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# Strategies to recover and minimize boil-off losses during liquid hydrogen storage

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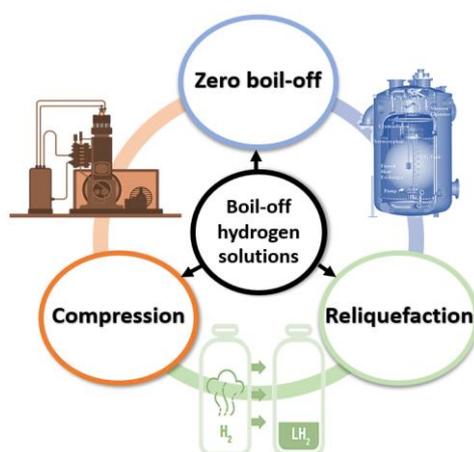
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## Graphical abstract



## Abstract

Liquid hydrogen (LH<sub>2</sub>) offers the highest storage density compared to other forms of storage, without requiring a chemical reaction. However, it requires the hydrogen be cooled to 20 K using an energy-intensive refrigeration process. LH<sub>2</sub> storage is associated with the unavoidable evaporation of a fraction of the LH<sub>2</sub>, known as "boil-off", which results in process inefficiency and energy losses. To ensure proper deployment and increased competitiveness of LH<sub>2</sub> storage, evaporation should be minimized as much as possible or, alternatively, recovered in liquid or gaseous form. This review covers, for the first time in a single document, the key elements including definition, current challenges, and state of the art of the hydrogen storage in the form of LH<sub>2</sub> and the three different recovery strategies to minimize hydrogen evaporation or recover boil-off hydrogen, namely: zero boil-off, hydrogen reliquefaction, and commercial solutions for boil-off hydrogen compression.

## **Highlights**

- Liquid hydrogen (LH<sub>2</sub>) offers the highest storage density among physical methods
- Minimizing or recovering boil-off hydrogen (BOH) is crucial to deploying LH<sub>2</sub> storage
- Zero boil-off (ZBO) is a well-established and evolving concept in the aerospace industry
- Reliquefying BOH can prevent the conversion of ortho to para hydrogen
- Non-mechanical compressors are key players in BOH compression

**Keywords:** boil-off, liquid hydrogen, zero boil-off, reliquefaction, compression, hydrogen storage

**Word count: 10897**

## Abbreviations

<b>BOG</b>	Boil-off gas
<b>BOH</b>	Boil-off hydrogen
<b>CAPEX</b>	Capital expenditures
<b>CHC</b>	Cryogenic hydrogen compressor
<b>COP21</b>	Conference of Parties
<b>DOE</b>	US Department of Energy
<b>EHC</b>	Electrochemical compressor
<b>EXE</b>	Exergy efficiency
<b>FOM</b>	Figure of merit
<b>IDEALHY</b>	Integrated Design for Efficient Advanced Liquefaction of Hydrogen
<b>JAXA</b>	Japan Aerospace Exploration Agency
<b>J-T</b>	Joule-Thompson
<b>KHI</b>	Kawasaki Heavy Industries
<b>LH<sub>2</sub></b>	Liquid hydrogen
<b>LHV</b>	Lower heating value
<b>LNG</b>	Liquefied Natural Gas
<b>MLI</b>	Multi-layer insulation
<b>MOF</b>	Metal organic framework
<b>NASA</b>	National Aeronautics and Space Administration
<b>OPEX</b>	Operational expenditures
<b>SEC</b>	Specific energy consumption
<b>SRIA</b>	Strategic Research and Innovation Agenda
<b>TRL</b>	Technology Readiness Level
<b>VCS</b>	Vapor-cooled shield
<b>ZBO</b>	Zero boil-off

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## 1. Introduction

The international environmental commitment made in the Paris agreement of the Conference of Parties (COP21) set clear benchmarks to develop a common global green agenda with the goal of limiting the increase in the Earth's temperature to below 2 °C this century by combating climate change through different means [1]. Reducing emissions of greenhouse gases, such as anthropogenic CO<sub>2</sub>, is essential to achieving this goal. CO<sub>2</sub> is one of the main products of any combustion reaction; therefore, to reduce CO<sub>2</sub> emissions into the atmosphere, fossil fuels must be replaced by increasing the production and use of renewable energy sources [2]. Hydrogen as an energy carrier can be both a promising alternative to traditional fossil fuels and a facilitator of the energy transition. However, to deploy a green hydrogen economy, certain technological and environmental challenges regarding its production and storage require special attention. H<sub>2</sub> is indeed mostly produced by methane reforming and not by green methods such as water electrolysis using electrical energy from renewable sources [3,4] and on the other hand the low volumetric energy density of H<sub>2</sub> along with its supercritical state under ambient conditions make its storage very challenging.

H<sub>2</sub> storage and distribution in liquid form may offer certain advantages over compressed H<sub>2</sub> in tanks: superior cargo transportable by trailers due to its higher volumetric density, reduced transport frequency and, therefore, costs [5], and more suitable large-scale transportation over long distances [6]. However, H<sub>2</sub> liquefaction requires refrigeration cycles to go from ambient conditions to 20 K, which is an energy-intensive process. At the industrial level, the main drawback of current liquefaction plants is their low production capacity, typically about 5 ton/day, and their relatively low exergy efficiency (EXE) indicating the room for improvement in both the production costs and the energy consumption [6]. Given the rising potential of the H<sub>2</sub> transportation sector, namely trucks, aircrafts, and ships [7], it is expected that larger capacity liquefaction plants (greater than 50 ton/day) will be built in the near future [8]. Moreover, if one considers liquefied natural gas (LNG) as a reference sector for the liquid hydrogen (LH<sub>2</sub>) industry, the perspectives of large-scale liquefaction plants can be even more encouraging, as larger LH<sub>2</sub> capacities are now needed. Large-scale LNG plants [9–11] currently offer production capacities between 8,200 and 13,700 ton/day for transnational commerce [12]. In the case of LH<sub>2</sub>, international energy markets could require H<sub>2</sub> liquefiers with production capacities ranging from 100 to 1,000 ton/day [13,14].

In line with the need to deploy LH<sub>2</sub> for different applications and to foster its long-

distance transport, the European hydrogen strategy foresees reducing the costs of importing H<sub>2</sub> from countries where its green production can be cost-effective due to abundant renewable energy resources. In the framework of the Horizon Europe plan [15], the development of a LH<sub>2</sub> storage container design for maritime transport in sizes larger than the current 1,250 m<sup>3</sup> (90 tons) is underway. The project will ultimately contribute to several of the goals proposed in the Clean Hydrogen Joint Undertaking SRIA [16] including: LH<sub>2</sub> tank capacities of 350 tons in 2024 and 2,800 tons by 2030; capital investment of LH<sub>2</sub> containments of 50 €/kg in 2024 and less than 10 €/kg by 2030; and boil-off rates of 0.5 % in 2024 and less than 0.3 % by 2030. Similarly, but focusing on the air transport industry, the OVERLEAF project, also supported by Horizon Europe, aims to develop an LH<sub>2</sub> storage tank that is 50% lighter than the current tank, as well as the propulsion system for H<sub>2</sub>-powered aircrafts. This ambitious project comprises a consortium of 10 partners from six European countries, including companies and academics from the aeronautical sector [17].

Regardless of the type of application, mobile or stationary, a major challenge in LH<sub>2</sub> storage is the mitigation of boil-off gas (BOG). Boil-off hydrogen (BOH) is the result of the evaporation of LH<sub>2</sub>, primarily due to heat leakage into the cryogenic tank. Although there are several strategies to mitigate or recover the evaporated gas, in many cases, H<sub>2</sub> is not used and the fuel is lost to the atmosphere, resulting in wasted energy. To improve the efficiency and cost reduction of LH<sub>2</sub> storage, it is important to recover or avoid this evaporated gas, as long as the recovery solution is cost-effective compared to the cost of BOH. Given the critical importance of deploying LH<sub>2</sub> technology in the transportation and energy sector to help decarbonize the global economy, in this paper we present a comprehensive review of the LH<sub>2</sub> storage issue, focusing on key elements such as BOH mitigation strategies, for example zero boil-off, and recovery solutions, including reliquefaction or direct compression of BOH. Although some of these topics have been addressed separately by other authors, to the best of our knowledge, this is the first time that the three BOH solutions mentioned above are contextualized together in a single manuscript. In the case of BOH gas compression, given the current complexity of compressing H<sub>2</sub> using traditional mechanical compressors due to its very low temperature, some data is also provided on commercially available non-mechanical compressors that could eventually be used to compress the gas.

## 2. Liquid Hydrogen storage

J. Dewar was the first to liquefy  $H_2$  in the late 19<sup>th</sup> century. Today, cryogenic gas liquefaction is a proven technology that can be used for gas storage [18]. Among the various well-established technologies for storing  $H_2$  by physical methods,  $LH_2$  offers the largest storage capacity per unit volume as well as safety advantages due to its low storage pressure (0.1013-0.6 MPa) [19–21]. Figure 1a shows the  $H_2$  storage capacity per cubic meter, referred to as volumetric density ( $kg/m^3$ ), together with the volumetric energy content (kWh/L), for the main physical methods of  $H_2$  storage. In terms of energy and volumetric storage capacity, the liquid form of  $H_2$  is more advantageous than gaseous storage.

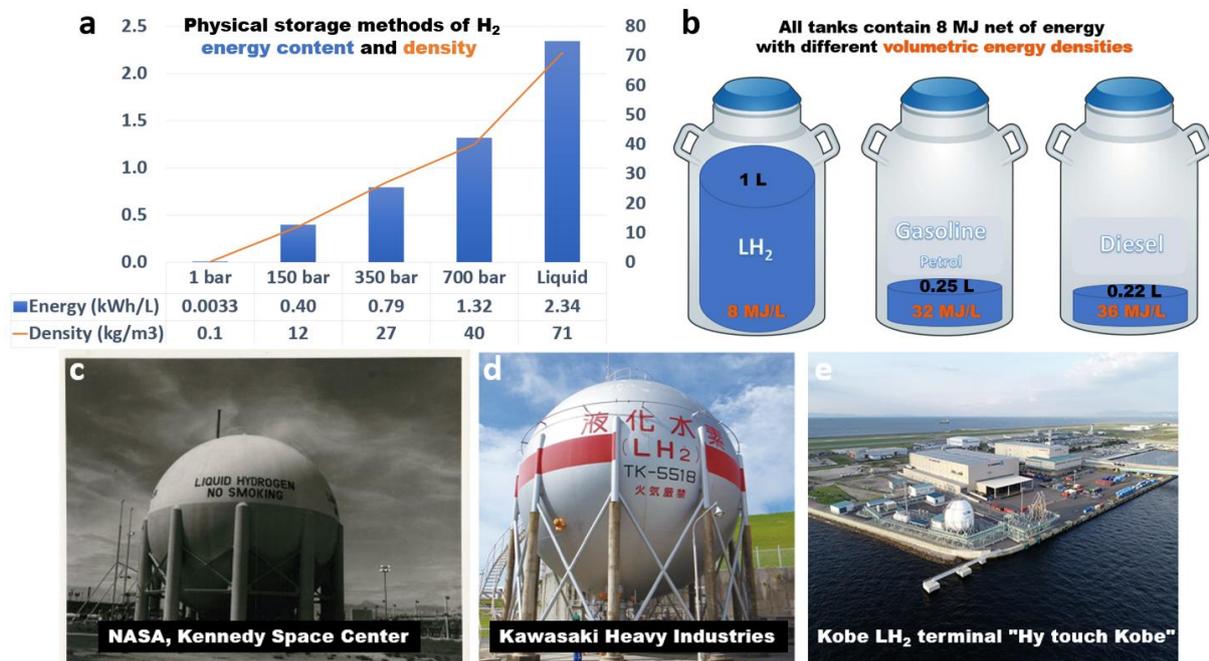


Figure 1. (a) Density and energy content of different physical  $H_2$  storage methods (after Ref. [22]); (b) graphical comparison of energy content per unit volume based on the lower heating values (LHV) of the fuels; (c)  $LH_2$  storage tank for the Apollo program at NASA's Kennedy Space Center in the 1960s; (d) Kawasaki Heavy Industries  $LH_2$  tank and (e) Kobe  $LH_2$  terminal "Hy touch Kobe" on Kobe Airport Island in Japan (Kawasaki Heavy Industries [23]).

As shown in Figure 1a, the density of  $LH_2$  can be about one to three times that of compressed  $H_2$  at pressure levels between 35 and 70 MPa, so smaller and thinner tanks can be used for its storage [24]. Nevertheless, due to the cryogenic conditions under which  $LH_2$  must be stored, the tanks require a more complex engineering design to prevent evaporation caused

by heat transfer from the environment. Since LH<sub>2</sub> is not corrosive [25], sufficiently insulated stainless steel and aluminum alloy tanks are used for its cryogenic storage [24].

H<sub>2</sub> is a supercritical gas at ambient conditions, so it must be cooled below its critical temperature, 32.94 K (for para-hydrogen, p-H<sub>2</sub>), to be transformed into liquid form. H<sub>2</sub> is typically liquefied at its normal boiling point, 20 K [26]. Reaching such low temperatures makes H<sub>2</sub> liquefaction an energy-intensive process of greater complexity than the high-pressure H<sub>2</sub> compression at room temperature. The energy consumption of H<sub>2</sub> liquefaction is estimated to be 30-40 % of the energy content of LH<sub>2</sub> [22,27,28], i.e., 8 MJ/L on a lower heating value basis [29]. Although LH<sub>2</sub> is the most densified version of all physical H<sub>2</sub> storage methods, its volumetric energy density is still lower than that of other common liquid fuels, such as gasoline or diesel, as illustrated in Figure 1b. For instance, 0.25 L of gasoline and 0.22 L of diesel have the same energy content as 1 L of LH<sub>2</sub>. However, H<sub>2</sub> has the advantage of having the highest gravimetric capacity.

Due to its high energy consumption, the application of LH<sub>2</sub> has long been limited to the spacecraft industry [19–21], where budgetary issues or market prices are not a concern [22]. The National Aeronautics and Space Administration (NASA) was one of the first developers of LH<sub>2</sub> technology to use H<sub>2</sub> as a propellant in its space flights. In the 1960s, NASA built two of the world's largest spherical tanks (see Figure 1c) to store LH<sub>2</sub> at the Launch Complex 39 at Kennedy Space Center in Florida, USA, to support the Apollo and space shuttle programs. Each spherical tank, consisting of two concentric spheres, has a volumetric storage capacity of approximately 3,200 m<sup>3</sup> [30–32]. The LH<sub>2</sub> is placed inside the stainless-steel inner sphere (16 m diameter, 1.75 cm thick) while the carbon steel outer sphere (21.6 m diameter, 2.95 cm thick) serves as a jacket [33]. The boil-off rate was estimated to be 563 kg/day [30], which translates to an evaporation rate of nearly 0.25 % per day [31].

Spherical tanks are considered the most suitable and efficient way to store LH<sub>2</sub> to avoid heat transfer from the environment, as they have the lowest surface-to-volume ratio [34]. In addition, another advantage of spherical tanks is that they have good mechanical resistance as long as the stresses and strains are uniformly distributed. However, LH<sub>2</sub> storage tanks can also be constructed in other shapes, such as cylindrical, conical or any combination of these shapes depending on the storage application or transportation medium. For example, cylindrical tanks are often used for transporting LH<sub>2</sub> in trailers or railroad cars due to limitations on the maximum allowable tank diameter [34].

In the late 1980s, Kawasaki Heavy Industries (KHI) also built two spherical LH<sub>2</sub> tanks with volumetric capacities of 540 and 600 m<sup>3</sup> [35], like the one shown in Figure 1d. These high-performance LH<sub>2</sub> storage tanks have been used since their construction in the JAXA Tanegashima Space Center in Japan. The LH<sub>2</sub> tanks are also concentric spheres like those at NASA with a void between the inner and outer walls. In addition, this double-hulled tank was built so that the outer spherical tank could contain the interior. The main design objective was to prevent as much heat transmission and conduction from the outside as possible and to maintain a certain vacuum in the interspace for long periods. In fact, according to company reports, the BOH rate has remained the same, at values below 0.2 %, with no sign of deteriorating performance over the past 30 years [36].

More recently, a 1,250 m<sup>3</sup> cylindrical marine tank and a 2,500 m<sup>3</sup> spherical land terminal tank have been commissioned [37]. The terminal, based on Kobe Airport Island as shown in Figure 1e, has been named Kobe LH<sub>2</sub> "Hy touch Kobe" and plans to become a first-class international demonstration of the hydrogen energy supply chain in the world [23]. KHI also announced the completion of the basic design of what the company claims would be the world's largest spherical LH<sub>2</sub> tank with a total volume of 11,200 m<sup>3</sup> and a H<sub>2</sub> storage capacity of 10,000 m<sup>3</sup> with a negligible boil-off rate of  $\leq 0.1$  % per day [38].

With the growing interest in H<sub>2</sub> as a fuel and energy carrier to reduce CO<sub>2</sub> emissions and mitigate the consequences of climate change, the prospects for the use of LH<sub>2</sub> have expanded to other applications. These include, for example, H<sub>2</sub> storage in filling stations for fuel cell vehicles or its large-scale transportation by ships via export from countries where this fuel is more abundant. Some attempts have also been made to implement on-board usage of LH<sub>2</sub> in small and medium-sized vehicles [24]. BMW, for instance, conducted pilot tests with an internal combustion energy vehicle, BMW Hydrogen 7©, and GM/Opel did the same but with a fuel cell vehicle, GM Hydrogen 3©. Both tests were conducted with LH<sub>2</sub> as the fuel. Despite the relatively good results of these pilot tests, the complexity of maintaining LH<sub>2</sub> at such a low temperature and the boil-off phenomenon prevented the widespread use of LH<sub>2</sub> in medium-sized vehicles [28].

### **3. The concept of boil-off gas**

The concept of boil-off gas (BOG) is closely related to the term cryogenics. Cryogenics is known as the science and technology of very low temperatures, i.e., temperatures often below 120 K [39]. Nonetheless, the value on the temperature scale at which refrigeration ends

and cryogenics begins is not well defined. According to Timmerhaus [40], temperatures below 125 K are considered a reasonable dividing line once the normal boiling points of most permanent gases, namely He, H<sub>2</sub>, Ne, N<sub>2</sub>, O<sub>2</sub>, and air, are below 125 K, whereas most common refrigerants have boiling points above this temperature. Cryogenic engineering deals with the industrial development, use, and improvement of low-temperature techniques, processes, and equipment [40]. A major challenge in cryogenic process engineering is the minimization of the inherent heat transfer from the environment to the cryogenic fluid in a given storage tank [39]. A consequence of this heat input to the storage tank is the generally slow but continuous vaporization of the cryogenic liquid due to the low boiling point of the fluid. The new gas phase in the container is known as boil-off gas (BOG).

### **3.1. Description of hydrogen boil-off phenomenon**

The low temperature required to maintain H<sub>2</sub> in the liquid state implies the use of cryogenic tanks that, in addition to being mechanically robust, must be able to minimize heat transfer from the environment to the Dewar in order to prevent BOG from LH<sub>2</sub> (BOH). Despite the technological evolution of cryogenic tanks in terms of thermal insulation and materials used to construct the tanks, heat leakage will eventually occur, especially when LH<sub>2</sub> storage is planned for long periods. Therefore, the design of cryogenic tank must also consider proper internal pressure control to safely release excess gas from H<sub>2</sub> evaporation [18,41]. H<sub>2</sub> is inherently a difficult molecule to maintain in the liquid state due to its low boiling point, which complicates its liquefaction, but also due to its low enthalpy of evaporation (0.45 kJ/g) that is almost 18 times lower than that of liquefied natural gas (LNG).

Standard Dewars for long-term storage of LH<sub>2</sub> are usually equipped with a pressure relief valve (as shown in Figure 2), which allows H<sub>2</sub> gas to be vented when the internal pressure of the tank has reached the allowable value, e.g., 0.1013 MPa (typically  $\leq 0.6$  MPa [42]).

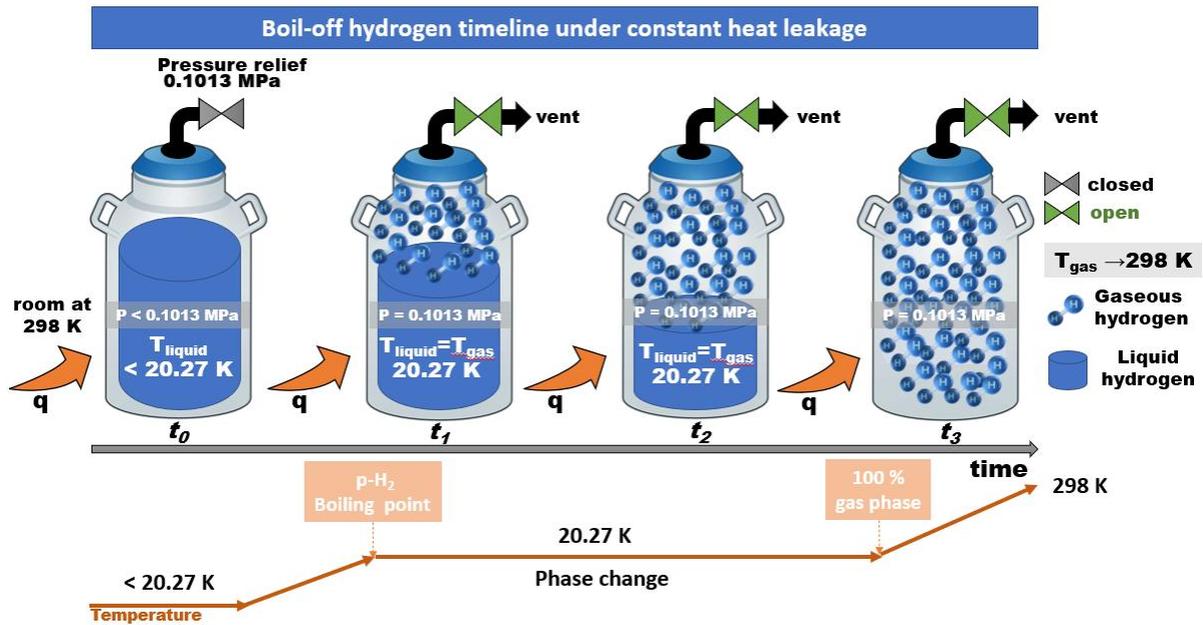


Figure 2. Graphical description of the boil-off hydrogen (BOH) phenomenon.

Figure 2 shows a sequential graphic representation of how a heat leakage,  $q$ , can result in BOH formation. Initially, at time  $t_0$ , the internal temperature of the system may be slightly below the boiling point of H<sub>2</sub> and the fluid is stored only in liquid form in a cryogenic tank equipped with a pressure relief device, which keeps the tank pressure at 0.1013 MPa or less. At any time between  $t_0$  and  $t_1$ , the heat may be able to overcome any energy transfer resistance imposed by the tank insulation layers. Although LH<sub>2</sub> evaporation is an endothermic process, the cooling provided by vaporization is insufficient to counteract temperature increase of LH<sub>2</sub> due to heat leakage. Thus, at a certain time  $t_1$ , the LH<sub>2</sub> temperature reaches the boiling point (20.271 K at 0.1013MPa for p-H<sub>2</sub>), which opens the safety valve and causes H<sub>2</sub> boil-off. The obtained BOH is in equilibrium with the LH<sub>2</sub> and, therefore, the density of each phase does not vary with time [43]. Once the allowable tank pressure is reached, the pressure relief device activates in order to control the internal tank pressure. As the thermal leakage continues inside the tank, the level of LH<sub>2</sub> (as shown at  $t_2$  in Figure 2) similarly decreases, causing the BOH to occupy the space that LH<sub>2</sub> no longer has. Finally, at a certain time  $t_3$ , the LH<sub>2</sub> will have completely transformed into gas, with the gas temperature increasing until it reaches ambient temperature.

### 3.2. Causes of boil-off hydrogen

BOH is an undesirable but somewhat unavoidable effect occurring in cryogenic tanks. Despite heat leakage is the most common cause of BOH, it is not the only one. According to Sherif et al. [34,44], BOH may be generated for the following reasons, detailed below:

- Ortho- to para-H<sub>2</sub> conversion
- Heat leaks (shape and size effect, thermal stratification, thermal overfill, insulation, conduction, radiation, cooling)
- Sloshing
- Flashing

During the hydrogen liquefaction process, H<sub>2</sub> is generally available under supercritical conditions at room temperature (~300 K) and must be cooled to 20 K. Under ambient conditions, the H<sub>2</sub> molecule is referred to as “normal H<sub>2</sub>”. The H<sub>2</sub> molecule has two atoms whose nuclei are rotating. Normal H<sub>2</sub> contains two spin isomers of H<sub>2</sub> of different composition: 75% ortho-hydrogen (o-H<sub>2</sub>) and 25% para-hydrogen (p-H<sub>2</sub>). In o-H<sub>2</sub> isomer, the hydrogen nuclei spin in the parallel direction while the nuclei of the p-H<sub>2</sub> isomer spin in the opposite direction, as illustrated in Figure 3a.

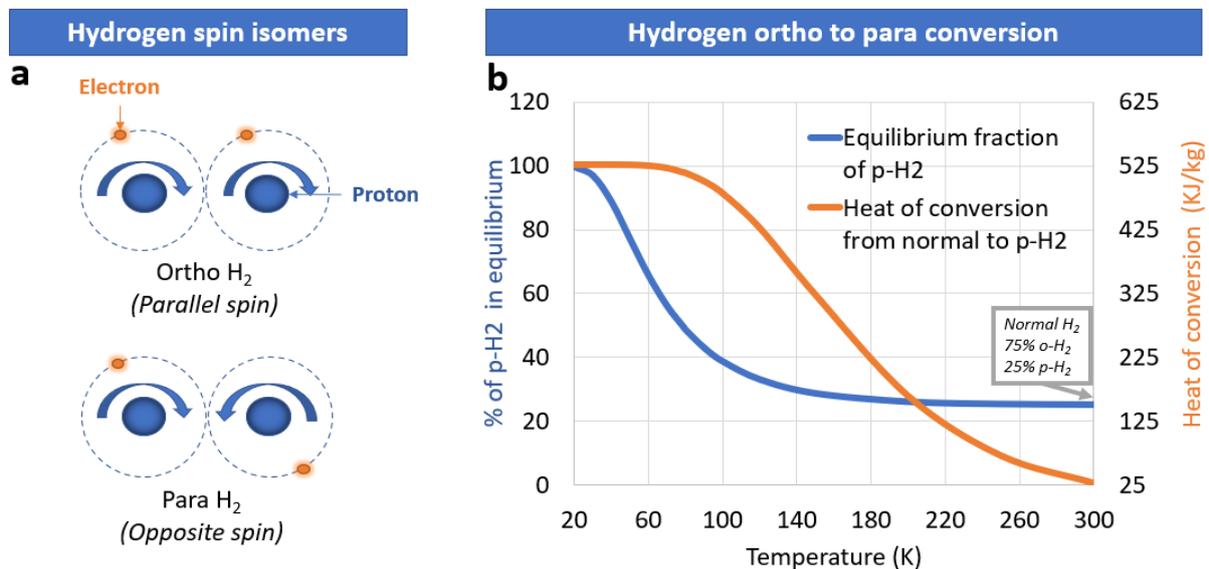


Figure 3. a) H<sub>2</sub> spin isomers; b) Equilibrium fraction of para-hydrogen (p-H<sub>2</sub>) and heat of conversion from normal to para-hydrogen as a function of temperature (after [45,46]).

The equilibrium concentration of o-H<sub>2</sub> changes with temperature. For example, as the temperature decreases, the equilibrium concentration of o-H<sub>2</sub> also decreases until the H<sub>2</sub> molecule is mostly p-H<sub>2</sub> at 20 K, when the H<sub>2</sub> becomes liquid. This reaction, known as ortho to para conversion, usually takes time since the perturbations involving the nuclear spins are small in magnitude [47] and a non-equilibrium mixture may occur [48]. The problem with storing LH<sub>2</sub> is that this spontaneous conversion is sufficient to vaporize up to 64% of the original LH<sub>2</sub> [49]. Catalysts are used at the industrial level to accelerate the rate of o- to p-H<sub>2</sub> conversion and avoid further boil-off losses during the H<sub>2</sub> liquefaction process. If H<sub>2</sub> liquefaction is carried out without catalytic conversion of o- to p-H<sub>2</sub>, the ortho isomer will be at a higher concentration than its equilibrium concentration and will thus spontaneously convert to the para isomer, generating a significant amount of heat [50]. The use of a catalyst generally requires a higher cooling load, and thus an efficiency penalty because the heat of conversion must be removed. Some catalysts include diamagnetic solids, such as germanium or silver [51], copper [52], oxides, including Fe<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, Gd<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub> [53], alumina-supported perovskites (LaFeO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>) [54] or gold nanoparticles [55] among others. Commercial oxide-based catalysts currently used for o- to p-H<sub>2</sub> conversion include IONEX® (Fe<sub>2</sub>O<sub>3</sub>.2%H<sub>2</sub>O) and OXISORB® (CrO.SiO<sub>2</sub>) [56]. The o- to p-H<sub>2</sub> conversion reaction is primarily due to magnetic properties [57], while the heat of conversion increases as the reaction from o- to p-H<sub>2</sub> proceeds, as shown in Figure 3b.

BOH formation due to heat leakage in cryogenic systems often occurs through radiation and conduction. Heat input can penetrate through insulation and conduction via pipes, access ports, internal shell supports, and instrumentation cables [40]. Materials with low thermal conductivity or the insertion of long heat transfer paths (e.g., by reducing the heat flow cross-section) can reduce convective losses, while various types of radiation shielding (e.g., multilayer insulation, boil-off vapor-cooled shields and opacifiers in powder insulation) can reduce radiation losses [40].

The type of insulation is critical to prevent BOH formation, i.e., the insulation design must be able to balance the savings from BOH reduction with the cost of the insulation system [40]. The boil-off rate can be different depending on the sophistication of the Dewar insulation technology, and the shape and the size of the tank. Since boil-off losses due to heat leakage are proportional to the surface-to-volume ratio, the boil-off rate decreases sharply as the storage tank size increases [58,59]. For spherical, vacuum-insulated, double-walled Dewars, boil-off losses are typically between 0.3 and 0.5 % per day for 50 m<sup>3</sup> storage tanks, 0.2 % for 103 m<sup>3</sup> tanks, and approximately 0.06 % for 19,000 m<sup>3</sup> tanks [60]. Nonetheless, the

BOH rate can even be higher than 0.5 % per day as reported by other authors. Klell [18] reported that most current LH<sub>2</sub> tanks may achieve boil-off losses between 0.3 % and 3 % per day. Similarly, BOH rate estimates around 1.5–3% per day have been reported elsewhere [58,61]. Linde, for instance, provides different types of LH<sub>2</sub> cryogenic tanks with different boil-off rates based on size, geometric shape and intended use. This company estimates that cylindrical tanks with a capacity of 300 m<sup>3</sup> can have boil-off rates of less than 0.3 % per day, while spherical tanks with a size between 1,100 and 2,300 m<sup>3</sup> have boil-off rates of less than 0.1 % per day [31,62]. Regardless of the BOH rate, the need for special design and more robust tank insulation to prevent LH<sub>2</sub> evaporation can increase the cost and the weight of the tank and thus reduce the gravimetric energy density of the system.

LH<sub>2</sub> tanks are generally of three types: *i*) double-jacketed tanks with liquid nitrogen on the outer jacket, *ii*) super-insulated tanks with reflective powder or multi-layer insulation (MLI), and *iii*) vapor-cooled shielded (VCS) tanks employing super-insulation [34,44] as graphically described in Figure 4. Multi-layer insulation (see Figure 4b) is considered the most effective thermal protection for cryogenic systems. The reason could lie in the fact that all types of heat transfer are mitigated by providing multilayer insulation with considerably low thermal conductivities. Thermal conductivity values of this insulation mode can be as low as 10 to 50 μW/mK at temperatures between 20 and 300 K. Typically, the alternating layers consist of reflective materials, namely aluminum foil or aluminized Mylar, and low-conductivity insulating materials, such as fiberglass mat or paper, glass cloth, or nylon netting, all under high vacuum [40].

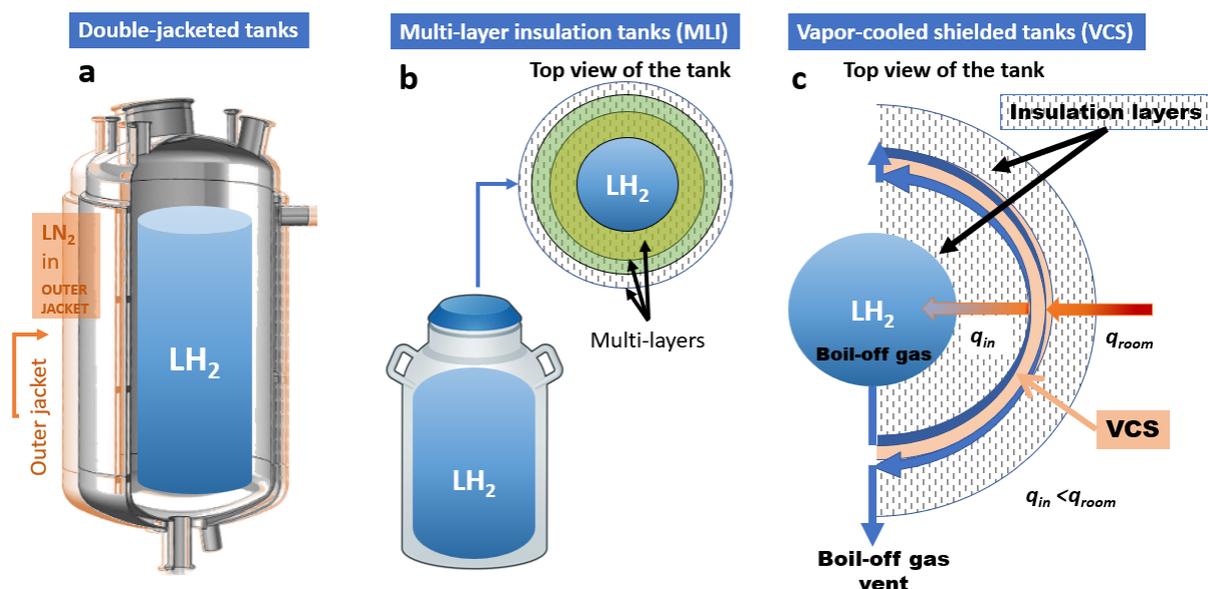


Figure 4. Illustrative examples of different insulations for liquid hydrogen (LH<sub>2</sub>) storage: (a) double-jacketed cryogenic tanks, (b) multi-layer insulation tanks, and (c) multi-

layer insulation with vapor-cooled shield (VCS) cryogenic tank. The terms  $q_{room}$  and  $q_{in}$  in Figure 4c refer to the ambient heat and the heat reaching the inner side of the tank, respectively.

Despite the effectiveness of multi-layer insulation systems, previous reports suggest that the addition of a vapor-cooled shield (VCS) will further reduce boil-off losses [34,44]. Xu et al. [63] estimated the optimization efficiency parameter  $\beta$  of a given VCS, which is defined as the decrease in the heat flux rate entering the cryogenic tank ( $q_{in}$  in Figure 4c) after the VCS is introduced into the insulation system. The results indicated that heat leakage can be significantly reduced once the  $\beta$  parameter can go up to 60.5 %. This substantial reduction in heat loss is determined by the heat exchange between the low-temperature BOH and the incoming ambient heat ( $q_{room}$  in Figure 4c), allowing for efficient use of the low-temperature sensible heat of the BOH prior to its reliquefaction or venting, as shown in Figure 4c [34,44,63].

Thermal stratification in the LH<sub>2</sub> can cause additional boil-off. Thermal stratification occurs when a fluid at different temperatures exists within a container, resulting in an increase in tank pressure [34,64]. Heat transfer from the walls and bottom of the vessel will always lead to an increase in the sensible enthalpy of LH<sub>2</sub>. If the heat leakage is sufficient to reach the interior of the vessel, the heat distribution tends to be uneven because the heat flow primarily occurs through free convection. Therefore, the warmer LH<sub>2</sub> rises to the surface, causing the temperature of the upper layers to be higher than that of the bulk liquid [44]. Under such conditions, the pressure inside the vessel corresponds to the vapor pressure of the temperature of the warmer upper layers of the LH<sub>2</sub>, which is in thermodynamic equilibrium with the BOH [34,64]. Therefore, the BOH must be vented to maintain the pressure of the tank, otherwise, the warmer stratified column of LH<sub>2</sub> can potentially cause cavitation and damage the LH<sub>2</sub> pump [44,64]. One way to reduce boil-off losses due to stratification is to use high-conductivity plates installed vertically in the tank. The plates produce low-resistance heat paths between the bottom and top of the tank and are therefore able to prevent excessive temperature gradients and pressures. Another way to overcome thermal stratification within the tank is to use a magnetic-type refrigerator to extract heat from the tank and maintain the LH<sub>2</sub> in subcooled or saturated conditions. Magnetic refrigerators are considered suitable for this task because of their high efficiency, reliability, and relatively low cost [34,44].

Transporting LH<sub>2</sub> by tank truck can also result in BOH due to hydraulic jumps that LH<sub>2</sub> may experience inside the tank. The movement of LH<sub>2</sub> due to acceleration or deceleration is known as sloshing and occurs when the impact energy due to the movement of LH<sub>2</sub> inside the

tank is converted into thermal energy. The thermal energy eventually becomes large enough to cause some evaporation of LH<sub>2</sub>. A possible solution to sloshing is the addition of cross baffles inside the tank to mitigate the impact forces during acceleration and prevent LH<sub>2</sub> movement [34,44]. Additionally, transport of LH<sub>2</sub> from high-pressure (between 0.24 and 0.27 MPa) to low-pressure Dewars (0.12 MPa) is another issue that can generate BOH [44]. The reason is the quick vaporization, known as the flashing phenomenon, occurring over the transfer of LH<sub>2</sub> from a tank to another with a difference of pressure. LH<sub>2</sub> transport at lower pressures (near atmospheric) is a way to mitigate boil-off formation due to flashing, though at the expense of storing a smaller volume of LH<sub>2</sub> [44,65].

In summary, the combination of different aspects, such as the heat leakage, low H<sub>2</sub> vaporization temperature, low pressure inside the tank, and transportation of the vessel itself, contribute to BOH generation during conventional LH<sub>2</sub> storage in Dewars [66,67].

#### **4. Boil-off hydrogen recovery solutions**

With the growing interest in using H<sub>2</sub> as an energy carrier, various storage options are being investigated and improved. In many LH<sub>2</sub> storage/transport applications, the BOH is simply released or vented to the atmosphere to prevent overpressure in the cryogenic tank. While it is true that this method can be the simplest way to eliminate BOH by avoiding investment in adequate infrastructure to use the gas for other purposes, venting a fuel is a waste of energy, especially for a gas that is expensive to liquefy [68]. Although H<sub>2</sub> venting is generally safe for the environment if the amounts released are small, venting can become hazardous when large amounts of BOH are vented into confined spaces. H<sub>2</sub> venting must be carried out with adequate safety precautions because of the risk of explosion if the evaporated H<sub>2</sub> meets oxygen or any oxidizing agent [68].

Since in most cases, the use of BOH requires additional infrastructure and energy, it is worth examining the feasibility of implementing a boil-off recovery solution. First, it is critical to minimize BOG generation whenever possible. State-of-the-art insulation systems are essential to prevent heat leakage into the LH<sub>2</sub> storage vessel. However, over extended periods, heat transfer is virtually unavoidable with passive cooling alone. To counter this, mitigation strategies incorporating active cooling with multilayer insulation, such as zero boil-off (ZBO), could be an attractive option. Nevertheless, ZBO may not be suitable for all types of applications since cryogenic tank design is quite sophisticated and is currently limited to

the spacecraft industry. Thus, boil-off recovery strategies, namely reliquefaction or compression of the  $H_2$  gas, must be considered. The choice of the type of recovery strategy depends on the industry, location and application of the  $LH_2$ , as well as the space available for additional facilities if required.

Reliquefaction can be an optimal option for  $LH_2$ -fueled applications or for  $LH_2$  transportation. The main drawback of this method is the need for additional adjacent space for the reliquefaction facility and the relatively high OPEX and CAPEX of the cooling process. Even though the BOH is initially at very low temperature, to convert BOH to  $LH_2$ , the gas must first be collected for further cooling [68]. During collection, the gas temperature increases, and thus the required cooling energy depends on the feed temperature of the BOH into the reliquefaction system. Compression can be a useful method to recover  $H_2$  in its gaseous state for various applications such as fuel cell vehicle refueling stations or high-pressure buffer storage. However, it is crucial to ensure that the recovery strategies employed are not overly expensive to maintain a positive OPEX, *i.e.*, the energy used to recover the BOH should not exceed its own cost [69].

#### **4.1. The Zero Boil-Off concept**

Since the 1960s, NASA has paid special attention to developing a solid understanding of the management of cryogenic propellants, such as  $LH_2$ , oxygen, and methane [70]. The primary motivation was NASA's interest in expanding human missions across the solar system, particularly the exploration of the planet Mars. For that purpose, space travel requires proper storage and management of cryogenics under microgravity conditions for long duration missions, which led NASA to implement cryogenic refrigeration systems such as the 20K cryocooler to achieve zero boil-off (ZBO) of  $LH_2$  [71]. In an attempt to achieve long-term  $LH_2$  storage on orbit, the ZBO storage system appears to be a combination of passive insulation technology (*i.e.*, multilayer and cooled shield) and active cooling technology, as described by Plachta et al.[72].

A cryocooler is a refrigerator that operates at cryogenic temperatures, and is therefore typically used to maintain a cryogen in its liquid state. In the case of  $LH_2$ , cryogenic refrigerators must be able to continuously remove a certain amount of "heat load" while maintaining the  $LH_2$  tank at 20 K. Thus, the main objective of the ZBO is to control the tank pressure without having to vent the BOH by using a cryogenic cooler and multi-layer

insulation similar to the scheme shown in Figure 5a. In other words, the ZBO system removes heat entering through the tank walls primarily by radiation, using a submerged finned heat exchanger coupled to the cooler [73].

A cryocooler coupled to a cryogenic tank must be able to remove the amount of heat load necessary to maintain the tank at the desired temperature. The maximum amount of heat load that a given cryocooler can handle is known as the “lift rate”. This rate is regularly given in units of energy per time, such as watts. For large propellant tanks in spaceflight, the main challenge is to increase the lift rate to achieve adequate removal of the heat load and, therefore, to achieve ZBO of the cryogen [71]. Although NASA has previously investigated two types of cooling cycles such as the reverse Brayton cycle and the Stirling cycle, in which the working fluid circulation directly cools the tank wall [71], the reverse Brayton cycle remains the preferred distributed cooling system [74]. ZBO in space propellant storage has evolved closely with advances in cryocooler technology under microgravity conditions in the 1980s and mid-1990s. The first ZBO proof-of-concept test was conducted at NASA Glenn Research Center in 1998 and the second was held at NASA Marshall Space Flight Center two years later. Both tests were conducted to evaluate the potential application of the ZBO using the existing components at the time [75].

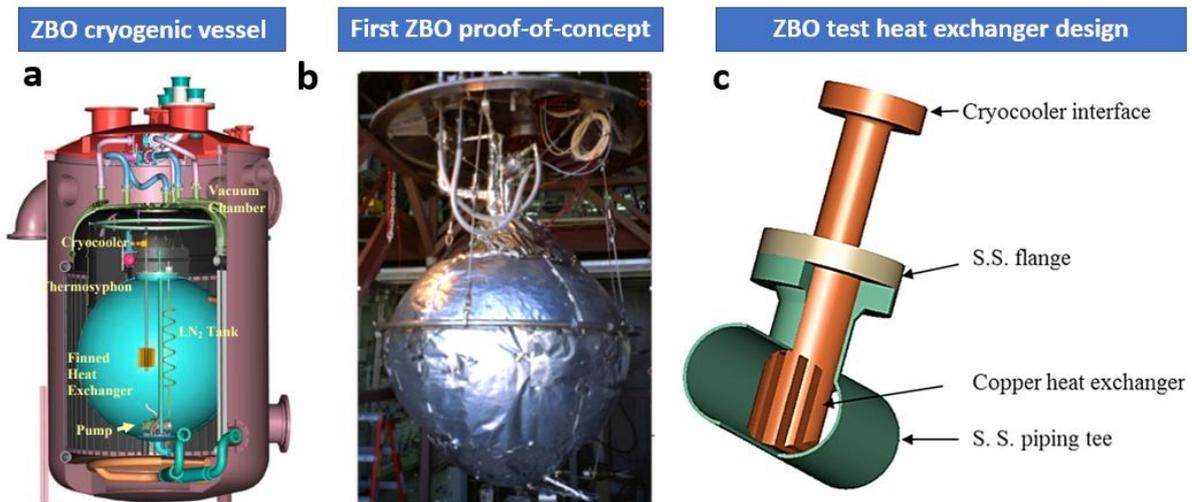


Figure 5. (a) Example of a cryocooler coupled to a cryogenic vessel (taken from Plachta et al. [73]), (b) First zero boil-off (ZBO) proof-of-concept tested at NASA Glenn Research Center facilities, and (c) LH<sub>2</sub> ZBO test heat exchanger design (Figures 5b and c were reprinted from Plachta et al. [71] with permission from Elsevier).

The Glenn Research Center test used an LH<sub>2</sub> cryogenic tank with multilayer insulation and a cooler, but under conditions not similar to those of a flight. The cryocooler was placed on top of the spherical cryogenic vessel, as shown in Figure 5b. Although the pressure record inside the tank showed a steady decrease demonstrating that the cryocooler could remove part of the heat load, the thermal gradient between the LH<sub>2</sub> and the cryocooler was high enough (~8 K) to cause a substantial loss of lift rate and thus an increase in power. At Marshall Space Flight Center, the ZBO test was conducted under more realistic flight conditions, since the LH<sub>2</sub> was pumped through a cooled bypass loop using a heat exchanger (see Figure 5c) coupled to the cryocooler. Although ZBO was easily achieved, some inefficiencies derived from heat leakage through the pump and bypass loop affected the successful operation of the system.

While each test had a purpose, the ZBO approach based on cooling the cryogenic fluid in the tank was abandoned in search of a better system to integrate the cryocooler for application in larger tanks. Therefore, new ZBO projects considering the integration of the cryocooler through a circulated gas loop coupled outside the tank have been proposed [76]. With this new cryocooler coupling system, heat removal was also achieved at the tank wall using a cooled shield placed in a multi-layer insulation [71]. ZBO systems for LH<sub>2</sub> storage in spaceflight are being consolidated. Open issues include the need to increase the lift rate while maintaining the cryogenic system at a practical size and weight suitable for NASA space missions. Promising results on the implementation of ZBO systems by NASA for liquid storage of oxygen [74] and nitrogen [77] have also been reported with boil-off reductions of almost 90 %.

## **4.2. Hydrogen reliquefaction**

The principles of reliquefaction are basically the same as those of liquefaction, except that the feed conditions can change. In this section of the review, before going into the details of current BOH reliquefaction strategies, some insights into state-of-the-art H<sub>2</sub> liquefaction processes are detailed.

Liquefaction of gaseous fuels is an inherently energy-intensive process, but it has the advantage of densifying the fluid and thus reducing storage volume and facilitating fluid transport. Of all the fuels that are gaseous under normal conditions, H<sub>2</sub> has the lowest boiling point. As an example, H<sub>2</sub> must be cooled to a temperature 90 K lower than natural gas (i.e., a boiling point of 110 K), which implies the use of more efficient thermally insulated tanks to

store the liquid [78]. Similarly, reaching a lower temperature implies a significant amount of additional energy to liquefy the gas. To give figures, liquefying  $H_2$  from ambient conditions theoretically and ideally requires about 10 times more energy than LNG, i.e.,  $3.92 \text{ kWh/kg}_{LH_2}$  versus  $0.31 \text{ kWh/kg}_{LNG}$  [79].

$H_2$  liquefaction can be divided into several steps, namely  $H_2$  compression, pre-cooling, cryocooling and liquefaction [80]. The  $H_2$  liquefaction process includes two cooling stages [81] as can be appreciated graphically in Figure 6a. In the first cooling stage, also called pre-cooling, the  $H_2$  feed gas is cooled to a temperature of around 80 K. In the second stage, the pre-cooled  $H_2$  passes through a heat exchanger to reach 30 K through a cryocooling system, which operates with refrigeration cycles such as the helium reverse Brayton cycle (possibly with  $H_2$  as well, but there is a minimum temperature limitation [80]) or the  $H_2$  Claude cycle [79]. Finally,  $H_2$  is liquefied by Joule-Thompson (J-T) expansion down to 20 K at atmospheric pressure. One of the main challenges in  $H_2$  liquefaction is the conversion of o- to p- $H_2$ . As discussed previously, this reaction is accompanied by heat release, which is greater than the latent heat of vaporization [82–84]. Therefore, to decrease the boil-off rate in storage tanks, catalysts are used during both cooling steps to accelerate the  $H_2$  conversion, as shown in Figure 6a (in yellow). The p- $H_2$  content after liquefaction processes is between 95 % and 98 % [85]. According to Aasadnia et al. [86], the specific energy consumption (SEC) of liquefaction plants is usually around 10-15  $\text{kWh/kg}_{LH_2}$  while EXE values are between 19 % and 24 % [6,86–89]. However, SECs can drop to values between 5 and 8  $\text{kWh/kg}_{LH_2}$  when considering large-scale conceptual liquefaction plants proposed in the literature [86].

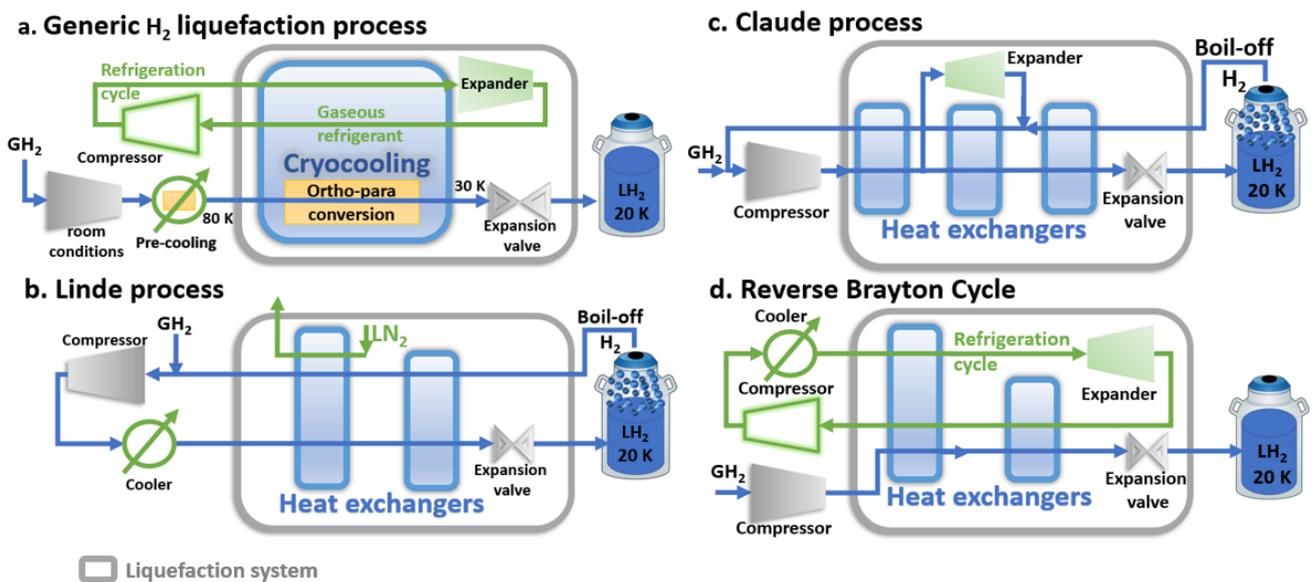


Figure 6. Simplified flow diagrams of: (a) a generic H<sub>2</sub> liquefaction system (based on Ref. [90]), (b) the Linde-Hampton process, (c) the Claude process, and (d) the reverse Brayton Cycle (Figures 6 b, c, d are based on Refs. [65,91]). LH<sub>2</sub> and GH<sub>2</sub> refer to liquid and gaseous H<sub>2</sub>, respectively.

Several refrigeration processes can be used for H<sub>2</sub> liquefaction, including the Linde process, the Claude process, and the reverse Brayton cycle. The Linde process, also known as the Linde-Hampson process, is similar to the refrigeration process pioneered by John Dewar, where liquid nitrogen (LN<sub>2</sub>) is used as the refrigerant. Since the boiling temperature of LN<sub>2</sub> is higher than that of LH<sub>2</sub> (77 K vs. 20 K), the primary purpose of nitrogen is to pre-cool H<sub>2</sub> below its J-T inversion temperature (200 K at atmospheric pressure) so that the H<sub>2</sub> can be expanded later via a J-T valve [65]. The J-T inversion temperature is defined as the point at which the J-T coefficient ( $\mu_{JT}$ ) becomes zero, indicating that an isenthalpic pressure drop no longer produces a change in temperature  $[(\partial T/\partial P)_h = 0]$  [92]. Any fluid expanding through a J-T valve will only cool down if it is below its J-T inversion temperature; otherwise, it will warm up. As a result, H<sub>2</sub> must not only be below 200 K, but its pressure must also be reasonably high before passing through the valve for successful liquefaction [91]. Chang et al. [91] thus conducted a study to determine the optimal pressure for maximizing the thermodynamic performance of a conventional Linde liquefaction system. They found that pressures of approximately 13 MPa are ideal, as indicated by the figure of merit (FOM). The FOM is calculated by dividing the minimum work required by the actual work, where the minimum refers to the exergy flow of H<sub>2</sub> and the actual work is the difference between the compressor input and expander output. Figure 6b shows a flow chart of the Linde-Hampson process where, in addition to LN<sub>2</sub>, low-temperature BOH is also used as a refrigerant.

The Claude process was first developed by Georges Claude in the early 20<sup>th</sup> century [93]. The main driving force for cryogenic cooling is an intermediate expansion step that uses a fraction of the compressed gas that is fed to the heat exchanger section, as shown in Figure 6c. The refrigerant in the heat exchanger section is H<sub>2</sub> gas from both the cooled expanded gas and the incoming cold BOH. The J-T expansion cannot be omitted because the expander (Figure 6c) is not intended for liquefaction but only for cooling since the expander usually does not handle liquid fluids [65]. Turbine expanders, such as radial flow turbines and axial flow turbines, are commonly used in H<sub>2</sub> liquefiers, leading to higher exergy efficiency. In industrial H<sub>2</sub> liquefaction processes, both types of expanders are used on the refrigeration side [89]. The Claude process configuration avoids the need for LN<sub>2</sub> cooling as in the Linde process. However, some authors have suggested that the introduction of an LN<sub>2</sub> pre-cooling

unit upstream of the liquefaction zone could lead to an increase in EXE of about 50-70% [94] since the mechanical energy of the turbine rotation can be recovered and better cooling is achieved [83].

In the reverse Brayton cycle, cryocooling is performed by a refrigeration cycle using helium as the coolant, as shown in Figure 6d. H<sub>2</sub> can be an alternative refrigerant, but helium is preferred because it has a lower boiling point and can therefore reach temperatures below 20 K in the gaseous state [91]. Reverse Brayton cycles can have various configurations depending on the arrangement and number of heat exchangers. For example, cycles can be simple (as in Figure 6d) with two heat exchangers, two-stage with an additional heat exchanger and an additional expander, and so on. The cycles can also include a pre-cooling section with LN<sub>2</sub> to reduce compressor work, although it is not mandatory [65]. In general, the reverse Brayton refrigeration cycle is less efficient than the Claude process, but it has the advantage of simpler and safer operation, because the pressure levels of the helium cycle can be much lower (1 MPa or less) [85,91].

Ejectors have emerged as useful devices for achieving high-efficiency refrigeration cycles in the liquefaction of liquid H<sub>2</sub> compared to conventional Claude, Linde or reverse Brayton cycles. An ejector is a work-producing device without moving parts that can enhance the efficiency of the refrigeration cycle by utilizing the high-pressure gas leaving the compressor to increase the cooling capacity of the refrigeration system [92,95]. Ejectors have a wide range of applications, including as jet pumps or compressors [92]. They are used to support vacuum operations [96] as well as for transfer and mixing pumps [97,98]. The use of ejectors can reduce throttling losses and increase the suction pressure of refrigeration systems, thereby reducing the compression work required for the process [99]. Rietdijk [100] was the first to suggest the implementation of ejectors in cryogenic cooling systems to generate sub-atmospheric pressure in a liquid helium evaporator, with the aim of achieving cooling temperatures below 4.2 K.

Cao and ter Brake [92] identified four main categories of ejector use in refrigeration systems:

- As a replacement for a compressor in a heat-driven refrigeration system [101].
- As a replacement for a J-T expansion valve in a refrigeration system [102].
- As a compressor in a vapor compression refrigeration system, providing a second step of compression to reduce the input energy required by a mechanical compressor [103].

- As a pump to drive a liquid recirculation loop, especially in refrigeration systems that use CO<sub>2</sub>, R134a, and R1234yf as working fluids [104–106].

During a typical J-T cryocooling process, a significant portion of the energy contained in the high-pressure gas is converted into kinetic energy, which cannot be used for work or expelled, and is instead dissipated as heat. As a result, a substantial part of the cooling potential associated with gas expansion is lost [107]. To illustrate the role of an ejector in a refrigeration cycle, a basic schematic of a Linde refrigeration cycle with an ejector and two heat exchangers is shown in Figure 7a, while the corresponding temperature versus entropy diagram of the refrigeration cycle with the ejector is presented in Figure 7b. In this cycle, the high-pressure gas (point 1 in Figure 7a) passes through heat exchanger 1 (HEX1), and is then split into two streams at point 2. One of the streams goes through heat exchanger 2 (HEX2) and is expanded by the J-T valve (between points 3 and 4), while the other stream is directed towards the ejector as the primary stream. The ejector, as shown in Figure 1c, primarily consists of a suction section with a nozzle, a mixing chamber and a diffuser. Figure 7d shows the pressure changes within the ejector as a function of its length. Inside the ejector, the high-pressure gas is initially passed through a nozzle in the suction section, which increases its velocity and reduces its pressure (2→X in Figures 7c, d). This low-pressure gas is then mixed with the secondary fluid coming from HEX2 (at point 6) in the mixing section of the ejector (X→Y in Figures 7c, d). Finally, the mixed gas is pressurized in the diffuser section, increasing its pressure and decreasing its velocity, before flowing to HEX1 at medium pressure (at point 7 in Figures 7c, d).

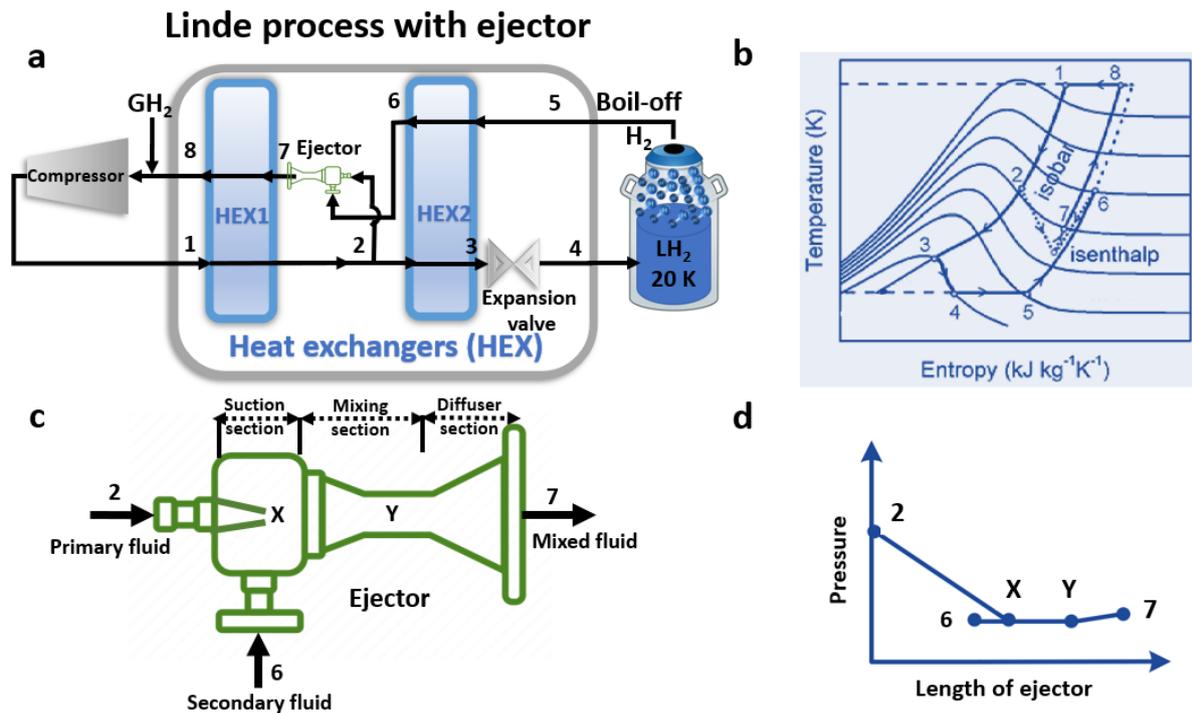


Figure 7. (a) Basic schematic of a Linde refrigeration process using an ejector with corresponding (b) entropy vs. temperature diagram (based on Ref. [107]); (c) schematic of ejector parts with example of a (d) pressure vs. length plot of the ejector (Figure c and d are based on Ref. [108] with the permission of the publisher John Wiley and Sons).

Most large-scale H<sub>2</sub> liquefaction plants are based on the Claude process with LN<sub>2</sub> pre-cooling, as reported by Bi and Ju [109]. This is primarily because of the lower specific energy consumption (SEC) of the Claude process compared to the other two fundamental liquefaction systems. Another reason is the simplicity of LN<sub>2</sub> pre-cooling, which, despite its low heat transfer efficiency, does not have a high investment cost. The maximum LH<sub>2</sub> production of existing plants worldwide is about 32 ton/day per liquefaction train [89]. For example, Praxair, a subsidiary of Linde, has several facilities in California, Alabama, Indiana and New York, in the USA, with production rates between 6 and 30 ton/day [93] and SEC values of about 12.5 and 15 kWh/kg LH<sub>2</sub> [84]. Praxair's new LH<sub>2</sub> plant in La Porte, Texas, USA, produces about 30 ton/day [110]. Linde's liquefaction facility with the Claude process in Ingolstadt, Germany, is capable of supplying 4.4 ton/day of LH<sub>2</sub> with a SEC of 13.58 kWh/kg LH<sub>2</sub> [111]. Also in Germany, Linde is expanding the existing H<sub>2</sub> liquefaction capacity of its LH<sub>2</sub> plant at the Chemical Park Leuna in southern Saxony-Anhalt. The company expects to produce 3,200 ton/year of LH<sub>2</sub> by the end of 2022 [112]. Air Liquide recently inaugurated its largest H<sub>2</sub> liquefaction plant in North Las Vegas, USA, with a production capacity of 30

ton/day to supply a wide range of industries, with future prospects in the growing fuel cell mobility market in California [113]. The company also plans to open a larger LH<sub>2</sub> production facility (90 ton/day) in South Korea after signing an agreement with SK E&S [114]. Available data on performance indicators such as EXE and SEC of current large-scale liquefaction plants are very limited [6]. On the other hand, small to mid-size liquefiers typically operate in a helium Brayton cycle or a hydrogen Claude cycle [115,116]. The choice of refrigeration cycle process is made based on plant capacity, location and electricity prices [6].

Refrigeration cycles for H<sub>2</sub> liquefaction are currently being extensively studied and modified with the aim of improving the EXE of the process and reducing the SEC of future large-scale liquefaction plants [84]. Numerous designs have been proposed to reduce both the CAPEX and OPEX of liquefaction plants and, consequently, the cost of the H<sub>2</sub> production chain [90]. Between 2011 and 2013, the IDEALHY (Integrated Design for Efficient Advanced Liquefaction of Hydrogen) project worked on the technological development of liquefaction plants at scales from 50 ton/day, aiming to reduce the SEC. The latter project, funded by the European Union's Seventh Framework Program, covered aspects including technology analysis and evaluation of the conceptual liquefaction process, process optimization, life cycle, economic and risk assessment, and preparation of a large-scale demonstration. In terms of technological advance, IDEALHY has demonstrated that it is possible to reduce the SEC from 11-15 kWh/kg<sub>LH<sub>2</sub></sub> to about 6.4 kWh/kg<sub>LH<sub>2</sub></sub> [117]. Other proposed H<sub>2</sub> liquefier designs have been published in the literature. Table 1 presents a summary of selected works with improved H<sub>2</sub> liquefaction system designs.

The performance indicators for the liquefaction plants presented in Table 1 were obtained from simulations performed primarily via Aspen Plus® or Aspen HYSYS®. SEC values below 10 kWh/kg<sub>LH<sub>2</sub></sub> and EXE values close to 50 % are higher than those of existing H<sub>2</sub> liquefaction plants, suggesting that, despite being merely theoretical estimates, they already give an idea of how much room for improvement there is in actual liquefaction plants. The US Department of Energy (DOE) has set the ultimate energy consumption target for H<sub>2</sub> liquefaction to 6 kWh/kg<sub>LH<sub>2</sub></sub> for large-scale 300 ton/day liquefaction plants [118]. Although this figure appears to be achievable by implementing process integration and proposed liquefaction design changes, the CAPEX for liquefaction systems remains an open issue [6], as they account for nearly 50% of the total liquefaction process assuming a plant capacity of 100 ton/day [90].

Table 1. Performance indicators for selected conceptual designs of H<sub>2</sub> liquefaction plants.

Author	Type of refrigeration process	Capacity Ton/day	SEC <sup>a</sup> kWh/kg <sub>LH<sub>2</sub></sub>	EXE <sup>b</sup> %
Asadnia et al. [119]	6-stage Linde-Hampson process and mixed refrigerant in a Brayton cycle for pre-cooling	100	7.69	39.5
Yin et al. [120]	Liquid nitrogen precooling and helium gas turbine expansion refrigeration	1.5	7.13	-
IDEALHY [121]	Mixed refrigerant (MR) pre-cooled Brayton cycle	50	6.7	32
Krasae-in [122]	Four cascaded H <sub>2</sub> Joule–Brayton cycles pre-cooled with a multi-component refrigerant.	100	5.91	39.1
Sadaghiani et al. [123]	Single mixed refrigerant cycle	130	7.64	32
Berstad et al. [124]	Mixed refrigerant (MR) Brayton cycle	86	5.91	39.1
Valenti and Macchi [125]	Cascade of four helium reversed, closed and recuperative Joule–Brayton cycle	952	5	47.73
Bi and Ju [109]	Helium expansion refrigeration cycle with mixed refrigerant (MR) pre-cooling	5	9.703	39.10
Jouybari et al. [126]	Compression-ejector refrigeration cycle is chosen to provide H <sub>2</sub> cooling from 298.1 K to 173.1 K, and cascade multi-component refrigerant cycle liquefies H <sub>2</sub> at 17.64 K	1930	7.405	23.59
Yin and Ju [127]	Helium gas turbine expansion refrigeration with LN <sub>2</sub> pre-cooling	1512	7.13	49.41

<sup>a</sup> Specific energy consumption, <sup>b</sup> Exergy efficiency

In the case where the H<sub>2</sub> gas feed comes from the boil-off, the process is called reliquefaction instead of liquefaction. The main advantage of boil-off reliquefaction is the possibility to perform cryogenic refrigeration without having to pre-cool the gas once H<sub>2</sub> is already at low temperature. This can result in substantial energy savings, as it is estimated that LN<sub>2</sub> production for the pre-cooling phase accounts for about 30 % of the energy consumption in H<sub>2</sub> liquefaction [128]. Another benefit is that the H<sub>2</sub> is already in the para isomer form, so catalytic conversion of o- to p-H<sub>2</sub> will not be necessary [81]. However, two issues that need to be considered in an LH<sub>2</sub> storage-reliquefaction facility to take advantage of the low BOH temperature. First, proper coupling of the reliquefaction system is vital to avoid collection of BOH in another tank and thus a significant increase in H<sub>2</sub> temperature. Second, a reliquefaction system must have the suitable volumetric capacity to handle the actual boil-off generation rate.

Lee et al. [129] assessed the potential use of a BOH reliquefaction system for LH<sub>2</sub> tankers using a hybrid LNG and H<sub>2</sub> propulsion system. The study considered partial BOH reliquefaction, i.e., a portion of the BOH was directly delivered to a fuel cell system at 0.1013 MPa, while the other portion was compressed to 4 MPa and then cooled by a reverse Brayton cycle before being expanded through a valve. Due to heat leakage in the pipes, the boil-off

feed was performed at 53 K to the reliquefaction system. The SEC was estimated at 3.30 kWh/kg  $\text{LH}_2$  [129], a value lower than the characteristic SECs for liquefaction processes from ambient conditions. Choi et al. [81] also performed a study of partial reliquefaction of  $\text{LH}_2$  with a reverse Brayton cycle. Similar to the work of Lee et al., the non-liquefied  $\text{H}_2$  fraction went into a fuel cell to generate electricity. The SEC values obtained ranged from 8.8 to 10.8 kWh/kg  $\text{LH}_2$  when the reliquefaction-to-generation fraction increased from 10 to 100%.

### **4.3. Hydrogen compression**

BOH can be compressed for direct use in fuel cells or for buffer storage. However, compressing BOH at cryogenic temperatures is a major engineering challenge, not only because current commercial compressors hardly work with fluids at such a low temperature (20 K), but also because of the energy required for possible upstream  $\text{H}_2$  heating. In an earlier work by our research group, Sdanghi et al. [130] extensively covered various aspects related to different types of compressors for  $\text{H}_2$ , such as those in Figure 8, including technical and design features, principle of operation, applications, performance level as a function of pressure range, and advantages and disadvantages.

In this section of the review, our intention is to revisit the different compression solutions that could be employed for BOH by identifying commercially available compressors, with an emphasis on non-mechanical compressors. Due to their compactness, negligible noise, superior efficiency, lack of wear and moving parts, non-mechanical compressors are considered a potential alternative to traditional mechanical compressors. Unfortunately, their diffusion on the markets is not yet sufficient because the level of maturity of the different types of non-mechanical compressors is different or because some of them do not yet have the appropriate  $\text{H}_2$  delivery capacity for certain high-pressure applications.

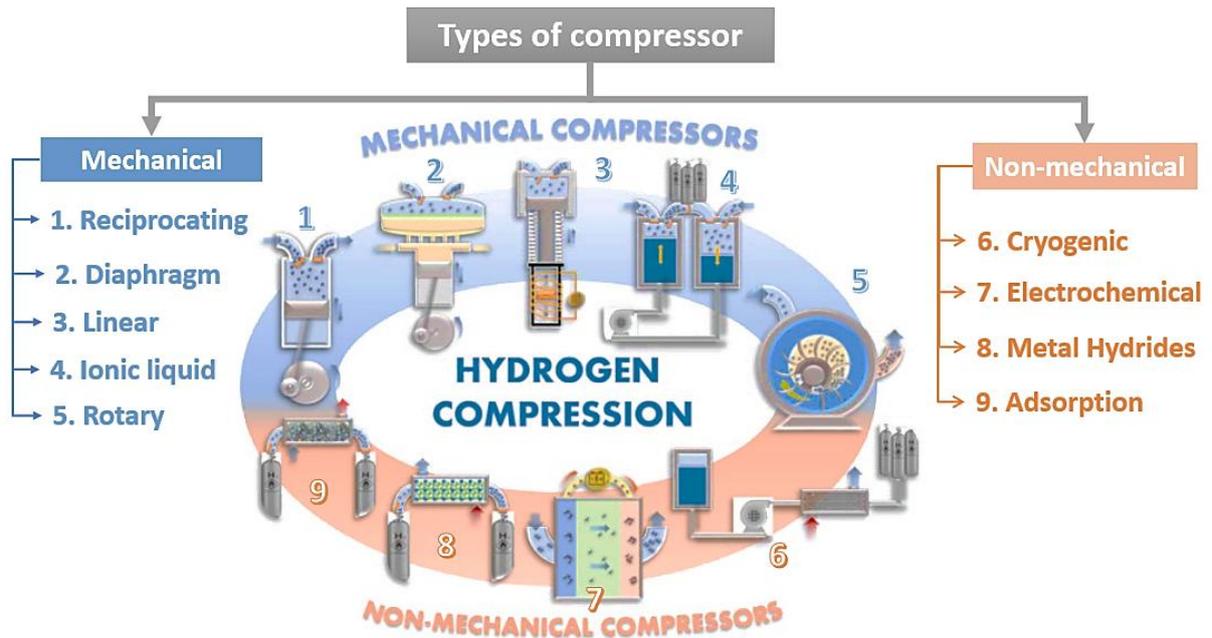


Figure 8. Graphical summary of the different types of H<sub>2</sub> compressors (reprinted from Sdanghi et al. [130] with permission from Elsevier).

Since there are many different types of compressors, it is not easy to decide which type would be the most suitable for a certain application because many aspects have to be considered: volumetric capacity and operating pressure range, compressor efficiency, energy consumption, footprint, additional infrastructure needed for operation, investment cost, noise level, among others. For BOH compression, there is also the question of whether or not the compressor can operate at 20 K. Figure 9 shows a basic scheme of an LH<sub>2</sub> gasification system. H<sub>2</sub> is stored in liquid form and, when needed, H<sub>2</sub> is pumped and vaporized to the target pressure.

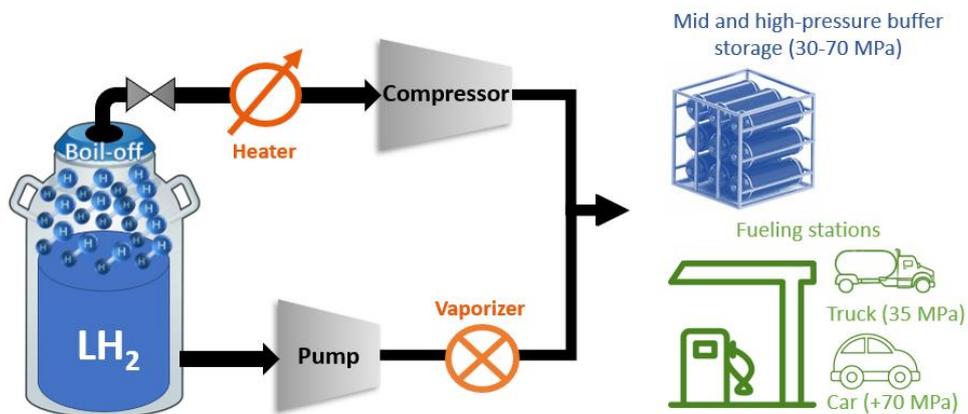


Figure 9. Basic scheme of an LH<sub>2</sub> gasification system.

To avoid boil-off losses due to venting, the BOH must be compressed to eventually rejoin the vaporized H<sub>2</sub> stream, as shown in Figure 9. In theory, the most practical solution for boil-off compression would be a compressor capable of handling BOH at its original temperature, as is the case in the LNG industry, where boil-off compression is a mature operation. However, to our knowledge, BOH compressors operating at 20 K do not exist commercially. One possible reason is that the boiling temperature of H<sub>2</sub> is nearly 90 K lower than that of natural gas, but also that H<sub>2</sub> poses additional operational challenges, such as material embrittlement or gas seal reliability at this temperature. Another likely cause is that the growing interest in LH<sub>2</sub> as a fuel or energy carrier is more recent than for LNG., i.e., the H<sub>2</sub> industry is technologically less mature than LNG. If BOH compressors evolve sufficiently from an operational and design standpoint, inserting a heat exchanger in front of the compressor (as in Figure 8) is an alternative way to increase the BOH temperature, allowing compressors to operate at higher temperatures. Nonetheless, this would imply additional energy expenditure.

#### *4.3.1. Commercial hydrogen compressors*

In this section of the review, we mainly provide information on non-mechanical compressors and atypical mechanical compressors, such as ionic liquid compressors. These compressors, which have been developed by private companies, are commercially available.

LH<sub>2</sub> shipping compressors and BOH compressors have already been tested on a 9,000 km journey from the eastern coast of Australia to Kobe Airport Island in Japan in 2020. A centrifugal compressor for BOH, designed by Atlas Copco Gas and Process, was set up to operate at 20 K in this LH<sub>2</sub> shipping pilot study conducted by Kawasaki Heavy Industries (KHI). The single-stage turbo compressor was used to ensure that H<sub>2</sub> remained at 20 K in liquid form. The BOH was stored on board after in situ liquefaction in a 116 m-long, 8,000-ton cylindrical tank in a 1,250-m<sup>3</sup> double-jacketed, vacuum-insulated, single tank [131].

While mechanical compressors are known to be noisy due to their numerous moving parts, ionic liquid compressors have the lowest noise level among mechanical compressors as they have fewer moving parts and mechanical seals, so they operate almost at isothermal compression. Linde's expertise in H<sub>2</sub> compression is based on ionic liquid systems. The company offers a broad portfolio of standardized compressors with H<sub>2</sub> delivery capacities of up to 900 kg/day at a maximum pressure of 90 MPa and up to 1,344 kg/day at a maximum pressure of 50 MPa [132]. The ionic compressor 90©, for example, has a flexible range of

allowable inlet pressures from 0.6 to 20 MPa and an energy consumption of up to 3.3 kWh/kg H<sub>2</sub> with a noise level of 70 dB at a distance of 10 m [133].

The US company Air Products is proposing a Cryogenic Hydrogen Compressor (CHC) system with a pump claimed to be able to operate with both vapor and liquid phases without the need of an additional compressor [134]. While most LH<sub>2</sub> pumps only work with liquids, Air Products appears to have designed a two-phase flow compression process capable of pumping LH<sub>2</sub>, capturing the BOH, and delivering this gas into the process at high pressures. All without the need to preheat the BOH. Additionally, the cryogenic compressor technology is load-following, which means the compressor supplies the required flow rate to the process at any given time. The CHC has a H<sub>2</sub> delivery capacity of up to 57 m<sup>3</sup>/h at 289 K under pressures up to 69 MPa [134]. Although this solution seems very advantageous since a single pump can compress both BOH and LH<sub>2</sub>, it is not clear whether the compression of both phases is performed at the same time or in alternating phases. Moreover, no information regarding footprint or power consumption is provided in the company's commercial brochure.

The Dutch company HyET Hydrogen offers modular designs of electrochemical compressors (EHCs) consisting of various stacks. The more stacks, the higher the compressor capacity. This company thus offers a wide variety of standardized EHCs with several H<sub>2</sub> flowrate capacities ranging from 2 to 600 kg/day and an outlet pressure of almost 90 MPa [135]. According to HyET Hydrogen, OPEX and CAPEX are very competitive with mechanical compressors: OPEX is around 0.30-0.60 USD/kg H<sub>2</sub> and CAPEX between 150 and 300 USD/kg H<sub>2</sub>/day (compared to a CAPEX of 1000-1500 USD/kg H<sub>2</sub>/day for mechanical compressors) [136]. Skyre Inc. offers smaller capacity EHCs, about 0.6 kg/day. The EHC, which was designed and proven for NASA, is based on a patented electrochemical technology for a wide range of applications in the emerging H<sub>2</sub> energy, fueling and storage markets. Additionally, as it is the differentiating characteristic of EHCs, the system is able to capture, separate and compress H<sub>2</sub> up to 20 MPa from a variety of mixed gas streams such as biogas, natural gas reformat, syngas or effluent from a given industrial process [137].

Giner ELX Inc, based in the USA but acquired in 2020 by Plugpower, also headquartered in the USA, has created standard EHC systems with H<sub>2</sub> flow rate delivery of either 10 kg/h or 0.5 kg/h, operating at inlet pressures of about 0.1-10 MPa and achievable outlet pressures up to 87.5 MPa. The company claimed to have made progress in addressing EHCs issues such as membrane durability and reproducibility, as well as substantially reducing H<sub>2</sub> back diffusion. Consequently, it has achieved stack efficiencies in the range of 2.0 kWh/kg H<sub>2</sub> at 350 MPa and 4.4 kWh/kg H<sub>2</sub> at 87.5 MPa [138].

Standard hydrogen metal hydride compressors from Hystorsys can operate with capacities ranging from 1 Nm<sup>3</sup>/h up to 12 Nm<sup>3</sup>/h (8.5 to 25.5 kg/day) and achieve pressure levels up to 25 MPa. The compressors are based on a flexible and expandable design. Hence, if more H<sub>2</sub> delivery capacity is required, additional compression chambers can be added to increase the volumetric capacity[139]. A metal hydride compressor requires thermal management since its operation is driven by absorption/desorption cycles. Hystorsys compressors use hot and cold water for that purpose. Typical inlet temperatures are 288-298 K (cooling) and 358-368 K (heating). No information on the type of alloy is provided by the manufacturer.

The most relevant features of the commercial H<sub>2</sub> compressors described above are summarized in Table 2 for comparison purposes. As shown in Table 2, with the exception of the Air Products cryogenic compressor system, all other compressors require BOH pre-heating because their minimum inlet temperature ( $T_{in}$ ) is above 258 K.

Table 2. Comparison of various characteristics of different commercial H<sub>2</sub> compressors.

Compressor type	$P_{in}$ (MPa)	$P_{out}$ (MPa)	Flowrate (kg/day)	$T_{in}$ (K)	Footprint	CEC* (kWh/kg H <sub>2</sub> )	Supplier/reference
Cryogenic	0.1	69	up to 129	20	No data	No data	Air Products [134]
Electrochemical	0.3-1.5	up to 90	2, 10, 120-200, 500-2000	$\geq 298$	For the 10 kg/day: 1.5m $\times$ 0.9m $\times$ 2.0m	For 10 kg/day: 8.5	HyET Inc. [135]
Electrochemical	0.1-10	87.5	up to 0.42	$\geq 298$	No data	4.4	Giner ELX [138]
Electrochemical	0.1-1.4	2-20	0.6	$\geq 298$	1.27m $\times$ 0.76m $\times$ 0.66m	No data	Skyre Inc. [137]
Ionic liquid	$\geq 0.8$	up to 70	216	$\geq 258$	8m $\times$ 2.4m $\times$ 4.1m	1-3.3	Ionic compressor 90©, Linde [133]
Metal Hydride	0.2-3	25	8.5-25.5	258-298	No data	No data	Hystorsis [139]

\* Compression Energy Consumption

The only type of non-mechanical compressor excluded in the previous table and section was the adsorption compressor. To our knowledge, no adsorption compressor is commercially available today. Although the adsorption compressor concept is not new, the technology still

requires more sophistication in terms of thermal management to reach a higher level of maturity. Adsorption compressors for applications other than H<sub>2</sub> compression have already been reported in the literature since the 1980s. In the field of cryocoolers, kinetic studies of adsorption compressors have been performed by NASA's Jet Propulsion Laboratories in Pasadena, California [140]. More recently, the concept has been applied to methane compression using metal organic frameworks and activated carbons as adsorbents [141]. Santori and Luberti [142] performed a thermodynamic analysis of the compression of multicomponent gas/vapor mixtures with a thermally driven adsorption bed using zeolites and activated carbons. Although the application of the compressor is unclear, the study can be considered a consistent thermodynamic investigation of adsorption compression of multicomponent gas mixtures based on adsorbed solution theory applied to closed vessels.

Sdanghi et al. [143] built a proof-of-concept compressor based on thermally driven adsorption/desorption cycles using activated carbons with high BET area ( $\geq 3,000 \text{ m}^2/\text{g}$ ). Cyclic experiments comprising a cooling and a heating step were performed from an initial pressure of 8 MPa at 77 K to a final pressure of 70 MPa in a single step when heating the compressor to 315 K. This thermally driven compressor, which consisted of a prototype cylinder of 0.5 L containing approximately 0.135 kg, demonstrated that several textural properties of the activated carbons, including high surface area, large micropore volume, as well as very narrow pores, are of utmost importance to its successful performance. In a follow-up study, Nicolas et al. [144] focused on the optimization of the latter compressor by performing a parametric study under a variety of possible thermal conditions by modeling and simulating the delivery operation of the compressor using an axisymmetric 2D geometry in COMSOL Multiphysics®. Different operating variables, such as H<sub>2</sub> flow rate, temperature and pressure, were investigated under three different power inputs for the desorption step (100, 200 and 300 W). The results indicate that the higher the power, the higher the H<sub>2</sub> discharge load, and that the amount of H<sub>2</sub> delivered has an almost linear relationship with the final set temperature, as long as it does not exceed 500 K. The authors concluded that increasing convective heat transfer with the surrounding air can reduce the time to reach room temperature by almost 75%.

## **5. Alternative solutions to boil-off and outlook**

In an attempt to minimize H<sub>2</sub> boil-off losses during storage, adsorbents have been used to confine H<sub>2</sub> in their nano-porosity. This approach allows for even higher H<sub>2</sub> densities than

those achievable by LH<sub>2</sub> and extends the dormancy period to higher temperatures than traditional cryogenic tanks. The use of highly porous adsorbents in cryo-adsorption-based storage systems offers a promising alternative for transporting H<sub>2</sub> over long distances while achieving high volumetric density that is comparable to LH<sub>2</sub> and reducing boil-off losses.

Oh et al. [145] found that the use of cryo-adsorption on Metal Organic Framework (MOF) pellets at 20 K could be advantageous for industrial applications compared to typical LH<sub>2</sub> storage. This is due to the wider operating temperature range without boil-off losses, up to 37 K. The researchers used MIL-101(Cr) MOF to control the pressure increase of BOH caused by heat leakage. In a separate study, Park et al. [146] explored cryo-adsorption H<sub>2</sub> storage on five different MOFs as a potential solution to minimize boil-off losses for the purpose of enhancing dormancy during continental transportation. They observed that van der Waals interactions between the adsorbate and adsorbent in these MOFs results in superdense H<sub>2</sub> adsorption at 20 K, compensating for the space occupied by the adsorbent skeleton, resulting in a volumetric storage capacity comparable to that of LH<sub>2</sub> tanks (~96 %). The temperature at which H<sub>2</sub> desorption starts depends on the textural properties of the MOFs, resulting in an extended dormancy time for the tank system. In support of their findings, in situ neutron scattering experiments revealed that H<sub>2</sub> molecules are firmly attached and immobile at the adsorption sites, even above the H<sub>2</sub> boiling temperature. Gi et al. [147] confirmed the superdense state of H<sub>2</sub> not only on MOFs but also on activated carbons at temperatures below 33 K and at 0.1013 MPa.

To mitigate effectively boil-off losses in LH<sub>2</sub> storage and enable more efficient and cost-effective H<sub>2</sub> utilization, improvements to the current strategies outlined in this manuscript are needed. One such strategy is the SEC reduction of existing liquefiers to values below 10 kWh/kg LH<sub>2</sub>, resulting in lower corresponding costs for the reliquefaction process. Advanced monitoring and control systems should also be developed to accurately predict boil-off rates, as accurate assessment of pressurization dynamics, thermal stratification, and boil-off rates in LH<sub>2</sub> storage are critical for the design and operation of storage tanks.

Transferring the knowledge, developed over the decades in ZBO technology, to applications other than the aircraft industry would also allow for the development of more efficient and cost-effective cryogenic storage and transfer systems. Furthermore, exploring the development of cold compression at 20 K at a Technology Readiness Level (TRL) of 5 or higher could be an alternative for utilizing the BOH generated, which can then be stored for

later use. Future research should also focus on innovative porous materials, with high adsorption capacity and thermal stability, for H<sub>2</sub> storage that can prolong the dormancy periods.

## **6. Final remarks**

In this review, the current status of the three most relevant pathways to minimize and recover H<sub>2</sub> evaporation, such as zero boil-off, H<sub>2</sub> reliquefaction, and H<sub>2</sub> compression, has been thoroughly described for the first time. ZBO is a concept involving the use of both passive and active insulation technologies by direct connection of the cryogenic cooler to the H<sub>2</sub> tank and multi-layer insulation. H<sub>2</sub> reliquefaction also implies that BOG must become liquid as in ZBO. The main problem with H<sub>2</sub> reliquefaction systems is the cost of liquefaction. In the space industry, budgetary issues are not a concern, while in reliquefaction systems, for example in stationary applications, it must be considered to what extent reliquefaction can be a cost-effective option. An important advantage is that H<sub>2</sub> is already at low temperature, so the o- to p-H<sub>2</sub> catalytic conversion is not necessary if the reliquefaction process is properly integrated into the cryogenic LH<sub>2</sub> tank. Finally, H<sub>2</sub> compression will play an important role in the deployment of the hydrogen economy, since many applications of gaseous H<sub>2</sub> require high pressures (> 30 MPa). Non-mechanical compressors are attracting a lot of attention because they are more compact, quieter, more efficient and less expensive than traditional mechanical compressors. However, most commercially available non-mechanical compressors are not suitable for operating at the boiling temperature of H<sub>2</sub>, which requires a heater to raise the inlet gas temperature. New non-mechanical compressors with inlet gas temperatures near 20 K may be beneficial in advancing LH<sub>2</sub> logistics and, in turn, contribute to the global energy transition.

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