this reason, hydrogen gas from LH₂ is already widely used in the semiconductor industry and is also relevant for the chemical industry. For example, using LH₂ as a hydrogen source eliminates the need for further purification processes.

The high storage density of LH₂ plays a crucial role in transport and logistics, especially from the point of view of energy-importing countries such as Germany. The energy for liquefaction must be provided in the H₂-producing country, where renewable energy is cheap and available in large volumes. This makes the transport of LH₂ and the regasification of LH₂ the only type of liquid transport of hydrogen in which no additional energy is required in the target country to utilize the gas – not only is hydrogen imported, but also its valuable cold. With an innovative regasification process, the available cooling capacity can be converted into mechanical and/or electrical output, and some of the liquefaction energy can be recovered.

The vector LH₂ has a high degree of technological maturity.

Compared to other liquid storage variants, the import vector LH₂ has a high degree of technological maturity with respect to a wide variety of transport routes and for the barrier-free provision of hydrogen:

- For example, the HESC pilot project (Hydrogen Energy Supply Chain between Australia and Japan) is the first to demonstrate time worldwide that LH₂ can be produced in large volumes, stored and transported safely over 9000 km, and finally utilized at the destination. This by no means has to be in the same location as the landing terminal.
- The transport of LH₂ by road has long been established in Germany and thus allows the prompt setup of a "virtual pipeline" between a LH₂ storage facility and any location where hydrogen is needed. Existing rail and waterways can also be used for this purpose. In particular, this "virtual pipeline" enables industries that already consume grey hydrogen, or can replace fossil fuels in their processes, to access green hydrogen more quickly. The same applies to the construction of infrastructure for the mobile applications described above. The fact that a "virtual pipeline" is based on available technologies and existing transport routes, makes it an accelerating factor in setting up the hydrogen economy.

Against the backdrop of the war-induced gas crisis of the winter of 2022/2023, the current efforts to develop an LNG infrastructure in Germany and, above all, its later usability for hydrogen import, must be addressed at this point.

LNG terminals serve not only as access points to the global liquefied gas market and strategic natural gas storage facilities, but also to stabilize the pipeline networks: The high variations in the amount of gas demanded by consumers throughout the course of the day are compensated for very quickly by the wide density ratio between liquid and gas (about 1:600). This so-called peak shaving in the gas network takes place in the terminal by connecting pumps in parallel, quickly multiplying the gas discharge rate into the pipeline network. The future terminals will reliably retain this essential functionality with liquid hydrogen (density ratio approx. 1:842), in contrast to all the other H₂ derivatives discussed, which are unable to guarantee this valuable functionality due to the slow downstream high-temperature dehydrogenation processes.

In addition to the previously described applications for liquid hydrogen, its low temperature of approx. -253 °C offers opportunities for new, innovative technologies. At this temperature, superconducting materials transport electrical energy without loss. Integrated into the construction of an LH₂ pipeline, electrical and chemical energy can be transported over long distances with superconducting lines in a highly efficient manner and in a single line. In addition, superconductivity opens up new prospects for increasing the efficiency and improving the performance of electrical machinery and applications in electrical energy technology. Finally, the cooling of the hydrogen itself provides added value if it is coupled with conventional applications and, in this way, reduces the energy requirement, for example, for process cooling or air conditioning in buildings.

In addition to the focus on LH₂ utilization and logistics discussed at the start, this white paper also deals with the essential basics for the liquefaction and storage of hydrogen. The physical properties of the fluid influence the process engineering, design and material selection for plants and components. The safety aspects are also highlighted, with particular attention paid to the properties of the cryogenic liquid and the cold vapour.

2

Fields of application for H₂, hydrogen production and import requirements

Transformation of the energy system

Like most industrialized nations in the world, Germany currently covers its primary energy needs largely through imports. In 2020, Germany imported around 70% of primary energy in the form of coal, mineral oil, natural gases and nuclear energy. The renewable components of the energy mix are only reflected in the remaining 30%, mainly in the form of electricity, ultimately contributing just 16% to the total demand in 2020.¹

The effect of these figures on the living conditions of the people is demonstrated by their connection to the land area. The result is that 1.5 GJ/km² of renewable energy density contrasts with a demand density of 36 GJ/km². Completely renewable electricity generation alone requires, for example, doubling the generation capacities with the associated encroachment on the landscape. Taking this into account, it is clear that achieving a self-sufficient supply of all energy sectors through production is both ecologically unacceptable and socially unfeasible. As a result, Germany, like most other industrialized nations, will continue to import energy in large quantities in the future.

The major challenges lie in the substitution of fossil fuels through a substantial increase in the production of electrical energy generated from renewable sources, and green hydrogen derived from it, from this, as well as the rapid construction of suitable transmission and transport infrastructures for electricity and hydrogen. In Germany there is a nationwide natural gas

infrastructure consisting of transmission and distribution grids, whereas hydrogen pipelines are currently mainly used in industrial networks and not for energy supply; a hydrogen network intended for energy supply is to be implemented by 2030.

The accelerated development of a global hydrogen economy desired by all, can only be achieved with the simultaneous expansion of transcontinental production and transport chains, as well as regional distribution networks tailored to local conditions.

Expected H₂ requirements in LH₂-related fields of application and application scenarios in Germany

At least since the judgement of the Federal Constitutional Court in April 2021, in which the Federal Climate Protection Act (KSG) of December 2019 was partially declared unconstitutional, Germany has reached an agreement on the principle of climate neutrality by 2045.^{2,3,4} As a result of this, several political and scientific institutions have commissioned or conducted studies on how Germany can achieve climate neutrality by 2045.

Table 2.1: Overview of studies investigating the path towards climate neutrality in Germany by 2045. Sources: ^{5, 6, 7}

	1	2	3	4	5	6
Name	Climate-neutral Germany 2045	Climate pathways 2.0	Embarking on climate neutrality	Long-term scenarios for the transformation of the energy system in Germany 3	Germany on the road to climate neutrality in 2045	Pathways for the energy transition
Commissioned by	Climate Neutrality Foundation, Agora Energiewende, Agora Verkehrswende	Federation of German Industries (BDI)	German Energy Agency (dena)	Federal Ministry for Economic Affairs and Climate Action (BMWK)	Ariadne - Copernicus Projects	
Produced by	Prognos, Oeko-Institut, Wuppertal Institute	BCG	EWI, FIW, ITG, University of Bremen, Stiftung Umweltenergierecht, Wuppertal Institute	Fraunhofer ISI (Fh-ISI), Consentec, TU Berlin, ifeu	PIK, MCC, PSI, RWI, IER, Hereon, Fh-ISI, Fh-ISE, Fh-IEG, Fh-IEE, DLR-VF, DLR-VE, DLR-FK	Forschungszentrum Jülich
Selected scenarios	KNDE2045	Climate pathways 2.0 target pathway	KN 100:	TN electricity TN-PtG/PtL TN-H2-G	REMIND-Mix, REMod-Mix, TIMES PanEU-Mix	Scenario 95

In this context, five of these studies ("Big Five", in table 2.1: no. 1-5) are often named and more have been added here. This covers a wide range of political, industrial and scientific discourses. Table 2.1 lists the commissioners and parties responsible for producing the studies considered. Only studies 4 and 6 consider 2050 as the target year, as these studies were written before the amendment of the KSG.⁵

The studies quantify the expected future hydrogen demand in Germany as shown in Figure 2.1 for the years 2030 and 2045/50. Despite the different origins of the investigations, the authors of the studies come to the following conclusion: The three energy sectors industry, national transport and the energy industry will especially need hydrogen in the future.

One of these studies also predicts a high hydrogen demand in the building sector. Due to the high efficiency and low costs, the remaining studies identify an advantage in the use of heat pumps in this sector; this trend is further supported by the current plans to install 500,000 heat pumps per year from 2024.⁸ The differences in the displayed energy quantities can be attributed to various factors— for example, the level of final energy consumption and gross electricity consumption in the respective sectors.

The specific utilization and quantities of hydrogen within the aforementioned sectors are still subject to debate. In this respect, the studies are less specific. One of the most prominent applications of hydrogen is its use in industry for the reduction of metal oxides, for example for steel production, as well as as a basic material, for instance for ammonia and chemical production.

For the transport sector, the studies primarily focus on utilizing hydrogen in trucks. Rail transport, as well as aviation and shipping are not addressed in this context. This is partly due to the potential use of synthetic fuels, which are listed separately.

In the energy industry, hydrogen is primarily intended for energy conversion. Here, hydrogen is suitable for energy storage for longer periods of time (seasonal storage), when electricity generation from solar and wind energy is not available in sufficient quantities. If the hydrogen is used for reconversion in gas turbines, some of the district heating is additionally decarbonised by hydrogen by means of combined heat and power.

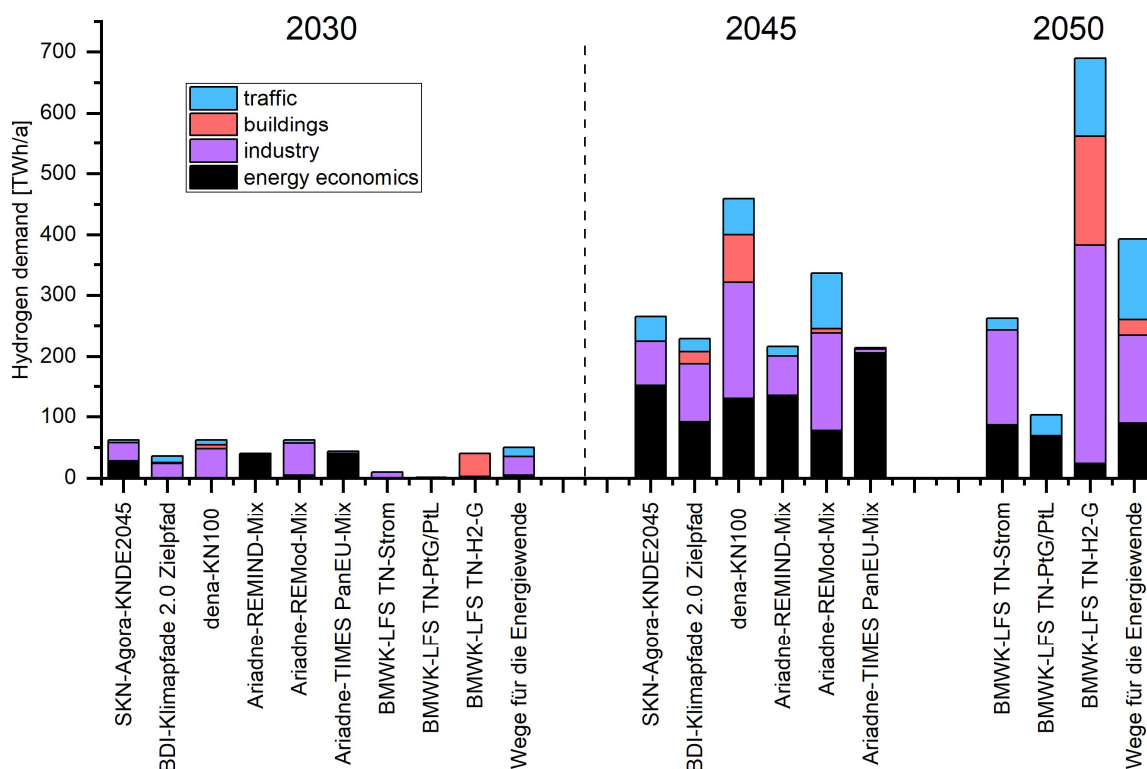


Figure 2.1: Use of CO₂-free hydrogen. Sources: 5, 6, 7

Details about the forms of hydrogen – whether gaseous or liquid – are not given in the studies listed. However, liquid hydrogen may play different roles in the above-mentioned sectors in the future. Although specific LH₂ requirements are still difficult to quantify throughout Germany, qualitative statements can be made about future LH₂ applications.

If stationary energy recovery or the use of hydrogen as a process gas is prioritized, as in the industrial sector, consumers are preferably supplied from a pipeline network. Designs of this type can be based on existing networks, for example, the one in the Leuna-Buna-Bitterfeld chemical triangle. These and similar sites can be decarbonised to great effect by supplying these local pipeline networks, from one or more feed-in points, with green H₂, e.g. from LH₂, instead of with reformed natural gas as before ("missing link"). If, as in the mobility sector, fuel stations, logistics centres with commercial vehicles, inland ports and airports are to be supplied with LH₂ as fuel hydrogen, their supply will also be based on LH₂. In mobile applications, the high storage density of liquid hydrogen is a crucial unique selling point for the use of LH₂ and is currently being implemented in the development of vehicles and aircraft (see also chapter 8). Ideally, it will be possible in future to maintain the hydrogen in its liquid state within the distribution chain as it is

transported across continents and countries, right through to the mobile end use, and avoid energy-intensive liquefaction process at the point of use.

Hydrogen transport options

The choice of the hydrogen transport system depends heavily on the production conditions, the requirements at the point of use and the distances to be covered between them. The continuous hydrogen production in a natural gas reforming plant ("grey hydrogen") in the chemical industry cannot be compared to an electrolysis plant in the H₂ mobility sector that is powered by excess offshore electricity. Unlike in the first case, where production and demand can be planned and coordinated, the "green" hydrogen produced from renewable sources in particular requires additional storage infrastructure and more extensive logistics.

LH₂ could be the "missing link" to accelerate the transition to green H₂.

The question of whether the most cost effective option is pipeline transport, containerized transport as compressed gas or liquid hydrogen or hydrogen derivative can only be answered with good knowledge of the geographical conditions, the respective supply and demand parameters and the market situation. Liquid hydrogen has advantages over other energy sources, especially for medium to large volumes and medium to long distances, as well as in geographical environments that are unfavourable for the construction of pipelines^{10,11,12} – quite apart from consumers that exclusively rely on LH₂.⁹ In addition, LH₂ technology has matured, not least due to the fact it has been used in space travel for decades.¹³

In addition to the transport aspect, LH₂ will have a special position in future networks and can be used in the current natural gas networks in a similar way to LNG: In H₂ supply structures, liquid hydrogen can act as another independent import source, strategic storage, and to cover peak shaving.

The available technology, reliable and established production (see chapter 5) and its versatility make LH₂ a crucial role in accelerating the hydrogen economy. The duration of the transformation period, measured in decades, is determined not only by the technical and geographical circumstances, but also by the reliance of hydrogen stakeholders on external factors which are virtually impossible to influence.

Along with the energy sector, industrial sectors such as chemistry, semiconductor, steel and glass production could either immediately meet their existing H₂ requirements from green hydrogen instead of grey as before, or could rapidly transfer their processes from fossil fuels to green hydrogen.

This is where LH₂ can act as a "missing link". The liquid supply system at the sites can be built up in the medium term, typically during the process conversion. The gradual conversion from "grey LH₂" to "green LH₂" occurs through the progressive expansion of renewable production sites both domestically and internationally. Then as soon as a hydrogen pipeline network is set up between the two ends of the hydrogen chain, local LH₂ infrastructures can either be dismantled or reused, for example, for regional distribution centres, filling stations, etc. In this respect, LH₂ has the characteristic ability to function simultaneously as an acceleration technology and a permanent pillar of the global hydrogen economy.

Nevertheless, is important to note that LH₂ technology has considerable optimization potential. For example, the liquefaction process currently still requires about 30% of the calorific value (see chapter 5). The cryogenic liquid boils at 20 K, whereby a small proportion of the storage capacity gradually evaporates over time (see chapter 5.3), depending on tank size and tank configuration. Ultimately, the boiling state also means that up to 25% of the volume is produced as so-called flash gas (evaporation loss) during transfer operations, which either has to be processed separately and recovered or is lost via blow-off or flare. These challenges are being addressed in current research. This work focuses on the re-use of the coldness at different temperature levels, the parallel transport of electrical energy in superconducting cables, the improvement of tank insulation by avoiding thermal bridges and the development of transfer pumps. As a result of this work, the efficiency of LH₂ logistics will increase significantly and the gap between this and alternative storage and transport methods will increase.

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3

Properties of H₂, LH₂ and H₂ derivatives

Basic properties and the phase diagram of hydrogen

Hydrogen is the lightest element and occurs in the three isotopes, protium (${}^1_1\text{H}$), deuterium (${}^2_1\text{H}$) and tritium (${}^3_1\text{H}$). The latter is unstable and hardly occurs in nature. As more than 99.9% of naturally occurring hydrogen consists of protium, only this isotope or the natural protium/deuterium mixture is considered below. Due to its small size, hydrogen exhibits relatively high diffusion rates in solids, which must be taken into account when selecting materials (see Chapter 4).

Hydrogen usually exists as a diatomic molecule (H₂). In ambient conditions (temperature ~ 20 °C, ambient pressure 1 bar) it is gaseous and has a very low density of 0.084 kg/m³ — a significantly lower value compared to the main components of air, nitrogen and oxygen. This is often beneficial, especially for example, when considering the safety aspects of hydrogen plants (see Chapter 4).

After helium, hydrogen is the element with the second-lowest boiling temperature, which is 20.4 Kelvin (-253 °C) at normal pressure (0.101325 MPa). The density of the liquid hydrogen at this temperature is 71 kg/m³, which is 842 times the density of gaseous hydrogen under standard conditions (15 °C, 1 bar). Nevertheless, the density of liquid hydrogen is significantly lower than that of other cryogenic liquefied gases, in particular liquid natural gas (LNG, 422 kg/m³). The triple point of hydrogen occurs at 13.8 Kelvin and

0.007 MPa. Figure 3.1 shows the phase diagram of para-hydrogen.

If one considers the amount of energy required to heat up liquid hydrogen (e.g. for subsequent use in a fuel cell), about 10% of the energy is required to evaporate the LH₂, and about 90% is required to heat up the cold H₂ gas. In other words: There is valuable "coldness" within the H₂ gas, which can be integrated into the overall system considerations to increase energy efficiency. Here, too, LH₂ differs significantly from LNG, where the ratio of the two energy contributions is nearly 1:1.

Depending on the nuclear spin configuration of the two hydrogen atoms in the hydrogen molecule, a distinction is made between ortho (o)- and para (p)-hydrogen, or the equilibrium mixture (e-H₂) which is made up of the two in thermodynamic equilibrium. As the equilibrium concentration is temperature-dependent and the conversion process from ortho- to para-hydrogen is exothermic (i.e. energy is released when o-H₂ is converted into p-H₂), particular consideration must be given to this when liquefying hydrogen (Chapter 5).

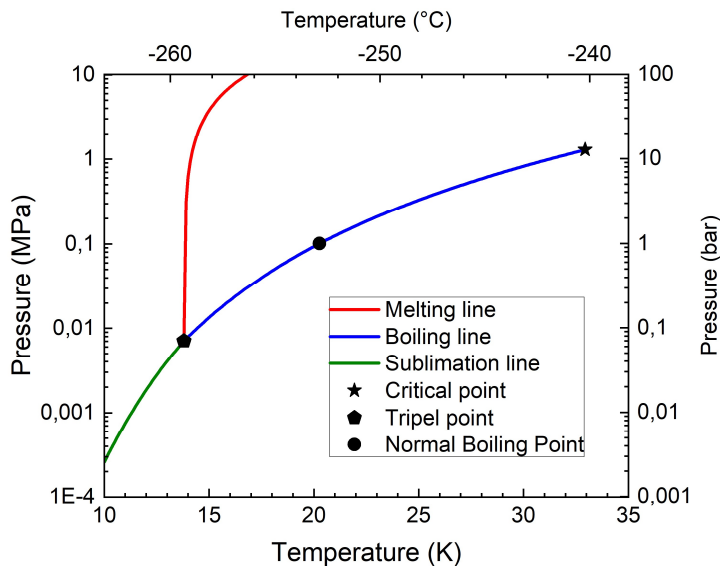


Figure 3.1: Phase diagram of (para)hydrogen. Data source¹

Hydrogen density

The liquid hydrogen density at equilibrium ranges from 77 kg/m³ at the triple point to 31.3 kg/m³ at the critical point (see Figure 3.2). This very pronounced decrease in the liquid density along the vapour pressure curve is a special feature of LH₂ and particular attention must be paid to this. In a sealed LH₂ container, for example, unavoidable heat input not only changes the pressure and temperature, but also the liquid density. Therefore, LH₂ storage containers must only be filled to such an extent that overfilling is prevented, even at a maximum working pressure which may be reached at a later point. Depending on the design, this limits the permitted fill level to 70-90% of the available volume.

Energy densities

For the energy-related use of hydrogen, its energy densities are of particular importance. Figure 3.3 shows the volumetric (left) and gravimetric (right) energy densities of relevant hydrogen-based energy carriers compared with some hydrocarbons.

Hydrogen has the highest gravimetric energy density of 33.3 kWh/kg based on the calorific value. This also surpasses hydrocarbons and hydrogen derivatives. Due to the low density under normal conditions and the resulting low volumetric energy density under normal conditions, the hydrogen must be compressed, liquefied or cooled and compressed for transport and storage.

The volumetric energy density of the liquid hydrogen at boiling point under normal conditions (20 K = -253 °C, 0.1 MPa) at 2.4 kWh/l exceeds that of the compressed hydrogen of 1.3 kWh/l at 70 MPa, 20 °C and below that of the cryogenic hydrogen compressed to 30 MPa at 30 Kelvin (2.8 kWh/l).

However, the energy density is generally significantly lower than that of liquid hydrocarbons (LNG, LPG, diesel).

Other hydrogen-based energy carriers such as ammonia or LOHC (liquid organic hydrogen carriers) also have high volumetric energy densities – for ammonia this is above that of all pure hydrogen transport forms - but their gravimetric energy density is significantly lower than for pure hydrogen.

Hydrogen regasified from LH₂ also has a very high purity of up to 99.9999% (grade 6.0), and can be stored, transported and transferred at low pressures.

LH₂ does not require reforming or processes for release at the place of use – ambient heat is sufficient – and is therefore immediately ready for use, which is particularly advantageous for mobile applications with limited space.

Another advantage of using LH₂ is that the energy required for liquefaction (see Chapter 5) is generated at the site of hydrogen production. This presents advantages thanks to the efficient and cost-effective provision of electrical energy from renewable sources, meaning the liquefaction can take place in a cost-optimized and greenhouse gas-neutral manner.

Some advantageous transport and storage applications are derived from the aforementioned physical properties of liquid hydrogen, for example hydrogen transport using ships, tank cars, trucks. Especially noteworthy are applications in CO₂-neutral aviation, ships, trains, large land vehicles, and synergies from the exploitation of the coldness of LH₂.

These are explained in more detail below.

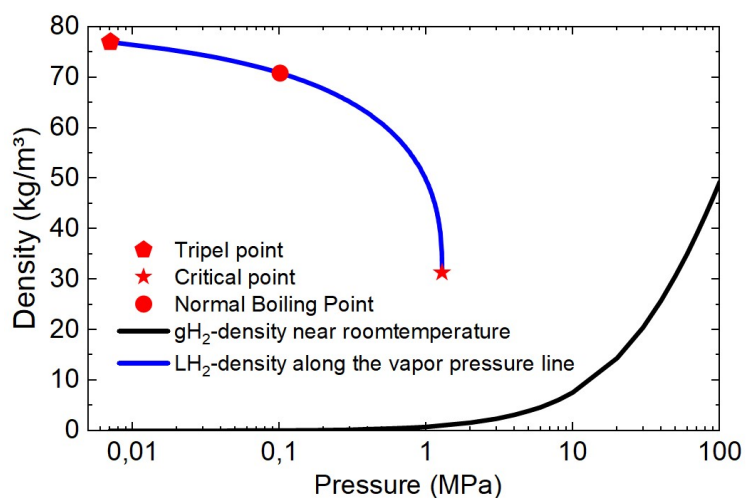


Figure 3.2: Liquid density along the vapour pressure curve (blue curve; critical point, etc., marked red), as well as the pressure-related H₂ gas density at close to ambient temperature (black curve). Own depiction based on data from¹

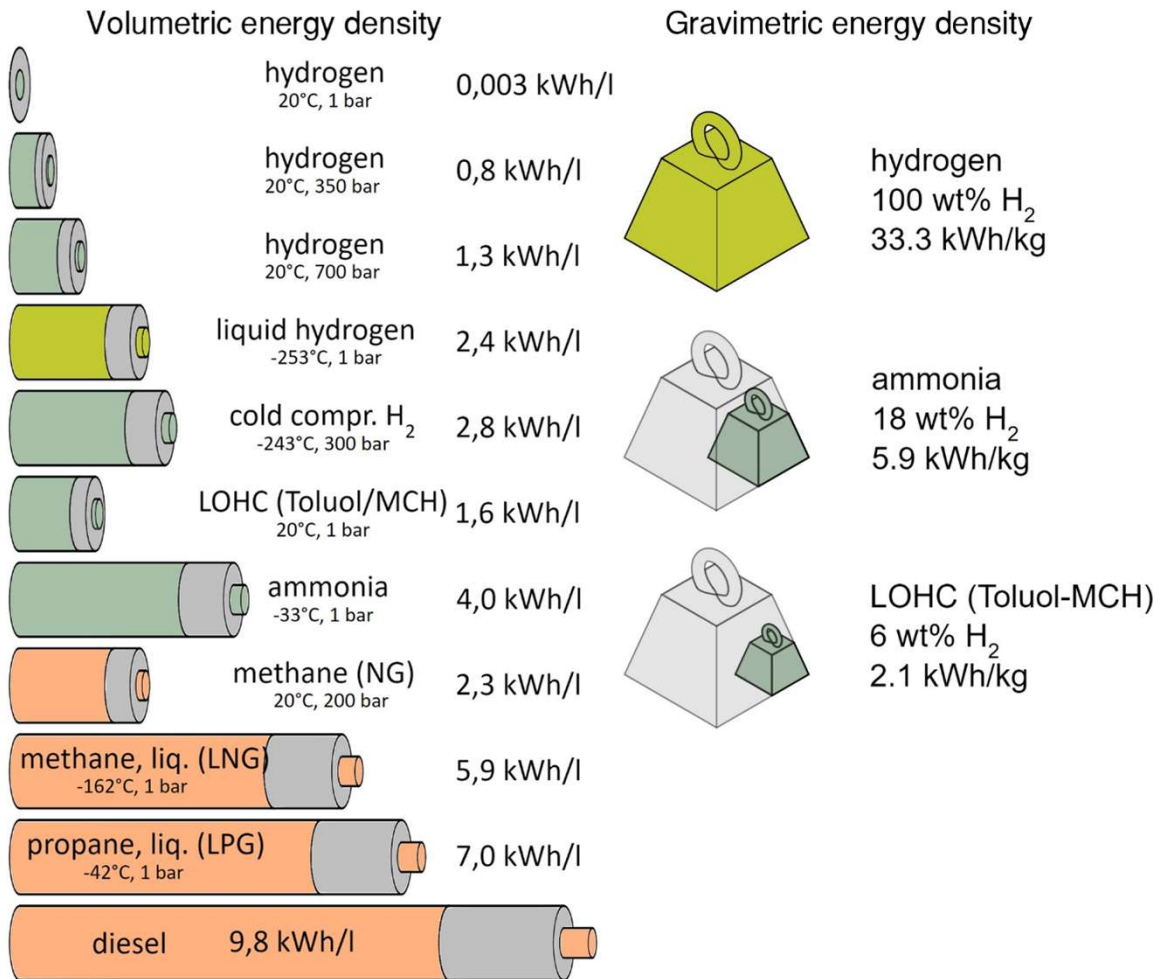


Figure 3.3: Energy densities of hydrogen-based energy carriers (green), in particular liquid hydrogen (light green) and of hydrocarbons (orange). Data sources 3,4,5

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4

Safety, materials and liquid hydrogen

Hydrogen safety

Hydrogen is not inherently more dangerous than other fuels, but it behaves differently in many respects. If it is handled professionally and its special properties are taken into account in the design and operation of corresponding systems, at least the same level of safety can be achieved with hydrogen technology. Safe handling of gaseous and liquid hydrogen is well-established in industrial environments. For cryogenic liquid hydrogen, the experience gained in space travel in particular is of great value. The use of LH₂ and liquid oxygen (LOX) as binary fuel for the rocket engines paved the way for the technical use of LH₂. To do this, LH₂ had to be safely produced, transported, stored and used in large volumes. However, these experiences are only partially transferable to new applications in non-industrial environments.

There are technological and safety advantages and disadvantages of using hydrogen in gaseous or liquid form for various applications, which can be inferred from the underlying physical properties.

Safety-related phenomena of compressed, gaseous and liquid hydrogen

Many safety-related properties are similar for compressed (cgH₂) and liquefied hydrogen.

Hydrogen is highly diffusible and can escape, for example via defective seals, and mix with air, forming highly flammable mixtures with a comparatively wide flammability range. However, the combustible cloud which forms after release or spillage of LH₂ is usually easy to see when the moisture in the ambient air condenses. Under normal conditions, the edge of the visible white cloud coincides with the lower flammability limit of 4 percent by volume of hydrogen in air. Due to its higher density (below 22 Kelvin, hydrogen is heavier than warm and dry ambient air) and the condensation of water vapour, the hydrogen released from the LH₂ reservoir experiences much lower buoyancy. It initially spreads along the ground. Within a comparatively short period of time, however, due to the further warming, the buoyancy forces become dominant and the visible, combustible cloud rises. The hydrogen-air mixture is then further diluted until it is no longer ignitable and no longer visible. This mixing process is partly driven by molecular diffusion forces, but essentially by turbulence in the ambient air.

The slightly different transport characteristics of cryogenic hydrogen play only a minor role in comparison to ambient-temperature hydrogen.

Hydrogen has the lowest minimum ignition energy (MIE), and it is to be expected that virtually any hydrogen released and mixed with air can be readily ignited. However, spontaneous ignition was never observed in any of over 500 experiments conducted by NASA in the 1980s, as part of the EU project PRESLHY 2017-2021. The ignition limits themselves and the temperature of hot surfaces necessary for ignition depend only slightly on the actual temperature of the premixed air-hydrogen mixtures. But overall, according to available databases, the low temperature of mixtures containing cryogenic hydrogen significantly reduces the tendency to ignite.

Due to the lack of carbon atoms, the kinetics of hydrogen-air combustion lead to a relatively rapid chemical reaction and flame propagation. Due to instabilities attributable to the low density, high diffusivity and low viscosity of hydrogen, hydrogen-air and hydrogen-oxygen flames have a strong tendency to accelerate. Lower temperatures reduce the laminar burning speed. However, as observed in the EU project PRESLHY, this is counterbalanced by the higher densities. The run-up to the transition to detonation is significantly shortened for cryogenic hydrogen. Overall, cryogenic and ambient-temperature hydrogen do not differ significantly with regard to the safety-critical characteristics of the combustion of premixed systems.

The radiant heat flow from hydrogen flames is much lower than

with hydrocarbons, due to the absence of carbon. Some materials, in particular high-strength steels, are susceptible to hydrogen embrittlement. Both effects are reduced for LH₂.

It is important to understand how the described safety properties of hydrogen are influenced by the technical form of storage, i.e. by the storage of hydrogen in compressed, gaseous or liquefied form.

Storage and unintentional release

The compressed hydrogen in a pressure vessel with a pressure of up to 100 MPa contains considerable mechanical energy, compared to the pressure of LH₂, which is stored in a cryostat at pressures typically below 1 MPa. In the immediate vicinity of a catastrophically failing pressure vessel, the pressure effect of the abruptly expanded gases outweighs that which can arise as a result of the combustion of the released gases. High-pressure releases, which sometimes carry small fragments of the fractured surface itself, can cause damage to other components or injure people.

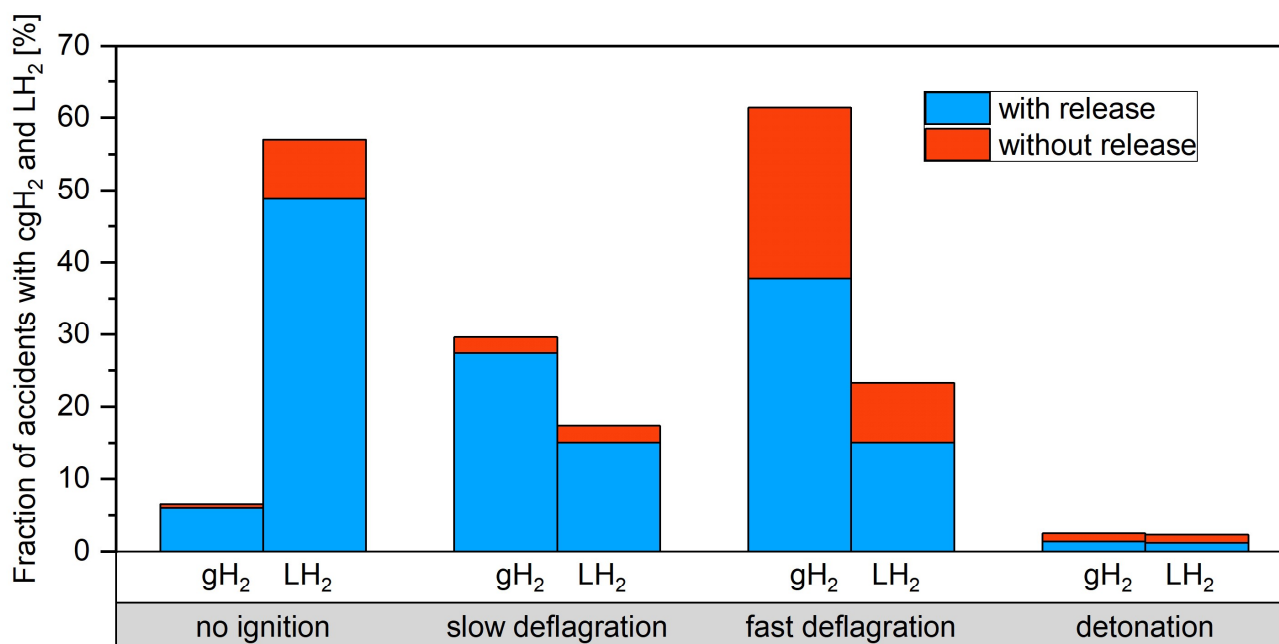


Figure 4.1: Proportion of incidents with gH₂ and LH₂. Own depiction based on data from ¹

The release of gases with high impulse leads to a strong recoil force on the pipeline or container.

These high impulse loads are expected in the event of a cryostat failure. However, particularly in the case of fire loads, the overheated LH₂ can spontaneously evaporate and ignite when the cryostat breaks open. This combination of a spontaneous phase transition, a steam explosion, and a chemical reaction (boiling liquid expanding vapour explosion, BLEVE) is known and feared from accidents with LPG. However, it is not yet clear whether BLEVEs are actually significant phenomena for LH₂, as the cryostat itself provides relatively good protection against overheating. However, rapid phase transitions (RPTs), which were observed, for example, when spilling LH₂ on water in the SH2IFT project, can be similarly high-energy. The explosive loads generated are considerable.

Both pressurized gas containers and cryostats must be protected against overpressure. In the first case, typically one or more thermal pressure relief devices (TPRD) are used; in the case of cryostats, a blow-off and safety valve as well as a burst protection membrane are used.

LH₂ is usually stored at moderate pressures well below the critical pressure of 1.3 MPa. However, the extremely low temperatures can render unsuitable materials brittle and lead to thermal stresses. If the cold surfaces are not carefully shielded, condensation of highly reactive oxygen or cryogenic burns can occur when people come into contact with these cold surfaces or accidentally released cryogenic hydrogen.

The higher density of the cryogenic liquid hydrogen means that the otherwise strong buoyancy forces acting on the warm hydrogen released into the atmosphere are absent at the initial stage of release. Up to 22 Kelvin, hydrogen is heavier than air at ambient temperature. Mixing with ambient air quickly leads to heating, on the one hand, and dilution on the other. The flammable gas mixture formed by the release of LH₂ into air can be detected by the visible cloud that forms when the released cryogenic hydrogen condenses the moisture in the ambient air. The flammable outer layer and the edge of the visible cloud match quite well.

Compared to cgH₂, LH₂ has a reduced risk potential, in particular with regard to compressive loads.

Research in the EU project PRES�HY has shown that the drop in concentration in impulse-dominated hydrogen streams at low temperatures follows the law of similarity, which is currently widespread in hydrogen safety technology.

During the combustion of cryogenic hydrogen-air mixtures, there are at least two competing effects. Compared to warm hydrogen, the density of cold hydrogen-air mixtures can be up to 4 times higher. This means that almost four times more chemical energy is available in the same volume. On the other hand, the low temperature slows down the flame propagation significantly, which leads to other instability phenomena in the flame front. This leads to somewhat more critical scenarios with liquid hydrogen in enclosed and obstructed spaces and the opposite for the scenarios with open spaces. This is also reflected in the statistics (see Figure 4.1) and was confirmed in the experiments carried out in the context of the PRES�HY project.

Phenomena such as BLEVEs or rapid phase transitions (RPT) observed in liquefied natural gas (LNG) and liquefied petroleum gas (LPG) have not yet been adequately studied for LH₂, as comparatively large amounts of LH₂ must be used, which involves relatively high costs for experiments and safety precautions. This would require the investment of financial and intellectual resources.

In the case of large-scale combustion, only a small difference in the size of the fireball, if any, is expected after the breakage of the hydrogen tank. The maximum size of the fireball scales with the stored mass at 1/3 potency and is probably largely independent of the storage state.

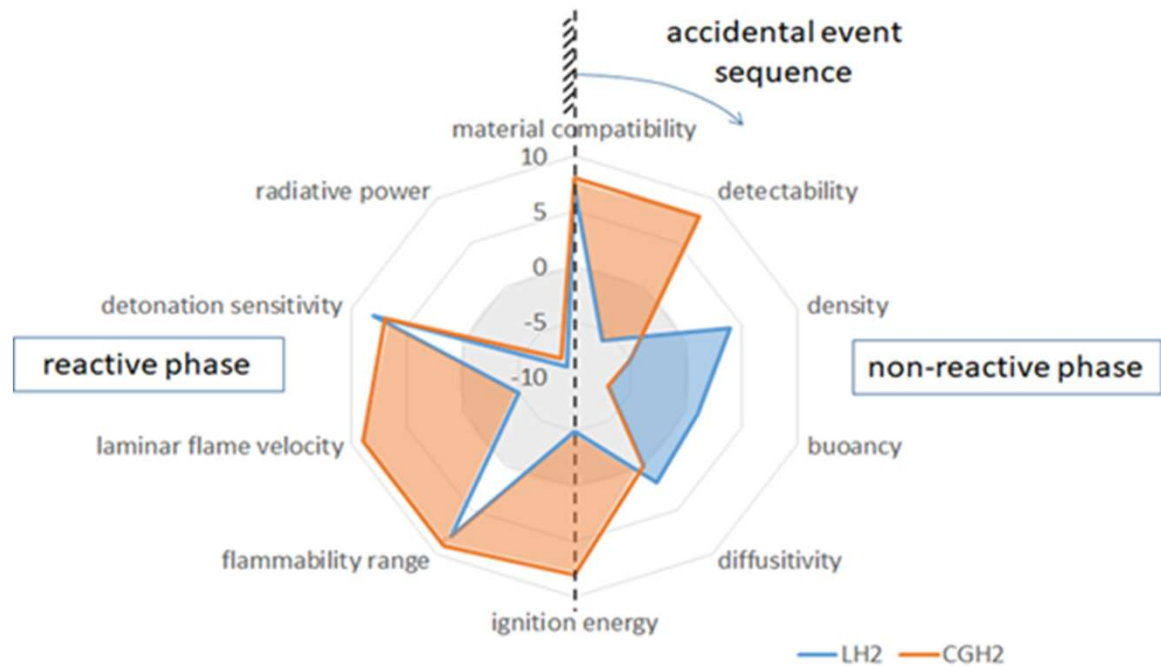


Figure 4.2: Comparison of the safety-critical properties of liquid hydrogen and compressed gaseous hydrogen along a prototypical accident sequence. Own depiction based on ²

The hazard distances for an ignited release from a pressure vessel or from a cryostat follow the same dimensionless flame length correlation that is already currently used by hydrogen safety engineers.

The direct comparison of LH₂ with compressed gaseous hydrogen shows some disadvantages, which in particular result from the greater spread of the hydrogen across the ground and the possible formation of oxygen-enriched zones. However, these disadvantages are compensated for the advantages resulting from the lower tendency to ignite and the generally slowed reactivity at the low temperatures. Figure 4.2 summarizes these findings in a property/hazard profile.

The safe use of hydrogen as an energy source requires a thorough understanding of the associated safety-critical phenomena, appropriate safety planning, monitoring of operating processes and overall safety management, as well as a generally proactive new safety culture for the use of hydrogen in the public sector.

In summary, the hazard potential of LH₂ is comparable to that of compressed gaseous hydrogen, with LH₂ showing slight advantages. However, with the knowledge of the different properties of gaseous

and liquid hydrogen and the basics of hydrogen safety technology, it is easy to develop a reliable hydrogen safety system that provides a similar if not better level of safety for people and the built environment.

Materials and LH₂

Before answering the question of which materials are suitable for use with LH₂, it is important to define both the operating conditions and possible extreme scenarios for use in the LH₂ environment: The components involved have to withstand complex loads in a wide temperature range between ambient temperature and cryogenic temperatures of 20 Kelvin and a pressure range of, for example, 0.1 to 1.3 MPa. Furthermore, if possible, there should be no negative impact from LH₂. These operating conditions ultimately dictate the various materials used in the manufacturing of the components, in order to ensure their safe, long-term use.

Avoid the negative influence of LH₂ on the material as much as possible.

In order to check the extent to which materials can be used in an LH₂ system, the following factors must be considered:

- I. Compatibility with hydrogen (with respect to hydrogen embrittlement, hydrogenation, bubble formation, porosity, permeation and diffusivity);
- II. Compatibility with the operating conditions (influences of temperature and pressure, e.g. on ductility, expansion/contraction, changes in properties);
- III. Failure behaviour (brittleness and ductility);
- IV. Compatibility with adjacent materials (properties to adapt to temperature and pressure changes, effects on shape and dimensions);
- V. Compatibility with the environment (e.g. a corrosive environment);
- VI. Manufacturing and processing possibilities (casting, rolling, bending, welding, additive manufacturing);
- VII. Cost-effectiveness and availability.³

The selection of a material for use is usually based on its mechanical and physical properties. The mechanical properties include, for example, the modulus of elasticity, tensile strength, impact resistance, ductility and notch sensitivity. Ideally, these properties should span the entire temperature range in a tolerable range according to the requirements.

In the high-temperature range, the materials should withstand, for example, a hydrogen fire in an emergency. For low-temperature application at 20 Kelvin, it is important to ensure that there is sufficient ductility. It is necessary to consider the physical properties, such as the different thermal contraction or conductivity of materials, in order to be able to compensate for them if required.

^{1,4}

Metal alloys are often used as structural materials in the low-temperature range. In this case, a stable structure is required, and changes in the structure, phase or crystal structure due to the load duration or the temperature cycles must be avoided. The crystal structure, for example, largely controls the low-temperature behavior of metallic materials. For example, alloys with a face-centered cubic crystal structure have high strengths with a small decrease in their ductility at cryogenic temperatures.

In addition to metallic alloys, fibre-reinforced composite materials and laminated structures are increasingly being used, which exhibit satisfactory behaviour in cryogenic operation.^{1,2}

Materials and their properties must therefore be carefully evaluated in order to find out how a hydrogen environment will influence them and to verify whether the requirements can be met or whether there are limits to their operation. It is advisable to look for materials in areas of related LH₂ technologies and cryo-technologies, such as medicine or space travel technology, which have already been successfully used for decades and are therefore suitably well developed. However, if data are incomplete or not available, it is advisable to use the existing expertise of cryo laboratories [e.g. CryoMaK⁵] and conduct experiments that replicate the corresponding operating scenarios. The further development and optimization of LH₂ technologies, e.g. by using even higher strength or lighter materials, is the subject of research, which is why the expertise should also be used to investigate and evaluate new materials for their LH₂ suitability.

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5

Liquefaction and storage

Hydrogen liquefaction

Minimum energy expenditure and influencing variables

The theoretical relationships are best illustrated in the following graph (Figure 5.1). Here the exergy is plotted against the temperature. The exergy represents the energy level of the hydrogen, in the respective thermodynamic state.

The exergy expenditure, or minimum energy expenditure is calculated according to the formula:

$$E_{min} = m \cdot [h_o - h_u - T_u(s_o - s_u)] = m \cdot (e_o - e_u)$$

with	E_{min} :	minimum (reversible) energy expenditure for change of state
	m :	hydrogen mass
	h_o, h_u :	specific enthalpy of hydrogen at the respective end or start temperature
	T_u :	ambient or start temperature
	s_o, s_u :	specific entropy of hydrogen at the respective end or start temperature
	e_o, e_u :	specific exergy value of the hydrogen at the respective end or start temperature

The derivation according to time then gives the corresponding minimum power requirement P_{min} for the liquefaction versus H_2 mass flow \dot{m} :

$$P_{min} = \dot{m} \cdot [h_o - h_u - T_u(s_o - s_u)] = \dot{m} \cdot (e_o - e_u)$$

The required enthalpy and entropy values can be found in corresponding tables of material values or, now routinely, from material data programs (the most known and established is REFPROP, published by NIST – National Institute of Standards and Technology, USA). These values correspond to the current accuracy standard, with deviations in the relevant section max. in the per mille range. The zero point of the exergy scale is set here (arbitrarily) to ambient conditions (300 K, 1 bar_{abs.}).

Influence of pressure and starting temperature

In Figure 5.1, the exergy values are plotted along individual isobars (1 ... 1000 bar_{abs.}). The two-phase region is also displayed. If, for example, hydrogen is isobarically cooled from a starting point of 1 bar_{absolute}/300 K, the liquefaction begins at 20 K / $e = 8$ MJ/kg, and the first drop of liquid phase condenses. The target point is usually complete liquefaction, more precisely the presence of almost exclusively para hydrogen in the liquid phase at approx. 1.05-1.2 bar_{absolute}.

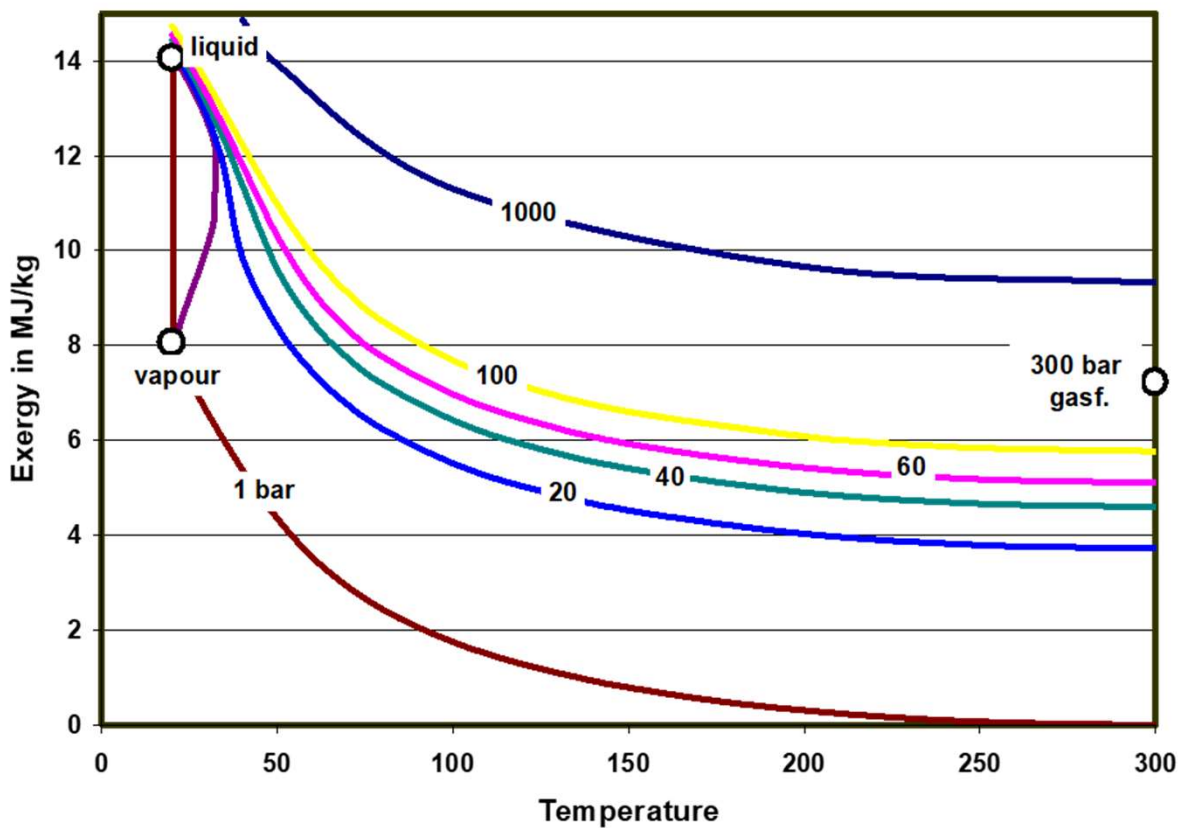


Figure 5.1: Minimum energy for the liquefaction of hydrogen, including o-p conversion (Created by: TU Dresden, H. Quack). The energy (exergy) state of the fluid is determined by pressure, temperature and aggregate state. Energy differences between different state parameters can be read directly on the vertical axis.

The minimum energy required for this is 14.2 MJ/kg. Converted, this is 0.279 kWh/l_{liq} or 11.8% of the calorific value of the given amount of hydrogen.

The graphic display makes the following points clear:

- Any variation in the starting temperature has virtually no influence. The reason for this is ultimately the Carnot factor: Only at very low temperatures does the cooling effort become very large and "expensive". It therefore makes very little difference whether the feed gas stream is supplied, for example, at 15°C, at 20°C or pre-cooled to 5°C. Even pre-cooling to 77 K using LN₂ brings certain process advantages, but only a limited effect with regard to the theoretical minimum energy expenditure.
- Omitting the o-p conversion would noticeably simplify the process. This is due to the fact that the necessary additional expenditure associated with the exothermic reaction is incurred particularly at low temperatures. However, the product n-LH₂ is difficult to use and barely marketable.
- In fact, significant energy savings are made when starting with

a higher input pressure:

- < 25% at an input pressure of 20 bar_{absolute} instead of 1 bar_{absolute}
- approx. 33% at input pressure 40 bar_{absolute} instead of 1 bar_{absolute}

Further advantages include more compact, smaller heat exchangers corresponding to the higher gas density, and thus smaller and cheaper liquefier cold boxes. However, all affected components must also be designed to be appropriately pressure-resistant, and any upstream compression costs must be considered in the overall assessment.

Therefore, an increased input pressure is usually the standard (e.g. 24 bar H₂ feed gas pressure).

Ortho-para ratio

During liquefaction, the two nuclear spin allotropes of hydrogen, ortho- or para-configuration, must be considered. At falling temperatures, such as in cooling and liquefaction, the equilibrium increasingly shifts in the direction of para-hydrogen, see Figure 5.2. The o-p conversion is a strongly exothermic process, especially at low temperatures.

The ortho-para (o-p) conversion is also included in the theoretical values shown above, i.e. the exergy values refer throughout to e-H₂, i.e. to hydrogen in the respective temperature-dependent o-p equilibrium. This means:

- Start with normal hydrogen (n-H₂), consisting of 75% o-H₂ and 25% p-H₂. This is the distribution present at ambient temperature and above, as well as after all relevant production methods;
- Cooling and liquefaction ideally take place precisely along the o-p equilibrium line, i.e. at each temperature level the associated o-p equilibrium ratio is present at the same time;
- at 20 K, hydrogen is finally present in liquid form with a p-proportion of 99.8%.

In the case of real liquefiers, catalyst material is used for this purpose. The current industry standard is iron oxide (Fe₂O₃), present or packaged as highly porous granules. Option a) is to place this between the individual heat exchangers in separate containers. This option can be found in liquefiers of an older design, as well as in modern liquefiers with a particularly large capacity. One disadvantage is that the re-adjustment of the o-p ratio then occurs in jumps, with the hydrogen being reheated by 5-10 K each time due to the exothermic reaction. Possibility b) is to fill this catalyst granulate directly into the respective flow channel of the heat exchanger. Scaling, effective dwell time and pressure losses must be

precisely calculated here. The hydrogen mass flow is then cooled continuously and always close to the e-line (for example, approximately to equivalent 2 K in order to keep required amounts of catalyst and pressure losses within limits). This form of conversion, continuously following the temperature, is thermodynamically more favorable, since the exothermically released heat can thus always be passed onto to the cooling unit at the appropriate temperature level and can therefore be "processed" on average with a more beneficial Carnot factor.

Losses due to the temperature jumps and mixtures mentioned are also eliminated. Modern liquefiers are also more efficient for this reason. The disadvantage here is that the large heat exchangers which already determine the coldbox volume again increase in the required structural size, as the granulate-filled fluid channels have to be made correspondingly larger for tolerable flow rates. According to current industry standards, the product LH₂ must have a para-content of at least 98% at the time of dispensing.

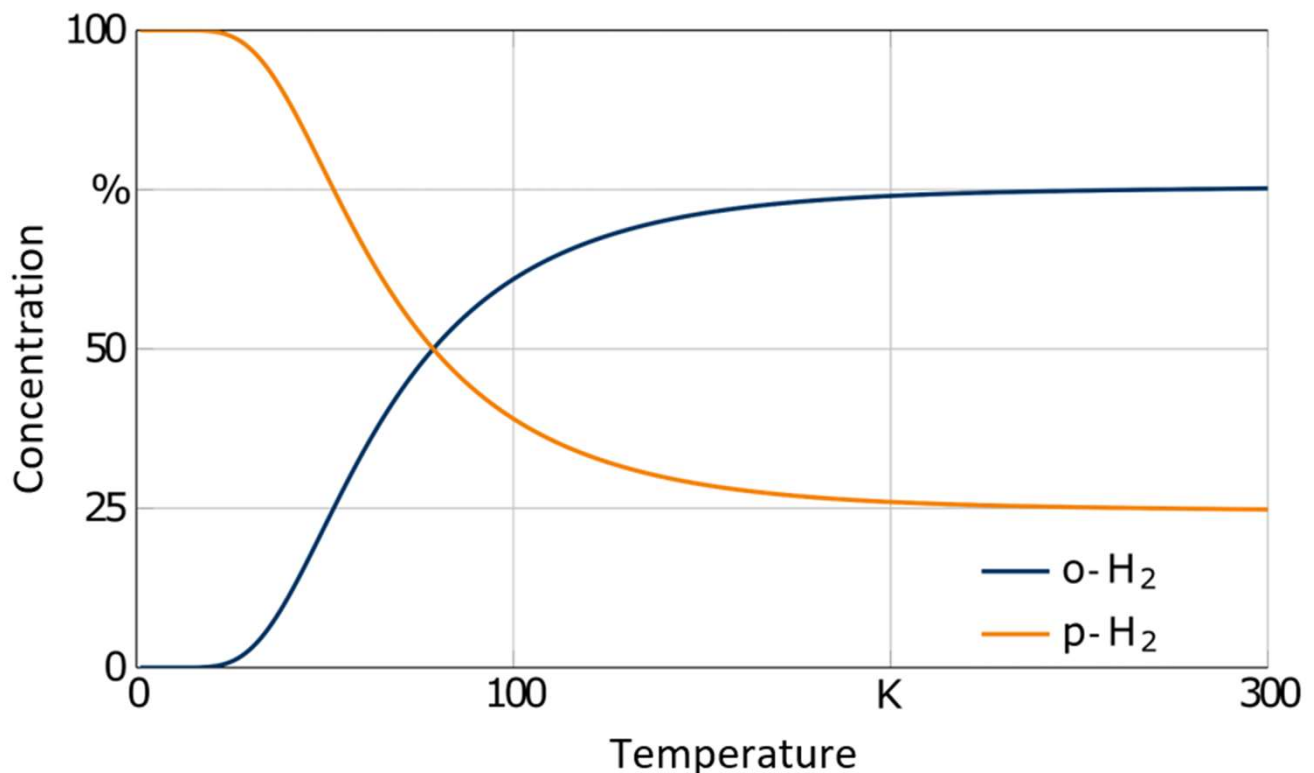


Figure 5.2: Equilibrium concentration of the H₂ allotropes.

Examples of hydrogen liquefiers

Current liquefiers worldwide

Known plants are listed in Table 5.1 below. The data comes from different sources^{1,2,3} and is sometimes slightly inconsistent. Different capacity specifications are additionally noted in brackets. In addition, US data are often likely to refer not to "metric" but to "short tons" (1 short ton = 2000 pounds ≈ 907.2 kg) – implying a 10.25% higher tpd value; as this is generally not specified, we rely on cross-comparisons here.

The list is not exhaustive. There are also some smaller plants, e.g.

- BLC, China, YOC 2007 and 2012, 1 tpd each
- Hainan, China, YOC 2011 (2.55 tpd),
- Xichang, China, YOC 2011 (1 tpd).

In addition, there are a number of small laboratory and test plants with liquefier capacities of 14-40 l_{LH₂}/h ≈ 1-3 kg_{H₂}/h.

In addition to the plants marked with *, some of the other old plants listed might no longer be in operation.

Table 5.1: Hydrogen liquefaction plants worldwide (tpd: tonnes or tons per day).

Location	Plant manufacturer	Capacity	Year of construction
Painsville, OH / USA	Air Products	3 tpd	1957 *
West Palm Beach, FL /USA	Air Products	3.2 tpd	1957 *
	Air Products	27 tpd	1959 *
Long Beach, CA / USA	Air Products	30 tpd	1958
Mississippi (Test Facility)	Air Products	> 36 tpd	1960 *
Ontario, CA / USA	Linde	20 tpd	1962 *
Sacramento, CA / USA	Air Products	(54) 60 tpd	1966 *
		6 tpd	1986
New Orleans, LA / USA	Air Products	34 tpd	1977 (1963)
	Air Products	34 tpd	1978
Niagara Falls, NY / USA	Linde	30 tpd	1981
Pace, FL / USA	Air Products	30 tpd	1994 *
Mcintosh, AL / USA	Linde	30 tpd	1995
East Chicago, IN / USA	Linde	30 tpd	1997
Sarnia, Ontario / Canada	Air Products	30 tpd	1982
Montreal, Canada	Air Liquide Canada Inc.	10 tpd	1986
Bécancour, Quebec /Canada	Air Liquide	12 tpd	1988
Magog, Quebec /Canada		15 tpd	1989
Kourou, French Guyana	Air Liquide	5 tpd	1990
Lille (Wazier), France	Air Liquide	10.5 tpd	1985
Rozenburg, Netherlands	Air Products	5 tpd	1986
La Porte, TX / USA	Linde	35 tpd	2020
Leuna, Germany	Linde	5 tpd	2008
	Linde	5 tpd	2021
Dresden, Germany	TU Dresden	10 l/h	2004
Baikonur, Kazakhstan Plesetsk, Russia	Cryogenmash	4 – 17 tpd	~1960
Amagashi, Japan	Iwatani	1.2 tpd	1978 *
Tashiro, Japan	Mitsubishi Heavy Industries	0.6 tpd	1984 *
Ooita, Japan	Pacific Hydrogen Co., Jpn.	1.4 tpd	1986
Tane-Ga-Shima, Japan	Jpn Liquid Hydrogen	1.4 tpd	1986
Minamitane, Japan	Jpn Liquid Hydrogen	2.2 tpd	1987
Kimitsu, Japan	Nippon Steel Corporation (Air Products?)	0.2 (0.3?) tpd	2004
Sakai, Japan	Iwatani Gas	1.1 tpd	2006
Osaka, Japan	Iwatani (Hydro Edge)	11.3 tpd	2006
Chiba (Tokyo), Japan	Iwatani (built by Linde)	10 (5?) tpd	2008
Yamaguchi (Shunan), Western Japan	Iwatani (built by Linde)	5 tpd	2008
Khi Akashi, Japan	In-house development by Kawasaki Heavy Industries	(5 tpd prototype plant)	2015
India	Asiatic Oxygen	1.2 tpd	n/a
Mahendragiri, India	ISRO	0.3 tpd	1992 no longer in operation
Beijing, China	CALT	0.6 tpd	1995

Substantial expansion of global liquefier capacities is planned by 2025.

A rapid expansion of this liquefier capacity is currently ongoing. Four or five other large industrial liquefiers are already under construction in the USA (10 - 32 tpd). A smaller liquefier (0.25 tpd) is already in operation in Port of Hastings, Australia. The commissioning of a 30 tpd liquefier in Southeast China was announced for 2022, and a 5 tpd liquefier in Doosan, South Korea for 2023. Further liquefiers with 30 tpd each are to be constructed in South Korea in 2023.

According to plant commissions already contractually agreed, in 2022-2025 alone a total of at least 135 tpd will be added to the liquefier capacity in the USA, and 120 tpd in the Far East. This represents an increase of 46% in North America and 360% in the Far East.⁴

Small plants

This class includes liquefiers with a performance class of typically $600 \text{ l}_{\text{LH}_2}/\text{h} = 1 \text{ tpd}$ up to a maximum of approx. $2000 \text{ l}_{\text{LH}_2}/\text{h}$ (3.4 tpd). Areas of application or operators are demonstration facilities, research centres or industrial users, if

- only moderate amounts of LH_2 are required,
- the liquefiers may be operated only in phases, and
- when low investment costs are more important than high efficiency.

Typically, a cooling circuit is used with helium as the refrigerant and with oil-lubricated screw compressors as a circuit (drive) compressor.

This allows the use of comparatively simple and well-established technology, along with reduced safety requirements. An H_2 input pressure (feed pressure) of 10-25 bar is used. The specific energy requirement of these small liquefiers is comparatively high:

- specific energy requirements (excluding LN_2 and compression feed):

$$8.05\text{-}9.5 \text{ kWh/kg}_{\text{LH}_2} = 29\text{-}34 \text{ MJ/kg}$$

- specific energy requirements (including LN_2 and compression feed):

$$12.3\text{-}13.4 \text{ kWh/kg}_{\text{LH}_3} = 44\text{-}48 \text{ MJ/kg}$$

- Overall characteristics:

low capital expenditure; high operating expenses

These small-scale H_2 plants are basically modified helium refrigeration plants: Cooling circuit including circuit compressor, medium pressure accumulator, expansion turbines and Brayton circuit within the coldbox work exclusively with helium as the refrigerant. There is only one further channel within the counterflow heat exchangers used, in which the H_2 feed gas flow is cooled and ultimately condensed – a concept that is well-suited for small plants, since it significantly reduces the safety requirements. Circuit compressor, cooling system components and piping are exposed exclusively to inert helium gas and are therefore not subject to any safety requirements or restrictions for combustible gases. Commercially available helium components can be used, the compressor chamber and affected building areas are not subject to ATEX regulations or the like. The components carrying hydrogen are kept to a minimum. This significantly simplifies the design, requirements, commissioning and subsequent maintenance; the plant and building can be produced at significantly lower cost. Figure 5.4 shows this type of liquefier.

In general, small H_2 liquefiers with LN_2 pre-cooling are used. An LN_2 tank, transfer pipe and removal of gaseous N_2 must therefore also be available (which, for example, means a major additional challenge for maritime applications currently being discussed – in this case for a desired re-liquefaction of H_2 exhaust vapour losses on tanker vessels). Calculations should be based on an LN_2 requirement of typically approximately $0.4 \text{ l}_{\text{LN}_2}/\text{l}_{\text{LH}_2}$.

In addition to "straight operation", LN_2 pre-cooling is also of particular importance when cooling the plant.



Figure 5.3: HYLIAL liquefier coldbox (source: Air Liquide⁵).

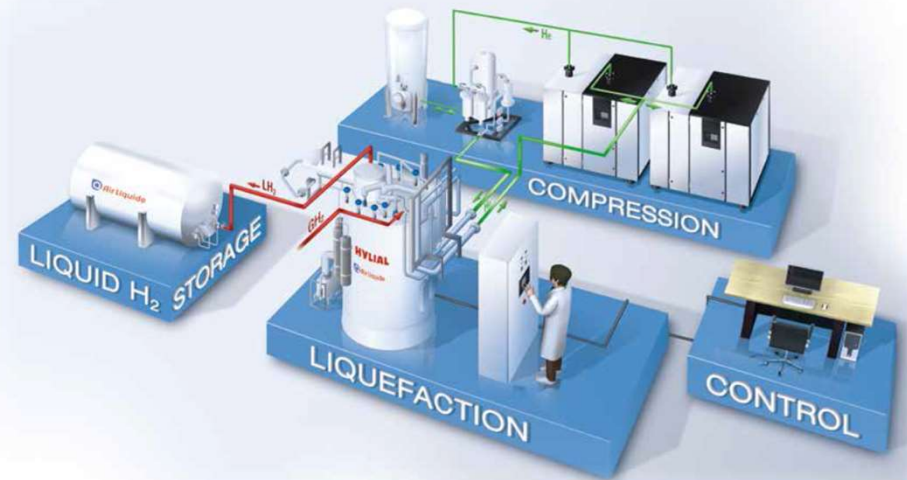


Figure 5.4: Design of H₂ liquefier layout, HYLIAL series (source: Air Liquide⁵).

Here, the full cooling capacity is available virtually from the first moment, while the Brayton circuit still operates far away from the respective nominal operating points and therefore very ineffectively. Due to the pre-cooling of the LN₂, the cooling time is significantly reduced. This applies to H₂ plants of all sizes. The reason lies, in particular, in the temperature-dependence of the heat capacity (debye temperature): More than 95% of the amount of heat to be extracted must be processed in the range between 300 K – 80 K.

Figure 5.3 illustrates one of the Air Liquide company's liquefiers of this size from the HYLIAL series. Figure 5.4 shows a schematic representation of this type of overall arrangement (a required LN₂ stand tank is not shown).

According to known figures, there is a specific energy requirement of 16.7 kWh/kg_{LH₂} for a HYLIAL 1500 condenser (capacity 1500 l_{LH₂}/h = 2.55 tpd). This figure consists of the electric drive output, plus the typical energy cost equivalent of LN₂ pre-cooling. This corresponds to 60.1 MJ/kg, equating to over half of the hydrogen's corresponding calorific value ($H_u = 119.95$ MJ/kg). Large liquefiers work with less than half of this quantity-specific energy requirement.

The figures refer in each case only to the stationary liquefaction operation at the design point, i.e. excluding cooling times, transient states, etc.

Industrial liquefiers: Example of Leuna system

These are understood to be plants with a capacity of 5-35 tpd, as are commonly operated in industry, in accordance with Table 5.1. An example of this is the Linde plant in Leuna.

The structure and flow chart are shown in Figure 5.5.

Basic data:

- two-stage compression (dry-running piston compressor, isothermal efficiency 65-70%; adjustable pre-compressor)
- 3 expansion turbines (oil-mounted), isentropic efficiency > 85%; first expansion stage alternatively switchable to dynamically gas-mounted turbine.
- cold ejector for withdrawing flash gas from the Dewar storage tanks.
- Feed input pressure: 24 bar; LH₂ discharge pressure: 1.3 bar
- Horizontal LH₂ storage tanks (2 x 250 m³ internal volume).

A specific energy requirement is stated for this liquefier (including an "LN₂ penalty" of 0.4 kWh/l_{LH₂}) of 11.9 kWh/kg_{LH₂} = 42.8 MJ/kg. This corresponds to 35.7% of H_u or almost exactly three times the theoretical minimum value stated above.

The specific energy requirement could be improved to 10 kWh/kg_{LH₂} = 36 MJ/kg $\approx 0.30 H_u$.

The cooling time for a plant of this type is typically about 3-5 days (with the plant conditioned and flushed ready for operation, and with the storage tank already or still LH₂-cold).

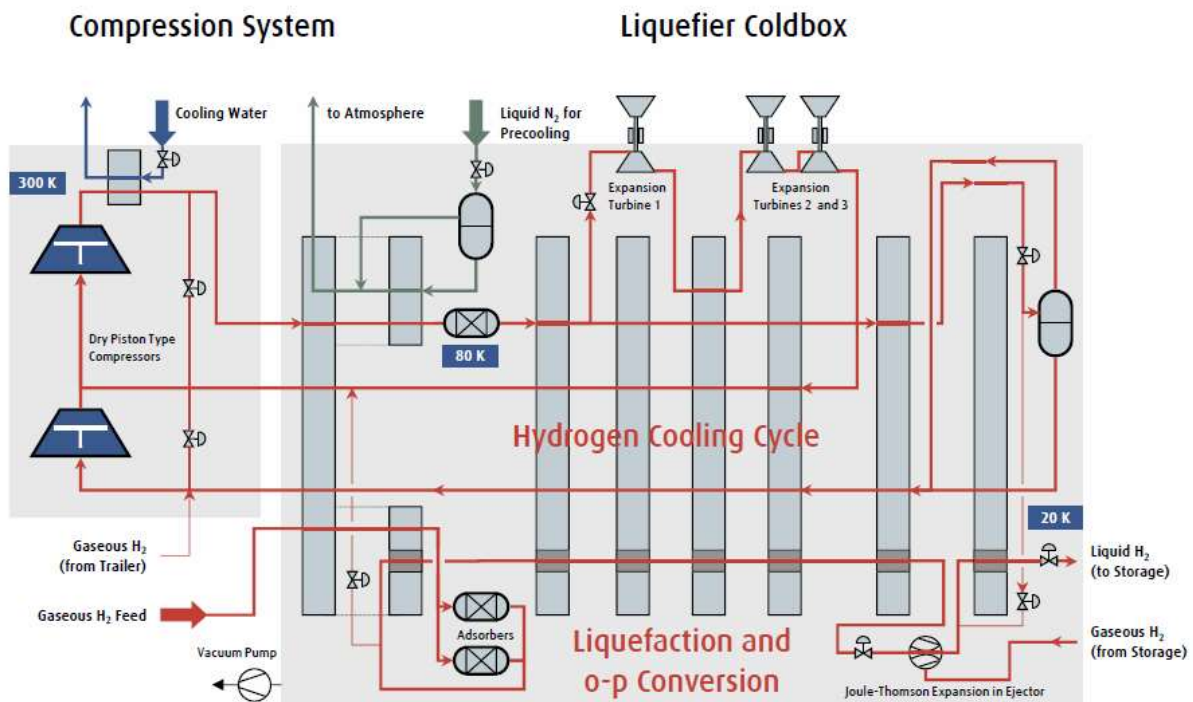


Figure 5.5: Flow chart of Leuna H₂ liquefier in a simplified form. Source: Linde 6

A regular, controlled shutdown of the system takes approx. half a day. Consequently, where possible, liquefiers of this type are run only in continuous operation, ideally at the best efficiency point. Peak shaving, running for a brief period, for example during times of excess electricity and temporary hydrogen provision, is very uneconomical (especially since almost the full drive and pre-cooling power is demanded during the cooling phase).

Large-scale hydrogen liquefaction plant designs (50-200 tpd)

Designs for future large-scale plants in the range of 50-200 tpd are planned. Here, the main focus would be on operating costs, i.e. on the realization of highly efficient circuits and components. Careful studies have been carried out with regard to new plant designs and the expected efficiencies.⁷

A specific energy consumption of 6.4 kWh/kg (or 6.76 kWh/kg incl. ancillary units), corresponding to 19-20% of H_{LH_2} , appears to be feasible. Liquefaction costs of (only) €1.72/kg_{LH₂} were calculated (as of 2013, based on a 50 tpd plant; this includes annuity/depreciation, maintenance costs, costs for electricity and LN₂, as well as costs for cooling water and gas losses). According to current experience, the liquefaction costs are likely to decrease further with increasing plant size, with an approximate scaling factor of (liquefier capacity)^{2/3}.

In the case of larger plants, a partial load capacity of 70-100% is achieved without additional outlay in terms of equipment and control technology. An even broader load range (50-110%) can be acquired by means of additional outlay in terms of equipment and control technology. In addition, certain efficiency losses in low partial load operation cannot be avoided.

Stationary storage

The technology for storing liquid hydrogen is highly developed. Mainly cylindrical and spherical containers are used. Flat bottom tanks, which are commonly used for large amounts of liquid natural gas, liquid nitrogen and liquid oxygen in the gas industry, do not exist yet.

Spherical containers

Spherical Dewar tanks with a volume of approximately 1000 m³ are typically used in larger liquefaction plants.

The largest existing liquid hydrogen storage tanks of this type are located at the space stations for the provision of LH₂ as rocket fuel. The largest two were installed on launchpads A and B at the Kennedy Space Center in 1965. The two identical tanks each have an internal volume of 3500 m³. For insulation, the space between the inner and outer tanks is filled with perlite and evacuated to between 130 mbar and 270 mbar. Remarkably, no degradation in the quality of the insulation was observed over 30 years of operation. The evaporation rate is stated in various sources ranging from 0.075 % per day to 0.18 % per day.⁸

Table 5.2: Typical evaporation rates in stationary liquid hydrogen tanks

Storage tank volumes	Boil-off rate per day
500 m ³	0.18% ¹¹
3500 m ³	0.07%
20,000 m ³	< 0.03% ¹²

The latest installation is located in Japan. It is a spherical tank with an internal volume of 540 m³. As with the previously mentioned tanks at the Kennedy Space Center, the insulation is made up of the combination of perlite and vacuum. The evaporation rate is stated as 0.18% per day.⁹

The main technology provider is the US company CB&I. Recently, a design for a 40,000 m³ tank was presented by CB&I. This size is considered as already available now. A study investigating 100,000 m³ spheres is also being conducted by CB&I between 2021-2023.¹⁰

The relative evaporation rate scales very strongly with the tank size. This is simply because the tank contents are cubic, the tank surface and thus a large part of the heat input scales quadratically with the dimensions. Table 5.2 lists the evaporation rates of typical storage container sizes.

Cylindrical tanks

In smaller liquefaction plants, as well as in the case of liquid hydrogen consumers, cylindrical Dewar tanks with a volume of up to 500 m³ are typically used. Large tanks are usually horizontal, smaller ones vertical for better use of space. These tanks are usually super-insulated (multilayer insulation with a high vacuum).

Tank systems with an integrated re-liquidation system (zero boil-off tanks)

The large tank systems are usually located at the sites of the hydrogen liquefiers. The evaporating hydrogen gas is recondensed there as standard via the liquefiers.

The large "stand-alone" liquid hydrogen tank systems (without liquefiers) can actually only be found at space stations, as large volumes of liquid hydrogen were used in space travel in the past and are still sometimes used today. The most modern commercial rockets such as "Falcon" and "Launcher One" do not use hydrogen as fuel, but the "New Shepard" rocket and the older heavy rockets such as "Ariane" and "Delta" are designed to use liquid hydrogen as fuel. In the future, similar "stand-alone" liquid hydrogen tank systems could be created at LH₂ import terminals. Based on NASA's assessment, there is a 50% loss during the transport and storage phase from the liquefier to the hydrogen utilized on the spacecraft. These volumes are mainly a result of longer storage times between individual launches.

To minimize these losses, NASA is working on storage tanks with an internal volume of 5300 m³, as well as on its own cooling system to compensate for the inevitable heat leak. Studies on this topic have been published since 1970, under the working title "zero boil-off". Recently, Fesmire et al.¹³ presented experimental results of a zero-boil-off storage tank (Ground Operations and Demonstration Unit for Liquid Hydrogen GODU LH₂).

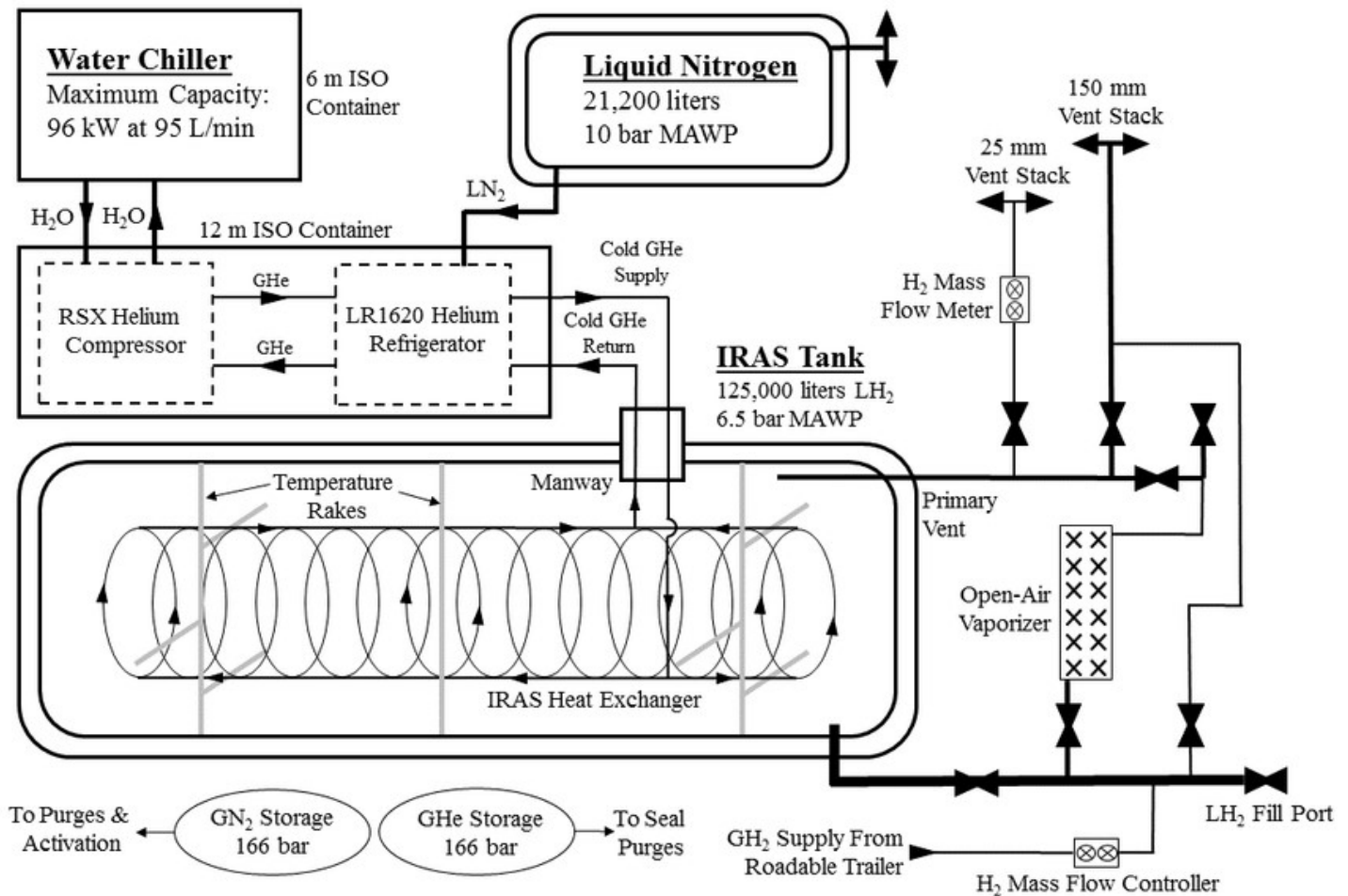


Figure 5.6: Cylindrical LH₂ tanks at the hydrogen liquefier in Leuna, Germany. Source: Linde

Figure 5.7: Photo of the LH₂ tank converted to a zero boil-off tank. Source: ¹³

Here, an integrated heat exchanger was developed and tested for a horizontal cylindrical LH₂ storage tank (internal volume 125 m³, heat input approx. 300 W). A separate cooling system provides a cooling capacity of up to 880 W at 20 K. In addition to compensating for the undesired heat input, the cooling system can be used to supercool the stored hydrogen down to 15 K. This achieves a density increase from 66.4 g/l to 76.2 g/l. The installation has received a highly positive economic evaluation.

In a statement from NASA, the ratio of energy costs to provide the necessary cooling capacity for hydrogen savings is stated at 1:5 (\$1 saving of LH₂ per \$0.2 energy costs).¹⁴ Further details can be found in the publication by W.U. Notardonato et al.¹⁵ Among other things, the study demonstrated zero-loss transfer activities, specifically, any loss of flash gas during the overfilling processes could be avoided.

Figure 5.8: IRAS tank USA, flow chart of the tank with internal cooling lines and re-cooling system. Source: ¹⁶

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6

Hydrogen transport options

A number of different factors form the basis of the global hydrogen economy: The spatial distribution of the demand and production regions with regard to renewable energy, the geographical conditions of the production regions for hydrogen production, as well as the political and economic conditions in the respective regions. Numerous individual constellations are derived from this, which have a direct effect on the choice of the transport system. Germany has already established partnerships or supply agreements for hydrogen imports with European countries such as Norway¹, as well as with non-European states or confederations such as Australia, New Zealand, Canada, and West and South Africa.²

This white paper focuses on the transportation of liquid hydrogen, compares and categorizes alternative transportation methods, and examines their respective interfaces. On the basis of the transported volume and distance between liquid hydrogen production and use, the following transport categories emerge, which are considered below:

- Intercontinental maritime transport
- European international transport
- Regional transport / distribution

Furthermore, different means of transport can be distinguished, for example ocean-going ship transport, rail, barge or truck transport, as well as pipelines.

Intercontinental maritime transport

In the intercontinental transport of hydrogen and hydrogen derivatives, distances of between 4,000 km (Morocco) and 15,000 km (Australia) must be covered by sea, meaning the selection of H₂ transport system is primarily based on the storage density and the specific transport costs.

When comparing the three CO₂-free liquid hydrogen carriers often discussed for ship transport, ammonia (NH₃), liquid organic hydrogen carrier (LOHC) and liquid hydrogen (LH₂), LH₂ has the highest gravimetric energy density and the second highest volumetric energy density, as explained in Chapter 3.3 and Figure 3.3.

Also in a comparison of the costs to be incurred in the overall chain from H₂ production to H₂ utilization, of the three options, LH₂ has some advantages³, while no significant cost advantage for any specific transportation form has been observed in various studies.

Finally, it is worth noting that for LH₂ only, the energy expenditure for liquefaction occurs exclusively at the place of generation, i.e. where renewable energy is available in large quantities and also at low cost. The separation of H₂ from the other two hydrogen transport options requires additional energy at the destination and reduces the amount of energy supplied with hydrogen accordingly, if this has to be obtained from the transported hydrogen.

"Hydrogen Energy Supply Chain" demonstrates LH₂ intercontinental transports.

This must be taken into account when considering the transport costs if it is intended to be used as H₂ and not, for example, directly as ammonia.

The intercontinental transport of large volumes of hydrogen can be carried out on the basis of LH₂. Accordingly, the composition of logistical structures between and in the H₂ recipient countries is based on the delivery of LH₂.

A recent example is the pilot project "Hydrogen Energy Supply Chain"⁴. HESC, from Japan, investigating and testing the supply of energy to Japan by means of liquid hydrogen imports from Australia. The hydrogen will be extracted from lignite in Australia, liquefied and transported to Japan by ship. Both the transport vessel itself and the loading and unloading infrastructure were developed between 2019 and 2021. The first liquid hydrogen delivery from Port of Hastings in Australia to Kobe in Japan was successfully demonstrated in 2022. This demo project marks the first phase of development, led by Kawasaki Heavy Industries (KHI). The pilot project initially involved a ship with two 1250m³ tanks, but for technical reasons, only one tank was installed in the 'SUISO Frontier'. The insulation design, featuring multilayer insulation in a high vacuum, is intended to maintain an evaporation rate of 0.2% per day. The ship was propelled with conventional fuels. An LH₂ tanker with 160,000 m³ capacity has been announced as the next step⁵, also insulated with high vacuum MLI, in order to achieve an evaporation rate of 0.2% per day. With an initial filling of 95% and a hydrogen density of 70 g/l, the liquid hydrogen inventory amounts to 10,640 tonnes. This results in 21.3 tons of hydrogen evaporation loss per day. During unloading, a sufficient amount of residual LH₂ is retained to maintain the tanks' temperature until they are refilled.

European international transport

Similar to the existing natural gas network, the transnational transport of hydrogen is based on the respective geographical conditions and distances. Thus, the long-term goal is to have a H₂ pipeline network for gaseous hydrogen on land, which is geared to the expected hydrogen requirements.⁶ Until this development target is reached, LH₂ transport by road, rail or inland waterways will again play the role of a "missing link" to cover the corresponding hydrogen requirements of consumers not (yet) connected to an H₂ gas network. In addition, liquid hydrogen transported by ocean-going ship (like with LNG and the natural gas network) can be regasified and fed into the European gH₂ pipeline network, whereby the valuable "low-temperature cold" of the LH₂ should be used sensibly, as is explained in more detail for mobile applications in Chapter 8. Transporting liquid hydrogen through pipelines requires substantial and consistent demand to justify the energy required for pipeline cooling, but would offer synergies in the coupling with electrical transmission networks, as outlined in Chapter 9.

Regional transport and distribution

First and foremost, the locations of hydrogen production and demand as well as the type of use are decisive for the question of how the future hydrogen transport network is to be designed.

Section 6.1 has already mentioned that some of the hydrogen will be imported from other European or non-European countries. In addition, hydrogen can be produced domestically, where the utilization of the electrolyzers would be greatest, in order to lead to favourable H₂ production. Transporting hydrogen through gas pipelines is usually the most cost-effective transport option; especially if existing natural gas pipelines can be re-purposed.

Wind energy at sea in northern Germany has the highest hours of full use of all renewable energy installations. Even if wind energy on the coast delivers lower full-load hours in comparison, H₂ production from onshore wind energy can also make sense, as shown by the Federal Government's long-term scenarios.⁷

On the application side, Busch et al. (2021) considered the supply of liquid hydrogen to German airports by trucks, trains and barges from a techno-economic perspective, and identified LH₂ supply by rail transport as the most cost-effective option.⁸

Reuß et al. (2021) investigated the costs of transporting hydrogen (carriers) by road to supply a hydrogen filling station network for the reference year 2050. They conclude that among the options considered, LOHC, gH_2 and LH_2 , for distances of 130 km or larger, road transport in liquid form is the most favourable and this increases almost linearly with the transport distance.⁹

LH_2 trailer

The volumetric energy density of liquid hydrogen is significantly higher than that of gaseous hydrogen (cf. Figure 3.3). Economic considerations show that for transport routes exceeding 200 km and delivery quantities surpassing one ton, the supply of liquefied hydrogen is more cost-effective.

In contrast to the transport of conventional fuels such as gasoline or diesel, the transport capacity for liquid hydrogen on the road is determined by volume, not weight. Liquid hydrogen trailers (see Fig. 6.1) typically have a nominal capacity of 2500 to 4000 kg, the largest with a storage volume of 65-70 m³. Typical working pressures are between 1 bar(a) and 4 bar(a)¹⁰, in some cases even up to 12.75 bar(a). The well-known manufacturers are:

- Linde
- Chart
- Gardner Cryogenics (part of Air Products)
- Schwingenschlögel GmbH
- MAN Cryo

Superinsulation (multilayer insulation in a high vacuum) is typically used for thermal insulation of the storage tank. In some cases, a combination of multilayer insulation and LN_2 shield cooling is also installed.

The unavoidable residual heat input results in a slow build-up of

pressure. The tank is designed to be pressure-resistant to avoid H_2 blow-offs. In the United States, the Department of Transportation has regulations that prohibit the blow-off of hydrogen on the road during transportation. The maximum permitted pressure in the trailer on the road depends on the fill level: a full trailer can only drive with a small overpressure, a half-full one with maximum pressure.

Unlike large stationary LNG tanks, stratification effects are virtually absent in road transport. According to Verfondern¹¹, the fluid movement ensures sufficient mixing, provided the vehicle is in motion. The price of an LH_2 trailer is quoted in Reuss et al.¹² as €860,000 per trailer in 2017 (for comparison: a high-pressure trailer was then in the range of €550,000, pressure level 250 bar for 670 kg hydrogen). In the meantime prices have become significantly higher, by a factor of 1.5-2.

The photo in Figure 6.2 shows the delivery of liquid hydrogen. The transfer losses consist of four components:

1. the displaced cold gas in the receiver dewar (replaced gas),
2. the evaporation losses during initial cooling of the transfer line and fittings
3. the evaporation losses due to heat input into the transfer system due to imperfect thermal insulation
4. as well as flash gas when the liquid is expanded from the higher to the lower pressure (since it is usually transferred by means of pressure difference).



Distribution

Efficient transit from source to service

Our hydrogen containers form the next link in the distribution chain. We offer containers exclusively for hydrogen as well as dual-use containers for LH_2 and liquid helium. In addition, we are currently working on semi-trailer solutions, and these are due to be launched in the near future.

Key Data for Dual-use Containers

Design pressure:	12 bar (174 psig)
Net capacity:	2.615 kg (at 10% ullage)
Holding time:	≥ 50 days to reach 11.4 bar(g) / ≥ 200 days with active LIN shield (i.e. dual-use container)
Design codes:	ASME VIII, Div 1
Approval:	ADR, IMDG code, ASME, TIR, CSC

Figure 6.1: Example of an LH_2 container.



Figure 6.2: Removal of displaced gaseous hydrogen via the chimney of the storage tank during LH₂ delivery. Due to the coldness of the discharged gas, moisture condenses locally from the air and a cloud of fog forms. Source: ¹³

In addition, evaporation losses occur during the transfer time due to the consistent heat input into the storage tank (usually covered by mixing with somewhat colder or somewhat warmer transferred fluid, as well as a change in pressure occurring in the target tank).

Often, all of these losses are collectively referred to as the boil-off gas (BOG).

Figure 6.3 illustrates the refilling process of a liquid hydrogen trailer at a filling plant. The trailer is filled up to a maximum of 90 % capacity, with the pressure typically maintained below 1.5 bar(a). No major evaporation losses occur during transport. The LH₂ transfer to the stationary tank takes place by means of the pressure difference. To build up and maintain pressure in the trailer, some of the liquid hydrogen is evaporated and used for pressurization. Pumps are not typically installed on board. The receiving tank is filled from below via a flexible transfer pipe with an internal diameter of approximately 0.025-0.05 m. The displaced cold gas is discharged to the outside via the corresponding pipes. At the Kennedy Space Center, the trailer is pressurized to 4.2 bar(a). According to Partridge¹⁴, experience has shown that 680 l of liquid hydrogen are evaporated in the trailer. The pressure in the trailer on arrival and after filling the tanker is not specified.

Partridge¹⁴ calculates the LH₂ losses resulting from the transfer from trailer to stationary storage at 13%. These values were determined

by comparing the weight of the tanker truck in the filling plant and the increase in fill level in the receiving tank. This loss covers the cooling of the transfer pipe, flow control valve losses, heat input during transfer and displacement of the cold gas (see Figure 6.3).

The filling time of an LH₂ trailer is between 4 hours and 6 hours; depending on the size of the receiving tank, between 1 and 2 hours are required for off-loading. Typical transfer parameters from the trailer to a stationary dewar are 1 bar to 2 bar pressure difference at a mass flow rate of approximately 0.5 t/h.

Pumps

The production, transport and use of cryogenic liquid hydrogen as an energy carrier necessitates numerous transfer operations of this cryogenic liquid.¹⁵ In order to minimize losses caused by evaporation, the use of suitable pump systems is essential. Various pumps are in development for LH₂, to enable a low-loss and sustainable transfer process to be established at all transfer stations in the future.

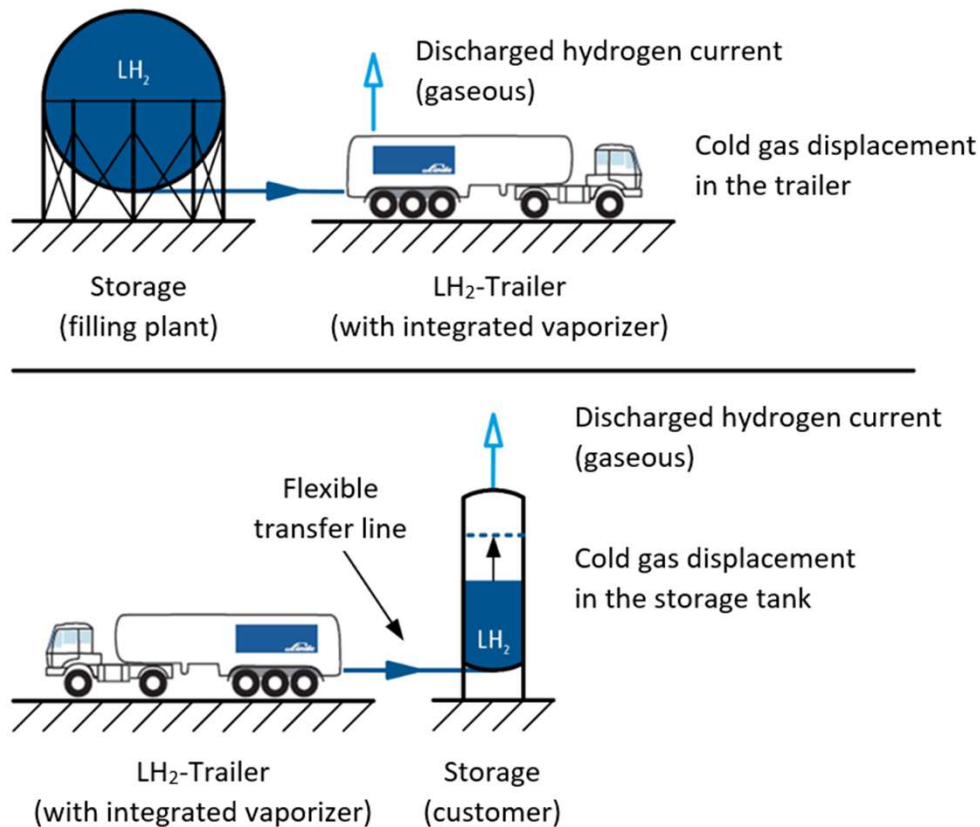


Figure 6.3: Schematic representation of LH₂ road transport. Top: Filling the LH₂ trailer from the filling plant storage tank. Bottom: Filling the customer's tank from the LH₂ trailer. Source [KS\(1\)](#)

Due to their fields of application, pumps for liquid hydrogen can be roughly divided into three types:

- 1. LH₂ high-pressure pumps:** These piston pumps have the task of bringing comparatively low mass flows (~100 kg/h) LH₂ to a high pressure of 350 bar to 700 bar. The liquid is then heated in order to fill (mostly mobile) tank containers with the high-pressure gas, for example at hydrogen filling stations for road vehicles. LH₂ high-pressure pumps are available on the market and are already widely used.
- 2. LH₂ pressurization pumps (fuel pumps):** These pumps have the task of bridging pressure differences between advantageous LH₂ tank pressure and required minimum input pressure at the consumer (fuel cell), and thus function as fuel pumps. Their specifications are defined by the consumer, the pressure increase is limited to a few bar (<20 bar), the flow rate is in the range up to <500 kg/h. Piston pumps are primarily suitable for use as LH₂ pressurization pumps, although a centrifugal pump configuration is also possible given the appropriate specifications. Some liquid hydrogen pumps are available on the market which can be used as pressurization pumps, however, there is still a need for further development across a wide range of pump specifications.
- 3. LH₂ transfer pumps:** This type of pump serves the purpose of moving large volumes of liquid hydrogen. A flow rate of up to 10 t/h is countered by a relatively small pressure buildup of <5 bar, which primarily only has to overcome the pressure losses in the pipelines. Due to the specifications, only centrifugal pumps are considered to be suitable as LH₂ transfer pumps. They are used for rapid filling of large volumes of LH₂, for example for refuelling ships, aircraft or locomotives in freight transport, but also in the distribution of liquid hydrogen from future LH₂ import terminals to the consumer. LH₂ centrifugal pumps of this size have so far only been used as prototypes in a limited number of pilot plants and are not currently commercially available. A multi-stage centrifugal pump was procured, tested and used for a project by Kawasaki Heavy Industries, for example. The prototypes tested so far have mostly been pump models which were originally designed for other cryogenic pumped media, but with the materials adapted for LH₂. The efficiency of such configurations is still low. There is a need for the development of efficient pump systems designed specifically to convey LH₂. Possible manufacturers could be commercial LNG pump manufacturers such as Cryostar / France, Nikkiso ACD or Ebara.

KS(1)

genaue Quelle?

Kasper, Simon (ITEP); 14.06.2023

Pressurization and transfer pumps in particular are used as cryogenic submersible pumps, i.e. all pump components are at LH_2 temperature within the LH_2 reservoir. The associated need for cryo-compatible drive systems and bearings offers an enormous advantage, in addition to solvable technological challenges: the possibility of using superconducting components without the need for additional cooling. The pump utilizes a passive, superconducting magnetic bearing system that consists of a combination of permanent magnets and superconducting material. This bearing is activated inside the target tank when cooled below the transition temperature and keeps the rotor floating permanently in a previously defined position. Thanks to its superconducting properties, the bearing system operates without consuming any

electrical power. Thus, high rotational speeds and load-bearing of the rotor can be achieved without any friction between solid objects. The bearing system generates sufficient supporting forces, eliminating the need for active control. Furthermore, superconducting coils and cage rotor systems can also be used advantageously and without additional cooling effort when driving the pump, resulting in increased the overall efficiency of the LH_2 pumps. These pump technologies enable highly efficient transfer operations during transport, as well as the provision of different consumer pressures for numerous LH_2 transfer and application scenarios.

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7

Stationary use of LH₂

Liquid hydrogen has been and is used as a fuel for rockets and the corresponding storage and refuelling infrastructure required on the ground have been instrumental in driving innovations and advancements in the large-scale use of LH₂ (see Chapter 5.3). However, the following chapters of the white paper will focus on LH₂ applications in the industrial and mobility sectors, aiming to contribute to the achievement of climate goals and refer to other work such as the study by *Verfondern*¹ and the references mentioned therein for use in space travel.

Semiconductor industry

Due to the intrinsically high purity of hydrogen regasified from an LH₂ tank (up to gas quality 6.0), it is already used today where these high degrees of purity are required anyway. Hydrogen is used in various process stages in the semiconductor industry, such as:^{2,3}

- Heat treatment of silicon wafers: The high thermal conductivity of the hydrogen gas helps to heat the wafers uniformly to up to 1000 ° C. In addition, the product is cleaned, as H₂ reduces and removes oxidic impurities on the surface.
- Production of monocrystalline layers: Hydrogen is used as carrier gas in various epitaxial processes. When monocrystalline silicon layers are built up, gaseous silicon compounds, for example, are introduced together with hydrogen. The gases react on the substrate, whereupon the individual silicon atoms formed can be deposited as a layer.
- Ion implantation: In order to influence the properties of a semiconductor layer, foreign ions can be introduced into the base material. Contamination with hydrogen ions and subsequent heating of the material leads to a clean layer splitting off, the so-called "ion cut".
- Stabilization: A hydrogen atmosphere helps extend the shelf life of some of the chemicals important to the semiconductor industry (such as Diboran B₂H₆ and Digerman Ge₂H₆).
- EUV lithography: In the photolithography process, the image of a photomask is transferred to a photoresist on the base material by means of exposure to light. This results in a mask that enables further processing, for example using etching. In photolithography with extreme ultraviolet light (EUV), tin droplets are bombarded with laser light in order to generate the UV light. This leads to contamination of the mirror surfaces by tin deposits. These are removed periodically by flushing the device with hydrogen gas to form stannane (SnH₄).

Gaseous hydrogen, which is delivered by truck with high-pressure tanks, can also achieve high levels of substance purity. However, in this case the transportable hydrogen mass is approximately one-fourth of that in LH₂ tankers. Similarly, storage on the semiconductor manufacturer's premises in LH₂ tanks offers a more compact solution compared to high-pressure tanks, the hydrogen is only regasified shortly before use in the process. Considering the high hydrogen demand of many semiconductor manufacturers, the supply and storage of the hydrogen in liquid form proves to be more efficient.

LH₂ storage for supplying hydrogen filling stations

In a filling station concept for refuelling vehicles with high-pressure hydrogen, the hydrogen is initially delivered in liquid form and stored in a liquid hydrogen tank directly at the filling station. To increase the pressure a hydraulic pump is used, which pumps the liquid hydrogen to the required high pressure before it is heated and the vehicle fuel tank is filled. In addition to the energy efficiency advantage, this pump is of a very compact design for the given output. The required installation space is 2.5 m³ per 120 kg/h of pumping volume. So far, Linde and Air Products have developed

this type of pump in-house.

Another filling station concept entails the gaseous hydrogen being compressed in a compressor. A filling station with an ionic compressor with a maximum flow rate of 35 kg/h is approximately the size of a 10-foot container.

Both concepts (liquid hydrogen pump and ionic compressor) require relatively high levels of maintenance. The maintenance-free times are between 200 and 1000 h.

The hydrogen losses at a filling station have been investigated by Petitpas⁵. The figures probably relate to an H₂ filling station with 320 kg/day of hydrogen output. The following details can be found in the study:

- 5.5 kg/day evaporation loss from the stationary dewar (725 kg)
- 0.3 kg/day loss from the transfer line from stationary tank to external pump
- 1.1 kg/day cooling the pump
- 0.06 kg/kg H₂ output, leakage at output of 700 bar gH₂
- Up to 0.07 kg / kg delivered LH₂ due to cold gas displacement



Performance Fueling Station

- Footprint: **very small 6.10 x 3.40m**
- Capacity: **50 - 100kg/hr (at 90 Mpa)**
- Refueling performance: **6 FCEV cars/hr.**
- Bulk storage capacity: **400kg LH₂**
- MAWP: **100 MPa**
- Energy consumption (total): **45kW**
- Specific energy consumption: **1.2 kWh/kg H₂**
→ Energy saving of around 70%vs. piston compressor
- Boil-off: **4 kg/day, utilized for stand-by cooling (no additional cooling system required)**
- Refueling protocol: **SAE J2601-A70 and CEP**
- High reliability, little maintenance and low costs
- Consequent development for installations at existing gasoline/ diesel retail stations, based on joint workshops with oil companies Shell, Total, OMV

Figure 7.1: Illustration of a hydrogen filling station with LH₂ tank. Source: ⁴

LH₂ terminals place higher demands on thermal insulation compared to LNG terminals, for example.

Costs

Hydrogen supply chains are analysed in Reddi⁶. Based on thermodynamic and economic modelling of the liquid hydrogen supply in space travel, the system has been adapted to road transport. The analysis provides detailed costs and estimates for each component involved. The liquid hydrogen scenario includes hydrogen production, liquefaction (using technology such as that described above) and LH₂ storage, road transport distribution, and the hydrogen filling station. In addition, this program can be used to combine transport as a high-pressure gas and via pipeline, or any combination of these three options.

Partial results, such as the costs for the LH₂ transport, are also calculated and presented. The LH₂ transport costs range from \$0.19/kg_{H₂} to \$0.25/kg_{H₂} depending on the scenario (transport routes, market penetration, etc.). The model is freely available as an Excel file and well documented. It is probably currently the most comprehensive economic analysis of a hydrogen infrastructure in the field of mobility. Individual aspects may not be considered as a general standard. For example, at the modelled cryogenic filling station (Figure 7.1), the H₂ flow conveyed via the cryopump is completely warmed up to room temperature and temporarily stored. For high-pressure refuelling, the hydrogen is cooled down to the filling temperature (-40°C) with a separate cooling system. It would be more efficient to use the existing cooling capacity from the LH₂.

Import terminals for LH₂

In chapter 6.1, the intercontinental transport of LH₂ was discussed as a relevant hydrogen import option. On land, corresponding LH₂ terminals play a vital role in the construction of a large-scale hydrogen infrastructure for unloading, storing and transporting the hydrogen that comes ashore.

The loading and unloading of an LH₂ tanker is designed based on LNG terminals. In contrast, all LH₂-carrying components require vacuum insulation. A so-called jetty line, up to 1 km in length, is used to transfer liquid hydrogen ashore and gaseous hydrogen back into the tank. The loading arm is usually made up of multi-flow transfer pipes. These are then merged on the jetty line. In line with the large volumes of liquid hydrogen, an LH₂ mass flow of 8 kg/s (28800 kg/h) and 3000 kg/h of gaseous hydrogen at 30 K to 40 K is to be expected here. Thermohydraulic modelling of the transfer line (diameter of LH₂ pipe approx. 215 mm, gH₂ pipe 270 mm) without the loading arm shows low evaporation losses up to a vapour mass fraction at the line inlet of $x = 0.15$. The proportion of vapour mass increases by a maximum of 0.007 kg_{gas}/kg_{liquid}. In absolute terms, this means an LH₂ loss of 201.6 kg/h – a very small proportion compared to the mass flows present. Loading arms with swivel joints and an emergency release device again cause the same amount of LH₂ loss.

The transfer of LH₂ by pressure difference alone would be inefficient at the scale of the required mass flows. In addition to the evaporation losses due to the continuous pressure reduction in the pipe, high mass flows can only be realized with large pressure differences. In the event of limited pressure stability in the tank, it is to achieve the required pressure buildup. For pressure differences of a few bar, centrifugal pumps (possibly multi-stage) are suitable as LH₂ transfer pumps for the given volume flows, see Chapter 6.3.

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8

Use of LH₂ in mobile applications

Mobile applications include

- Trucks/cars, buses (road transport)
- Mining and construction vehicles
- Locomotives for passenger trains as well as for the transport of goods
- Ships
- Aircraft

Means of transport with a required hydrogen tank load on board of less than 50 kg typically utilize pressurized hydrogen tanks with a range of 300-700 bar. These include, for example, cars, small and medium-sized trucks and buses.

It is also safe to assume that the larger machines with more than 500 kg of hydrogen on board are preferably equipped with a liquid hydrogen tank. These include mining and construction vehicles, locomotives for the transport of freight, ships and aircraft. In the range between 50 kg and 500 kg, both technologies can be used. The choice between the two technologies often depends on local conditions and requirements.

Filling stations catering to vehicles equipped with liquid hydrogen tanks are supplied with cryogenic liquid hydrogen. The supply of filling stations for means of transport with pressurized hydrogen tanks is currently carried out either with liquid hydrogen or with high-pressure hydrogen trailers. In the future, when hydrogen sales

at H₂ filling stations increase and the level of about 1 ton per day is exceeded, the supply of filling stations and the corresponding infrastructure will most likely be switched to liquid hydrogen LH₂.

Estimating the efficiency of energy chains and drive train

The energy efficiency of a fossil energy chain has deteriorated significantly over the past few decades, as exploration and transportation have become increasingly complex and energy-intensive. Although the efficiency increases in fossil fuel internal combustion engines have partly compensated for this, only about 18% to 33% of the energy stored in the crude oil reaches the drive axle of vehicles. If compressed H₂ gas is used as the fuel in a hydrogen engine, approximately 27% of the energy content can be converted to propulsion without the emission of CO₂; if the hydrogen engine is replaced by the combination of fuel cell and electric motor, approximately >28% makes it to the drive axle.¹

If liquefied green H₂ (LH₂) is used as fuel, then - without further system improvements - about 29% of the energy content reaches the drive axle via fuel cell and conventional electric motor (Figure 8.1).¹

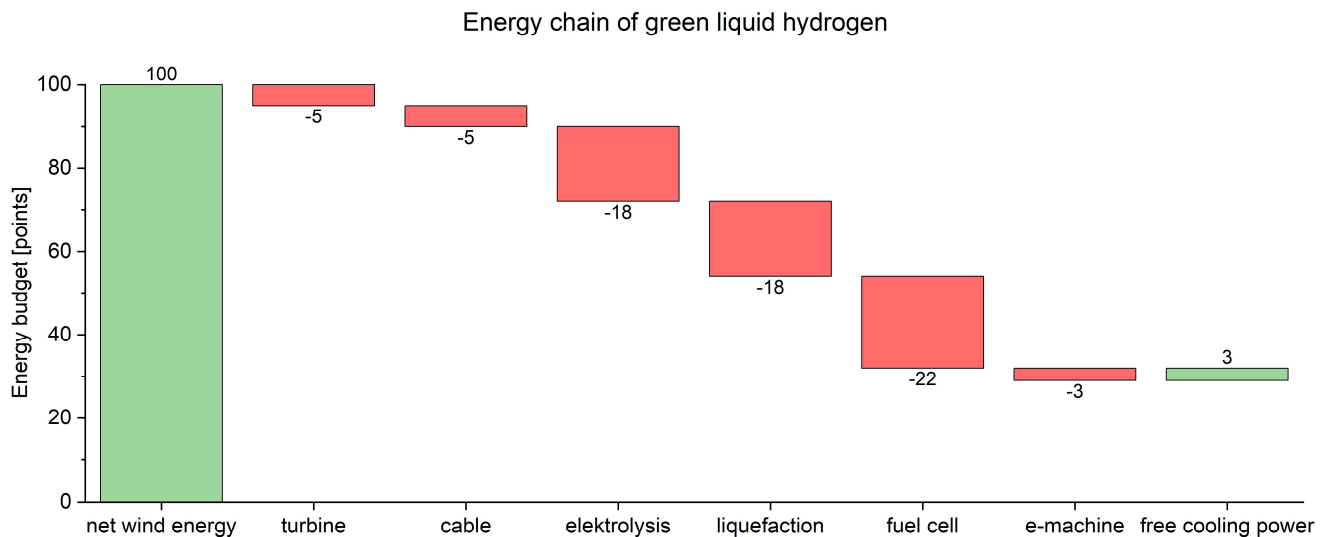


Figure 8.1: Energy chain of green liquid hydrogen for vehicles.

Depending on the efficiency of the fuel cell (currently 50%-60%), the utilization of LH₂ can provide a cooling capacity increase of over 3 percentage points, resulting in 32 % of the initial energy budget reaching the drive train.

The corresponding cooling technology offers further potential for increasing the efficiency of the drive train by means of optimized designs.

The initial energy budget of 100 points is provided via renewable energies (here: wind power). The electric power generation operates at about 95% efficiency and leads to an availability of only 95 points. Transmission by cable, hydrogen production by electrolysis, and liquefaction (all still using renewable energy!) each reduce the count- by 5, 18, and 18 points.

The fuel cell and the drive motor in the vehicle reduce it by 22 and 3 points respectively.

Using the "free cooling" of the liquid hydrogen before feeding into the fuel cell instead of elaborate dedicated cooling technology for the electric drive train results in an increase in the available energy for the drive axle of 3 points, ultimately achieving an efficiency of 32 vH. points.

Vehicles and energy requirements

The vehicle size and the surrounding medium, especially, result in particular requirements for the type of energy storage. Estimations suggest that when transitioning diesel locomotives, aircraft and large construction machines to hydrogen operation, the required amount of energy can only be carried in the form of LH₂. Table 8.1 provides an overview.

The fuel cell in vehicles

A filling station infrastructure is essential for H₂-powered vehicles to penetrate the market. As of 2020, there were approximately 540 H₂ filling stations worldwide, most of them in Japan, Germany, China and the USA.

Table 8.1: Typical power and energy requirements of different vehicles with important parameters.

Vehicle	Typical power requirement	Typical energy requirement	Specific parameter(s)
Car	30 kW	45 kWh	Efficiency of the energy chain
Truck	< 0.4 MW	<5 MWh	Volumetric and gravimetric energy density
Ship	(2-20) MW	240 MWh	Volumetric energy density, CO ₂ -free
Local train	< 0.4 MW	<5 MWh	CO ₂ -free
Locomotive	(1- 3) MW	(20- 60) MWh	Volumetric energy density
Aircraft	(4-25) MW	51 MWh ²	Gravimetric (and volumetric) energy density

LH₂ enables long ranges in heavy vehicles and provides cooling capacity.

Although the number of fuel cell electric vehicles (FCEVs) is growing, the annual growth rate fluctuates. At the end of 2020, there were approximately 34,800 FCEVs worldwide, with around two thirds located in Asia. The use of FCEV as a mobile sector-coupling element for the decentralized supply of various buildings with electrical and thermal energy is the subject of current research.

For fuel cells in vehicles, their suitability for everyday use has been proven, with a realistic H₂ consumption of approximately 1.2 kg per 100 km, and no significant increase in maintenance costs compared to Internal Combustion Engine Vehicles (ICEVs) is expected. The cooling of the fuel cell is still a challenge (especially in trucks, see below). Research is still needed with regard to cost reduction potential, service life and efficiency. Legal framework conditions to promote the environmentally relevant system properties (e.g. toll exemption) seem helpful and appropriate.

Hydrogen engines in vehicles

In the case of hydrogen engines, spark ignition internal combustion is state of the art, such cars were commercialized by BMW as early as the 2000s, but H₂ vehicles from Daimler and Opel with hydrogen engines have also reached the commercialization phase. The poor anti-knock properties of hydrogen were a particular obstacle to the transition to hydrogen. In order to achieve a high degree of efficiency, the spark-ignition and compression-ignition combustion (also for supercharged engines) must be further developed. Proof of the lifespan of modern hydrogen engines and their compatibility with modern materials has not yet been fully confirmed. However, cars with hydrogen engines are already offered for sale by Toyota in car dealerships. NO_x emissions are already at a very low level and can be reduced below the lowest level of EURO6d diesel engines. Political acceptance as zero-emission is still widely pending.

Although the maintenance costs appear to be higher than in the case of an electric drive train, it is generally possible to use established technologies and the hydrogen engine appears to be advantageous for high-load applications.

Hydrogen & drive train

In electric vehicles it is not only the electromagnetic design of the components that is important. An advanced cooling strategy is particularly relevant for high efficiency. For example, the current Audi e-Tron GT has four connectable cooling systems for the battery, power electronics, electric motors, charging technology and air conditioning. The importance of heat dissipation also becomes clear in relation to patents on electromagnetic design for cooling electric motors (2021 research): 3080 to 63021. We expend about 20 times more development effort on cooling electric motors than on electromagnetics.

LH₂ can significantly reduce this technical cost, because of its ability to absorb thermal energy (approx. 1.2 kWh/kg) until it is used in the fuel cell.³ From a purely mathematical point of view, an LH₂-powered truck would no longer need dedicated cooling systems for the drive train after the fuel cell. There is still a need for research to optimize the overall system.

Summary

Depending on the increase in production and vehicle type, FCEV and BEV will be cheaper than ICEV in 2021-31.^{4,5} Expansion of the H₂-filling station infrastructure and other legal framework conditions seem sensible. Vehicles with green H₂ as their fuel contribute to the conversion and unburdening of a sustainable electrical energy system and fit into a sustainable energy supply strategy under the constraints of sector coupling and including primary energy imports. The hydrogen engine represents an option in high-load applications. The use of LH₂, not only as a fuel but also as "free cooling", can significantly increase the efficiency of energy chains and vehicles. Furthermore, LH₂ provides an optimal "habitat" for high-temperature superconductors (HTS), which do not need to be kept at a low temperature using other technologies and which, due to the loss-free high current density, lead to a further considerable increase in efficiency and compact power in the drive train.

Deep penetration of the market with these technologies should be supported by political framework conditions that appreciate the entire range of advantages (e.g. CO₂-free mobility and transport by means of toll exemption) or pricing of environmental costs into fossil fuels

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9

Combination of LH₂ and superconductivity

The use of superconducting materials in conventional applications in particular opens up opportunities for technical progress. In all previous applications of superconductivity, e.g. in energy and medical technology, the required cryogenic temperature must be realized by means of complex cooling. Lossless energy transport occurs only when the superconductor is cooled below the transition temperature and kept at this temperature. Typically, liquid helium at 4.2 Kelvin (- 269 ° C.) is used for this purpose and liquefied as well as continuously recondensed with high energy expenditure. This coldness is supplied with the LH₂ at about 20 Kelvin, virtually without any additional expenditure. The selection of suitable superconductors for motors, magnetic field generators, bearings, etc. allows a variety of technical innovations. Within the logistics chain, the use of superconductivity has the potential to "recover" the energy used in the production of LH₂ to a large extent by avoiding losses.

Combined transmission of LH₂ and electrical energy ("Hybrid Energy Transmission")

The expected hydrogen demand in Germany by 2045-2050 varies greatly between different studies and scenarios depending on the framework conditions, ranging between about 100 and 900 TWh. ^{1-2,3,4,5,6,7,8,9,10,11} As considered in Chapter 8, due to its energy density,

liquid hydrogen is a possible fuel for large and difficult to electrify mobile applications, such as heavy trucks, ships or aircraft.¹² If significant proportions of the above-mentioned mobile applications are realized with liquid hydrogen as the fuel, liquid hydrogen requirements in the order of more than 100 TWh or several million tons of hydrogen per year could be reached in Germany by 2045-2050 (according to in-house calculations based on ⁷ and ⁹).

Germany's total hydrogen demand will largely be covered by imports, including overseas imports by ship. ^{3,5,6,7,8,11,13} Liquid hydrogen can be a relevant import vector (see also Chapter 6). ^{14,15,16,17,18} In order to minimize the demand for electrical power in Germany for the liquefaction of hydrogen and to derive further benefits from the cryogenic liquid, liquid hydrogen imported by ship in particular should be transported onward within Germany to the LH₂ users in liquid form. This could prevent conversion losses.

LH₂ is currently transported by means of container vehicles, for example by truck. Future transport to highly localized customers could be carried out, with a continuously high LH₂ demand, via LH₂ pipeline – for example at large airports.^{19,29}

"Hybrid pipelines" combine the transport of electricity and LH₂.

LH₂ pipeline transport is currently already being implemented in various applications, including rocket refueling²¹ and industrial liquefaction plants.

In addition to the expected strong increase in hydrogen demand, the electrical energy demand and transmission demand in Germany will also increase in the coming years.^{1,2,3,4,5,6,7,8,9,10,11} Therefore, the transport of chemical energy in an LH₂ pipeline can be combined with the particularly efficient transport of electricity in a superconductor to form a "hybrid pipeline". The cryogenic temperature of LH₂ is used to cool the superconductor and provides a superconducting current path with little additional expenditure to the LH₂ pipeline. This bundling of paths is particularly advantageous in regions of dense development or with a high transit requirements.

Technical superconductors currently in use require cooling below -163 °C (110 K). To achieve this superconductive state, cryogenic, liquefied gases such as helium (boiling temperature 4.2 K or -269 °C at ambient pressure) and nitrogen (boiling temperature 77 K or -196 °C at ambient pressure) are commonly employed for cooling in addition to refrigeration machines.

Once the state of superconductivity has been reached, the material no longer has any electrical resistance and high currents, in particular direct currents, can be transmitted with low electrical losses. The maximum current carrying capacity, the so-called critical current I_c , of a superconductor is temperature-dependent and decreases with increasing temperature.

The high-temperature superconductor REBCO is superconducting below approx. 90 K (-183 °C) and is produced as a flat strip – for details refer to ²². When cooled with liquid nitrogen, a four-millimetre-wide REBCO band can transmit currents of 160 amperes without electrical losses. When cooled with liquid hydrogen, this value increases to almost 1000 amperes.²³

Stranding them to form a cable increases their current-carrying capacity, enabling electrical transmission outputs of 100 megawatts or higher when operating at medium voltage, such as 20 kV.

Superconducting DC and AC cables, cooled with liquid nitrogen have been developed and in some cases operated successfully in the grid for several years. The SuperLink project, initiated in 2020, addresses a 12 km superconducting 110 kV cable for 500 MVA in Munich.²⁴ The advantages of superconducting cables over conventional solutions include the reduced space requirement for routes, lower electrical losses, higher power densities and the possibility of transmitting a predetermined power at a lower voltage level by means of higher currents.²⁵

Due to minimal electrical losses in a superconducting DC cable, the integration of a superconducting transmission line into an existing LH₂ pipeline for LH₂ transport adds only a negligible thermal load to the pipeline when operating in its cooled state. Consequently, the integration allows for a further increase in the already high transmission power of an LH₂ pipeline.

The combined use of a pipeline carrying cryogenic liquid for cooling superconductors was already proposed in the 1970s²⁶, in particular in combination with high-temperature superconductors (MgB₂) with transmission capacities in the GW range^{27,28,29,30,31,32} and intensified infrastructure integration was proposed.³³ The first successful demonstrators of combined energy transport with the superconductor MgB₂ with electrical and liquid-hydrogen transmission capacities ranging from approximately 50 to 75 MW, took place between 2013 and 2015.^{34,35,36,37}

Advances in the production of the REBCO superconductor also make this material interesting for applications in hybrid energy transmission, . The high critical temperature of REBCO allows for a significantly wider temperature margin, enhancing operational safety and providing a larger reserve compared to the previously tested material MgB₂.

The development and testing of a hybrid cable and its components in a demonstrator environment, as well as the evaluation of its profitable use, are the subject of current research within the project.

LH₂ + HTS in energy technology

A further, second approach is the adaptation of the electrical equipment to the new cooling options using LH₂. One example is the use of cryogenically cooled intermediate circuits (using superconducting components) in converters or the design of galvanic isolation (transformers,

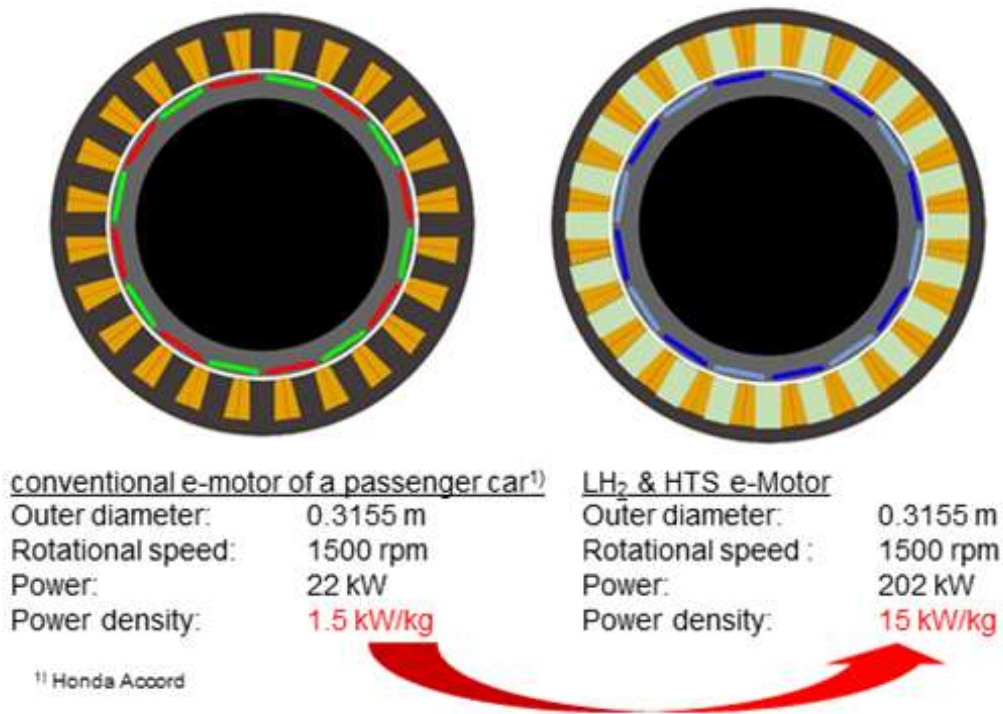


Figure 9.1: Left: Cross section of a conventional synchronous electric motor in a Honda Accord with conventional rare earth magnets in the rotor, iron teeth and copper windings in the stator and corresponding performance data.

Right: Cross section of an LH₂-cooled synchronous electric motor of the same diameter with an HTS field coil excited rotor, air teeth and copper windings in the stator and corresponding performance data.

coils) at the terminals of electrical transmission lines, which thus also avoid the input of parasitic heat.

LH₂ + HTS in mobile applications

Multiple demonstrators have shown the superior efficiency of electric rotating machines based on high-temperature superconductors (HTS). As HTS conduct the greatest electrical current densities (up to >600 A/mm²) without loss, no ohmic waste heat is generated in these machines. This is shown in machinery already in use in applications ranging from generators to marine motors, and recently also in electric drive units for aircraft. By harnessing the electromagnetic advantages of HTS, such as larger usable current densities and magnetic fields, these machines are designed to be highly efficient and compact, boasting a high power-to-mass ratio.

If the LH₂ fuel is used to cool the electric machines, no further cooling technology is required, resulting in a reduction of losses by over 80% compared to conventional machines

For example, a simple, basic electromagnetic design with HTS was produced for a (somewhat older, but well known) electric motor of a Honda Accord, which led to an increase in power density by a

factor of 10 with otherwise identical operating parameters (Figure 9.1).

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