Liquid

L Bonadio, Luigi Bonadio & Associates, East Brunswick, VIC, Australia

© 2009 Elsevier B.V. All rights reserved.

Introduction

Interest in the broad application of hydrogen as a fuel or energy carrier is largely attributable to the unique physical and thermodynamic properties of the gas, the diversity of resource and energy sources from which it can be derived, and its potential for reducing environmental impacts. Hydrogen can be obtained via a broad range of conversion processes that include the steam reformation or partial oxidation (together with a water–gas shift reaction) of fossil fuels such as natural gas, liquefied petroleum gas (LPG), diesel fuel, methanol and ethanol; the gasification of coal or biomass; the dissociation of ammonia; the electrolysis of water (using fossil fuel, renewable, and nuclear energy); and biomass conversion processes (gasification, photo-biochemical, fermentation). Hydrogen can be transported by pipeline, tanker, barge, ship, or airplane and dispensed to end users via dedicated fueling stations.

In addition to a broad range of industrial uses, hydrogen can be employed as a versatile fuel for land, sea, and air transportation, as well as for stationary and portable power generation applications. Hydrogen can fuel either an internal combustion engine or a gas turbine to produce mechanical power and heat, or a fuel cell to produce electricity and heat. The implementation of hydrogen-based technologies, when considered across the entire energy supply chain, has the potential to reduce the global and local environmental impacts of conventional energy supply and transportation infrastructure. Hydrogen is also regarded as a comparatively safe fuel.

The development of efficient and practical hydrogen storage technologies is critical to the technical and economic viability of hydrogen and fuel cell technologies. Hydrogen can be stored in a number of physical states, namely, as compressed gaseous hydrogen (CGH_2), cryogenic liquid hydrogen (LH_2), cryo-compressed hydrogen (CcH_2), or in a solid-state form. The selection of the most suitable hydrogen storage technology for a given application is dependent on energy, power, and hydrogen purity requirements, the scale and complexity of the engineering system where the hydrogen is to be used, and the capital and operating costs.

Hydrogen Liquefaction

Consideration of the unique physical and thermodynamic properties of normal, compressed, or liquefied states of hydrogen, as presented in **Table 1**, is fundamental to the technical design and efficient operation of hydrogen liquefaction plants and LH_2 storage systems. Since all gases occupy less volume at low temperatures, hydrogen gas can be cooled to form LH_2 via the process of cryogenic liquefaction. Cryogenics, derived from the Greek word *kryos* meaning 'icy cold', is the study of matter at very low temperatures (below 120 K).

The first systematic investigations of low-temperature phenomena were conducted by Francis Bacon in 1627. Refrigeration techniques for gas liquefaction were developed by Werner Siemens in 1857 and other pioneers of applied thermodynamics that included Claude, Hampson, von Linde, Kirk, Coleman, and Solvay. In 1883, Zygmunt von Wroblewski achieved the static liquefaction of oxygen and air and, in 1885, he accurately reported on the critical temperature, critical pressure, and boiling point of LH_2.

On 10 May 1898 at the Royal Institution in London, the Scottish chemist and physicist Sir James Dewar (**Figure 1**) applied a regenerative cooling process in a vacuum-insulated, double-walled, silvered-glass vessel not only to liquefy hydrogen at its normal boiling point (NBP), but to sustain the gas in the liquid state over a few days. He precooled gaseous hydrogen with liquid nitrogen under a pressure of 18.2 MPa, and then passed the hydrogen through an expansion valve. The outer jacket of the 'Dewar flask' or 'dewar' was filled with liquid nitrogen under vacuum to provide additional cooling and insulation from heat leakage. Dewar accurately determined the density of LH_2 at 70.973 kg m^{-3}. In 1904, a hydrogen liquefier designed by Dewar was exhibited in St Louis, USA. Hydrogen liquefaction plants were in operation from 1905 in Germany and France, and from 1907 in the United States. The work of Dewar made a significant contribution to present-day cryostats that are used for the industrial storage and bulk transport of LH_2 and other liquefied gases such as oxygen, nitrogen, air, fluorine, and helium. Refinement and miniaturization of his design also led to the common domestic vacuum flask, or 'thermos' bottle.

In 1929, the hydrogen diatomic molecule was discovered to exist in two isometric forms: hydrogen with odd rotational levels (symmetric nuclear spin function or parallel nuclear spins), called *ortho*-hydrogen (o-H_2); and hydrogen with even rotational levels (antisymmetric nuclear spin function or antiparallel nuclear spins), called *para*-hydrogen (p-H_2). Hydrogen liquefaction involves the progressive conversion of o-H_2 to p-H_2 with

Table 1 Physical and thermodynamic properties of hydrogen

General data	Chemical formula	H_2
	Molecular weight	2.016g mol^{-1}
	Liquid/gas equivalent at 288 K, 0.1 MPa	844 vol/vol
	Expansion ratio, liquid to gas, NBP to 293 K	1–845
Gaseous hydrogen (GH_2)	Density, gas at 293 K, 0.1 MPa	0.083 76 kg m^{-3}
	Density, gas at 273 C, 0.1 MPa	0.089 88 kg m^{-3}
	Energy density, gas at 293 K, 35 MPa	2.88 kJ m^{-3} (0.8 MW h m^{-3})
	Energy density, gas at 293 K, 70 MPa	4.68 kJ m^{-3} (1.3 MW h m^{-3})
	Specific volume at 293 K, 0.1 MPa	11.93 m^3 kg^{-1}
	Specific gravity, gas (air = 1) at 293 K, 0.1 MPa	0.069 98
	Latent heat of vaporization at NBP, 0.1 MPa	0.446 MJ kg^{-1}
	Flammable limits in air	4–75 vol%
	Autoignition temperature at 0.1 MPa	297.85 K (571 °C)
	Normal boiling point of H_2	20.39 K (−252.76 °C)
Liquid hydrogen (LH_2)	Normal boiling point of *para*-H_2 at 0.1 MPa	20.27 K (−252.88 °C)
	Triple-point temperature at 0.1 MPa	13.9 K (−259.3 °C)
	Inversion temperature	193 K (−80.15 °C)
	Triple-point pressure	0.007 2 MPa
	Critical pressure	1.298 MPa
	Critical temperature	33.0 K (−240.2 °C)
	Critical density	30.12 kg m^{-3}
	Density at NBP, 0.1 MPa	70.973 kg m^{-3}
	Specific gravity at NBP [water = 1 at 293 K]	0.071 0
	Specific heat at NBP, 0.1 MPa	0.009 7 MJ kg^{-1} K^{-1}
	Specific energy (LHV)	120 MJ kg^{-1} (33.33 kW h kg^{-1})
	Specific energy (HHV)	142 MJ kg^{-1} (39.47 kW h kg^{-1})
	Energy density at 26 K, 0.4 MPa	7.56 MJ m^{-3} (2.1 MW h m^{-3})
	Ideal work of liquefaction (hydrogen)	11.62 MJ kg^{-1} (3.228 kW h kg^{-1})
	Ideal work of liquefaction (nitrogen)	0.745 MJ kg^{-1} (0.207 kW h kg^{-1})
	Heat of transformation from normal LH_2 to *p*-H_2	0.526 MJ kg^{-1} (0.146 kW h kg^{-1})
	Heat of liquefaction	0.443 MJ kg^{-1} (0.123 kW h kg^{-1})
	Entropy at 300 K	37.695 9 kJ kg^{-1} 1 K^{-1}
	Entropy at 20 K	−3.3529 kJ kg^{-1} 1 K^{-1}
	Enthalpy at 300 K	0.0047 MJ kg^{-1}
	Enthalpy at 20 K	0.4087 MJ kg^{-1}

HHV, higher heating valve; LHV, lower heating valve; NBP, normal boiling point

simultaneous cooling. The equilibrium between *o*-H_2 and *p*-H_2 is temperature dependent, as presented in **Figure 2**. Hydrogen consists of 25% *o*-H_2 and 75% *p*-H_2 at room temperature, and 52% *o*-H_2 and 48% *p*-H_2 at the NBP of nitrogen, 77.4 K. In theory, LH_2 would exist as 100% *p*-H_2 at 0 K.

Liquefaction is an exothermic cooling process owing to the difference in the energy state, and therefore the enthalpy, between the two hydrogen spin states. The ideal heat of transformation, 703 kJ kg^{-1}, is greater than the heat of vaporization, 445 kJ kg^{-1}, so any *o*-H_2 remaining after liquefaction will evaporate. As much as 50% of the initial LH_2 in a standard-sized static system will evaporate over approximately 10 days if the dewar is not constantly cooled or insulated. This evaporation of hydrogen is commonly referred to as 'boil-off'.

The simplest liquefaction process is the Linde cycle and is characterized by the five ideal thermodynamic steps as presented on the temperature (T)–entropy (S) diagram as presented in **Figure 3**, namely: isothermal compression (step 1–2), isobaric cooling (2–3–4), isenthalpic expansion (4–5), cryogenic liquid extraction (5–6), and isobaric warming (6–7–1). The Linde cycle applies to gases, such as nitrogen, that cool upon expansion at room temperature, but hydrogen warms upon expansion at room temperature. Thus, the ideal Linde cycle for hydrogen liquefaction is modified with precooling of the hydrogen to allow it to cool upon expansion, and with constant removal of the heat of transformation that is generated throughout the *o*-H_2-to-*p*-H_2 conversion. As in the experiments conducted by Dewar, precooling involves contacting gaseous hydrogen with a working fluid, such as liquid nitrogen, that requires less energy to liquefy than hydrogen. Further cooling by contact with either recycled hydrogen or helium through a number of counterflow heat exchange stages reduces the hydrogen temperature to below its inversion temperature (193 K) and enables conversion to the desired equilibrium concentration of *p*-H_2. Modern hydrogen liquefaction plants operate at low pressure (down to

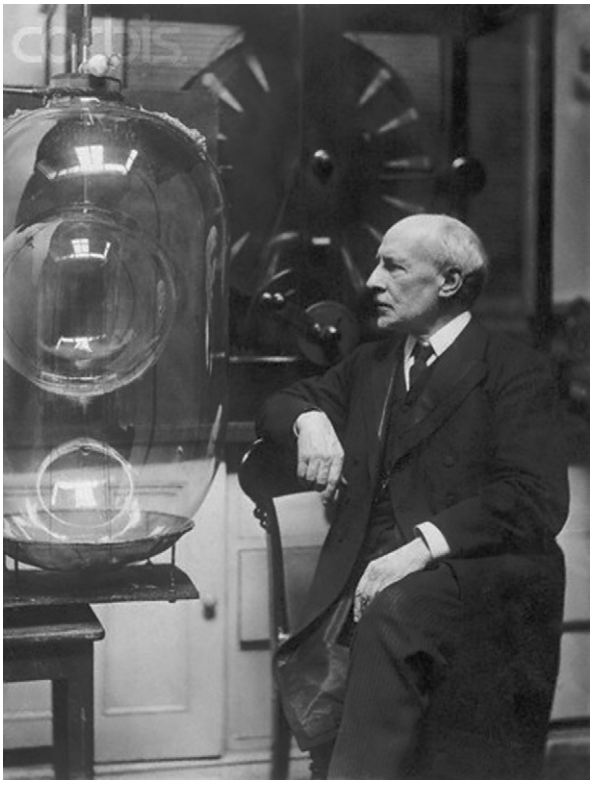

Figure 1 Sir James Dewar, FRS, 1842–1923, beside his vacuum-insulated, double-walled, silvered-glass, experimental apparatus developed for his pioneering work in hydrogen liquefaction.

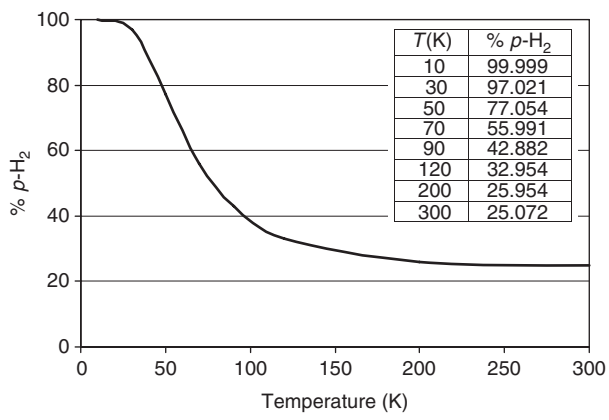

Figure 2 Temperature dependence of *para*-hydrogen and *ortho*-hydrogen equilibrium.

1 MPa) and low temperatures (down to 20 K) to produce between 95 and 99.79% p-H_2.

A simplified flow sheet of the precooled Linde cycle is presented in Figure 4. The corresponding thermodynamic steps are as follows.

Step 1′–2: Compression

Hydrogen is compressed (C1) from ambient pressure up to between 2 and 5 MPa.

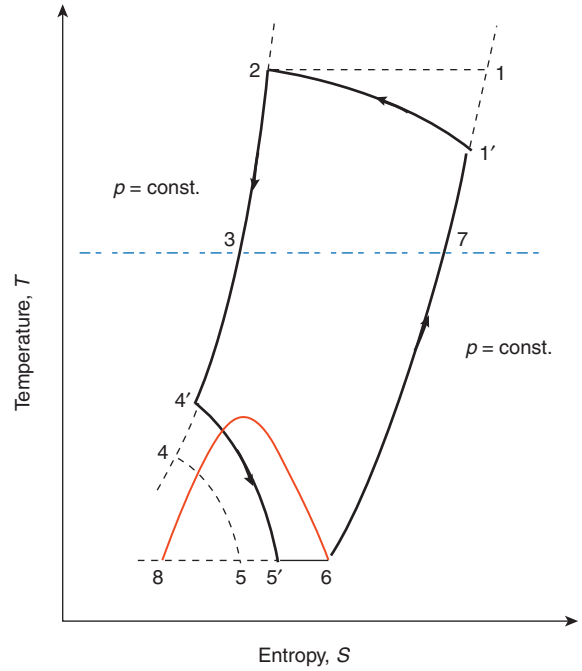

Figure 3 Temperature–entropy diagram for precooled Linde cycle. The dashed line through points 3 and 7 represents the normal boiling point (NBP) of the working fluid; p = const. represents isobars.

Step 2–3: Precooling

The compressed hydrogen is precooled in the first counterflow heat exchanger (HE1) by a working fluid, such as liquid nitrogen or helium, to below the NBP of this fluid. The working fluid flows in a closed loop.

Step 3–4′: Cryogenic cooling

The hydrogen is further cooled by the recycled hydrogen fraction from the liquid separation unit (LSU) or flash drum in a second counterflow heat exchanger (HE2) to below its inversion temperature of 193 K).

Step 4′–5′: Isenthalpic expansion

The cryogenic, compressed hydrogen undergoes isenthalpic Joule–Thompson expansion as it passes through either a throttle valve or an expander (reciprocating or tube) according to the scale and complexity of the liquefaction system. The expansion cools the hydrogen to 20 K ($-253\,^{\circ}$C) where it is converted to LH_2.

Step 5′–6: Liquid separation

The liquefied and unconverted hydrogen are stored in the LSU.

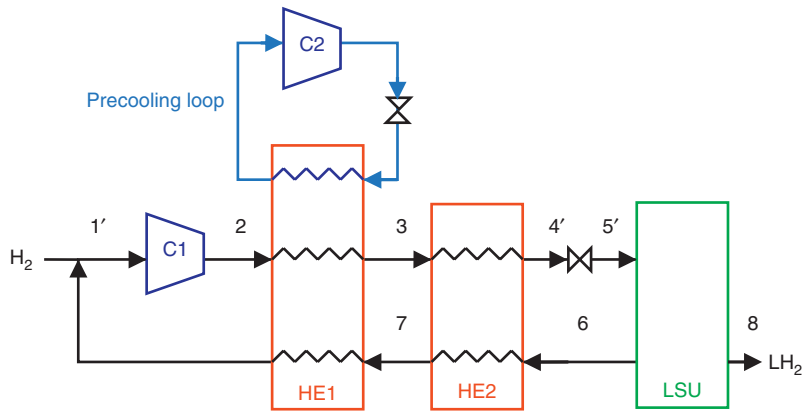

Figure 4 Simplified flow sheet for precooled hydrogen liquefaction process. HX, heat exchanger; C, compressor; LSU, liquid separation unit.

Step 6–8: Liquid extraction

The LH_2 fraction (commonly 10% of the total stored volume) is separated in the LSU where the LH_2 is recovered as product.

Step 6–7–1′: Warming

The unconverted hydrogen vapor stream is recycled back through the counterflow heat exchange stages to the compressor (C1).

Before undergoing liquefaction, hydrogen must be dried and purified up to 99.999%. This involves the removal of carbon dioxide, carbon monoxide, methane, and water via either pressure swing adsorption or the use of cryogenic membranes. Modern hydrogen liquefaction plants are complex unit operations with sophisticated thermal management and control systems to optimize the simultaneous conversion and cooling of the liquefaction process. Different liquefaction processes can be applied and combined, but generally they are variants on the Linde, Joule–Thompson, Claude, Brayton, Haylandt, and Collins cycles. Industrial-scale liquefaction plants commonly employ multistage compression, expansion, and counterflow heat exchange stages with energy recovery by expansion turbines, as illustrated in the process flow diagram given in Figure 5. Fixed-bed reactors for continuous and simultaneous conversion and cooling by a counterflow refrigerant stream have been actively developed since the early 1960s.

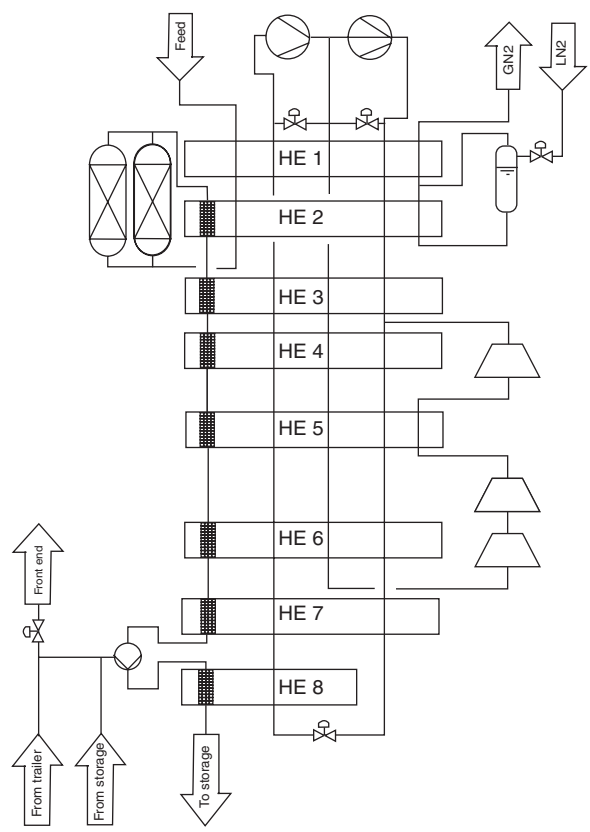

Figure 5 Process diagram of a typical industrial-scale hydrogen liquefier. HE, heat exchanger; GN_2, gaseous nitrogen; LN_2, liquid nitrogen.

Design Parameters

The storage efficiency and performance of either a large hydrogen liquefaction plant or a small LH_2 storage dewar is dependent on a number of design parameters that include dewar size and geometry, storage period, the rates of *ortho*-to-*para* conversion, heat and mass transfer, and electrical power consumption of the hydrogen compression system.

Specific Energy and Energy Density

Hydrogen has the highest specific energy of any fuel at $120.6\,MJ\,kg^{-1}$ ($33.5\,kW\,h\,kg^{-1}$) and the highest specific combustion energy release of any commonly occurring

material. On the other hand, the energy density of hydrogen is very low; for gaseous hydrogen it is 2.88 kJ m^{-3} (0.8 MW h m^{-3}) at 35 MPa and 4.68 kJ m^{-3} (1.3 MW h m^{-3}) at 70 MPa, whereas for LH_2 it is 7.56 MJ m^{-3} (2.1 MW h m^{-3}) at 0.4 MPa. The storage system energy density is a useful measure, adopted by the industry, for comparing different hydrogen storage options for practical engineering applications. The parameter is defined as the mass of hydrogen contained in a storage medium per unit mass of the complete storage unit including vessel shells. The storage system energy density of present LH_2 storage technology (7–8 wt%) already exceeds the US Department of Energy (USDOE) 2010 target of >6 wt% for hydrogen vehicle performance.

The advantages of LH_2 over other hydrogen storage media are the result of its higher energy density, higher purity, low-pressure operation, and the simplified transport logistics associated with handling a liquid particularly when compared with gaseous hydrogen. As a propulsion fuel, LH_2 provides the highest fuel payload and therefore the longest cruising range of any hydrogen storage medium. The compact nature of LH_2 minimizes the on-site hydrogen storage area for an industrial plant or fuelling station, and the number of transport vehicles required to distribute hydrogen from a production facility to consumers. The specific energy and energy density of various fuels are presented in **Figures 6** and **7**, respectively. A plot of specific energy versus energy density serves to compare the current and anticipated performance of various hydrogen storage media as presented in **Figure 8**.

Work of Liquefaction

The NBP of hydrogen is lower than that of any substance except helium, so hydrogen liquefaction is a highly energy-intensive process. The work of liquefaction of a cryogenic fluid quantifies the energy requirement to remove heat throughout the liquefaction conversion process and is dependent on the difference between the condensing temperature and ambient temperature of the gas. Based on the Carnot cycle with a heat sink at 300 K, the ideal work of liquefaction can be expressed as

$$W_L = \Delta H \frac{(T_a - T_e)}{T_e} \quad [1]$$

where W_L is the ideal work of liquefaction = 11.62 MJ kg^{-1} (3.228 kW h kg^{-1}) for LH_2; ΔH the change in enthalpy between initial (gaseous) state and final (liquid) state; T_a the ambient (or heat sink) temperature; and T_e the equilibrium condensing temperature of the o-H_2-to-p-H_2 conversion.

The ideal work of liquefaction can also be represented as the sum of work inputs:

$$W_L = W_{cooling} + W_{conversion} + W_{condensation} \quad [2]$$

where $W_{cooling}$ is the work input to reduce the hydrogen gas temperature; $W_{conversion}$ the work input to convert o-H_2 to p-H_2; and $W_{condensation}$ the work input for gas-to-liquid conversion.

In practice, the work of liquefaction, and therefore the energy requirements, are reduced by system inefficiencies and losses that are dependent on the complexity and capacity of the liquefaction plant or dewar. For hydrogen at its NBP, W_L is 16 times greater than that for nitrogen and 43 times greater than that for standard refrigerants such as Refrigerant R-22 at 233.15 K.

The supply of electrical power for hydrogen compression is a major operational cost of LH_2 systems and varies greatly according to the scale of the liquefaction process; modern large-scale plants are the most efficient and consume 30 MJ (8.3 kW h) per kg of LH_2, or 25% of the specific enthalpy or lower heating value of the hydrogen fuel; figures as low as 20% are anticipated in the near term and 5% over the medium term. Older large-scale plants with LH_2 production capacities of up

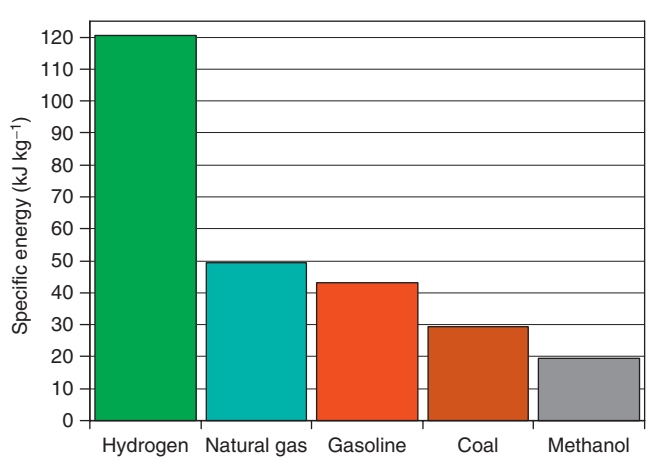

Figure 6 Specific energy for various fuels.

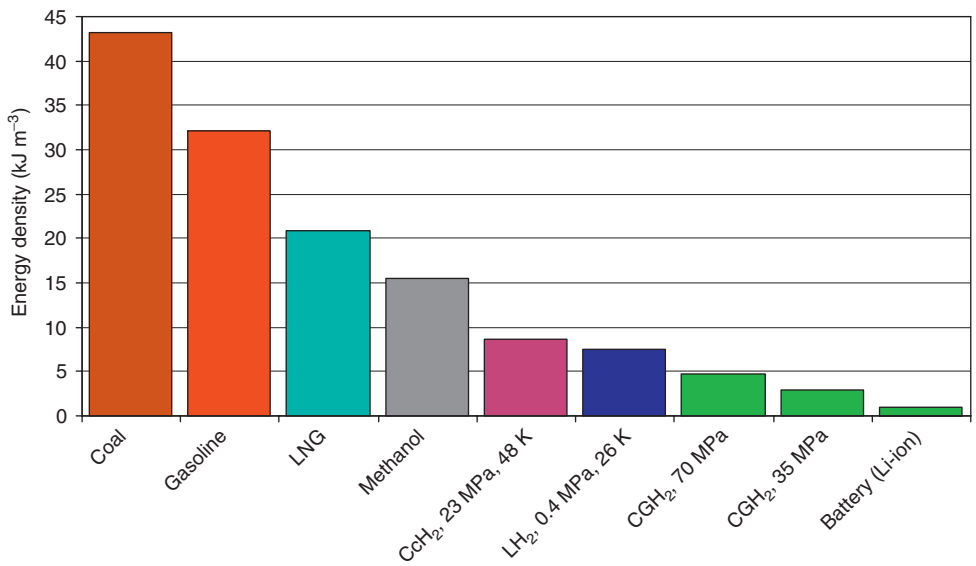

Figure 7 Energy density for various fuels (kJ m^{-3}). LNG, liquefied natural gas; CcH_2, cryo-compressed hydrogen.

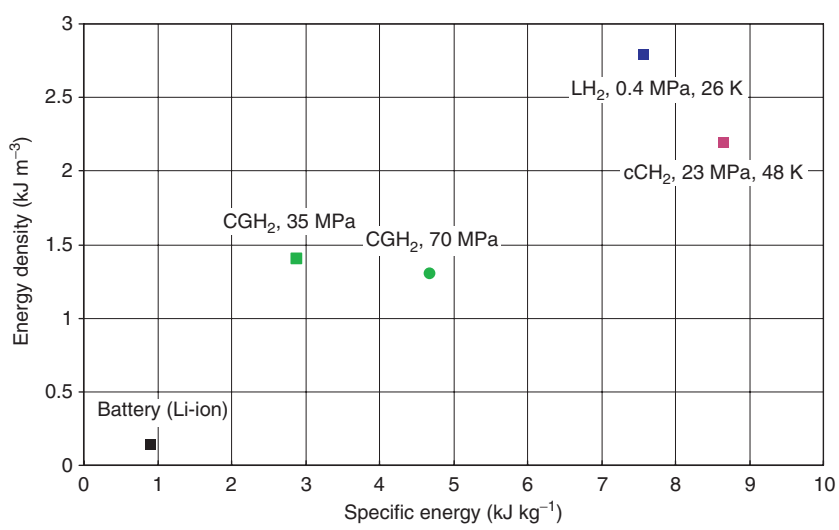

Figure 8 Comparison of system specific energy and energy density for various hydrogen storage options. Data are based on the total storage system volume. CcH_2, – cryo-compressed hydrogen.

to 12.5 t h^{-1} (300 tonnes per day (tpd)) consume 40 MJ kg^{-1}. The specific energy consumption for a medium-scale liquefaction plant with a capacity of 0.18 t h^{-1} is 50 MJ kg^{-1}, whereas for a small-scale dewar with a 10 kg h^{-1} capacity it is in excess of 100 MJ kg^{-1}.

Heat and Mass Transfer

Liquid hydrogen is extremely sensitive to thermal changes in its surroundings. If exposed to heat, LH_2 will expand when warmed by only a few degrees and will therefore undergo significant evaporation. Hydrogen boil-off from the liquefier results in a net loss in system efficiency and, consequently, higher operation costs. The rate of fuel depletion is proportional to both the *o*-H_2 content and the overall LH_2 mass initially contained in the dewar. In a parked car, a full LH_2 storage vessel of 5 kg capacity would lose all of its hydrogen in 3 weeks; complete evaporation would occur over 4 days if the vessel initially contained only 1 kg.

Hydrogen liquefaction system design and process operation therefore endeavor to minimize heat leakage into the LH_2 dewar. This can be sourced from the exothermic *ortho*-to-*para* hydrogen conversion, mixing or pumping energy, radiant heating, and convective and conductive heat transfer processes.

Conversion of ortho- to para-*hydrogen*

The dominant mechanisms for conversion of o-H_2 to p-H_2 have been investigated extensively since the 1960s. Assuming that LH_2 is stored with a specified final o-H_2 concentration and neglecting all other losses, the conversion and boil-off rates for a continuous-feed system can be calculated from the following set of equations:

$$\text{Continuity equation:}\ \frac{\mathrm{d}m_{\mathrm{L}}(t)}{\mathrm{d}t} = m_{\mathrm{c}} - \frac{\mathrm{d}m_{\mathrm{v}}(t)}{\mathrm{d}t} \qquad [3]$$

$$\text{Conservation of energy:}\ \Delta H_{\mathrm{v}}\frac{\mathrm{d}m_{\mathrm{v}}(t)}{\mathrm{d}t} = \Delta H_{\mathrm{c}}\frac{\mathrm{d}m_{\mathrm{o}}(t)}{\mathrm{d}t} \qquad [4]$$

$$\text{Conservation of mass:}\ \frac{\mathrm{d}m_{\mathrm{o}}(t)}{\mathrm{d}t} = m_{\mathrm{c}}x_{\mathrm{oc}} - m_{\mathrm{L}}(t)\frac{\mathrm{d}x_{\mathrm{o}}(t)}{\mathrm{d}t} - x_{\mathrm{o}}(t)\frac{\mathrm{d}m_{\mathrm{v}}(t)}{\mathrm{d}t} \qquad [5]$$

$$\text{Conversion rate:}\ \frac{\mathrm{d}x_{\mathrm{o}}(t)}{\mathrm{d}t} = -Kx_{\mathrm{o}}^{2}(t) \qquad [6]$$

where m_{L} is the mass of LH_2 in container, m_{v} the mass of hydrogen vapor leaving container, m_{o} the mass of liquid o-H_2 in container, m_{c} the constant LH_2 addition rate, ΔH_{v} the heat of vaporization, ΔH_{c} the heat of transformation, x_{o} the o-H_2 concentration in container, x_{oc} the o-H_2 concentration of added LH_2, and K the reaction rate constant, and t the time.

Given that the energy requirements for conversion of o-H_2 to p-H_2 represent a significant portion of the total work of liquefaction, the simultaneous conversion and cooling is tightly controlled to minimize both the energy required for liquefaction and the boil-off losses during storage. For each initial o-H_2 concentration, there exists a breakeven storage time for which the liquefaction energy is equal to the energy lost as hydrogen boil-off. The optimum yield of p-H_2 to minimize energy consumption is obtained by stage-wise conversion, with removal of the heat of transformation at the highest possible operating temperature.

Hydrogen liquefiers are equipped with catalytic reactors to accelerate the relatively slow, second-order kinetics of self-conversion. If the catalyst is well mixed with the hydrogen, the conversion approaches a first-order reaction for the gaseous phase. The rate constant is dependent on the catalyst used and the temperature and pressure of the hydrogen. If the catalyst is added to the liquid phase, the conversion approaches a zero-order reaction. Whereas hydroxides of Fe(III), Co(III), Ni(II), Cr(III), Mn(IV), as well as active charcoal, have been used as catalysts, either iron oxide or nickel–silica catalysts are preferred in most hydrogen liquefaction systems.

Dewar size and geometry

Boil-off rates vary according to the geometry of the dewar and are inversely proportional to the dewar size. The very large dewars are spherical in shape because spheres have a lower surface area for heat transfer, and therefore result in less boil-off per unit volume of stored LH_2. Nevertheless, the majority of industrial dewars are cylindrical in shape as they are easier and cheaper to construct and their volume-to-surface area ratio is almost the same as for spherical geometries. In most cases, dewars are double walled, with the inner container holding the stored LH_2 and isolating it from any large sources of heat leakage. Convective heat transfer is reduced by application of a high vacuum pressure, approximately 10^{-3} Pa at 20 K in the cylindrical annulus between the inner and the outer shells.

Insulation and shielding

Dewar insulation techniques such as foam materials, superinsulation foils, and radiation shielding minimize conductive, convective, and radiant heat transfer from the outer jacket to the isolated inner container. Following the technique adopted by Dewar, the annuli of modern stationary and transportable dewars are often filled with liquid nitrogen to restrict heat leakage by convection. Vacuum super-isolated dewars for large stationary storage can confine evaporation rates to between 0.06 and 0.4% of the stored hydrogen volume per day, and between 1 and 3% per day for small portable dewars. A typical boil-off rate for large industrial dewars is 0.1% per day with an industry target of 0.03% per day.

To prevent radiant heat transfer, thermal superinsulation is positioned between the inner and outer walls of the dewar. Thermal effectiveness and cost are critical factors in the selection of the most suitable insulation strategy. Other considerations include convenience, ruggedness, volume required, mass involved, ease of fabrication and handling, specific characteristics of the dewar system such as the physical properties of LH_2, whether the storage is intermittent or continuous, the environmental conditions surrounding the dewar, and the safety of the system. In the main, however, the choice of insulation material is governed by balancing the higher capital cost of installed, insulated system with the savings gained from lower energy requirements.

The insulation material consists of multiple (between 30 and 300) layers of reflective, low-emittance heat shielding, such as aluminized plastic films or foils that provide an area weight of 1.5–3.0 kg m^{-2} and thermal conductivity of around 10^{-4} W m^{-1} K^{-1}. These materials provide up to 300 times greater thermal resistance than expanded polystyrene, but are considerably more expensive. A cheaper alternative is perlite (colloidal silica). In some of the more recent designs, insulation foils are separated by glass fiber spacers to improve their resistance to heat transfer.

The design of a dewar also aims to optimize the conductive heat transfer between the LH_2, the working

fluid of the precooling loop, and the internal components of the heat exchangers. The shell walls are therefore thin, with a minimum thickness of between 2 and 4 mm, and are made of stainless steel for required strength. The internal support structures that align the inner and outer shells are another source of conductive leakage of heat. On the other hand, the coaxial tubes of the internal heat exchangers maximize surface area and therefore heat conduction between the counterflow hydrogen streams and the working fluid.

Venting and Recycling

Evaporative losses can be significant even for LH_2 storage systems with optimum heat transfer. As the hydrogen fuel expands over time, the gas pressure in the dewar will gradually rise. If this pressure exceeds the design limit, the boil-off must be vented to the atmosphere, recycled back to the liquefier, or transferred for captive use in other on-site processes. Minimization of boil-off is therefore particularly critical in applications, such as road vehicles, that require long-term storage or intermittent supply of LH_2.

The design and development of LH_2 systems also focus on maximizing the length of time it takes for LH_2 to begin evaporating, commonly referred to as the 'dormancy' or 'lock-up time'. The evaporative LH_2 losses from a conventional, low-pressure (0.5 MPa) dewar for road vehicles are significant if the vehicle is driven less than about 25 km daily. Advanced cooling systems are anticipated to increase the present lock-up time for a standard dewar from 3 to 5 days of inactivity to more than 12 days.

Large-scale industrial dewars are often fitted with tall dispersement stacks to capture, compress, and reliquefy any hydrogen boil-off. The energy consumed during this recycling process is less than that required to liquefy a fresh feed of gaseous hydrogen.

Storage Period

Unlike electricity, hydrogen can be stored in large quantities over long periods of time and thus it is ideally suited as an energy storage medium for several industrial uses. Unless the system is kept supercool, however, the tendency of LH_2 to boil-off can make long-term storage both difficult and costly. The desired storage time before the decanting and transferal of LH_2 is therefore a key parameter in the design and operation of a dewar system. For example, LH_2 supply systems for space craft, military rockets and other airplanes must be primed well in advance of the scheduled launch. The optimum storage time is dependent on the frequency and scale of LH_2 consumption and the cost of the electrical power required for compression. In any case, the operating cost of a standard LH_2 storage system over an extended period is small with respect to its capital cost.

Transfer and Decanting

The rate at which LH_2 is transferred from the dewar is also an important design and operational feature. The refueling of road vehicles with LH_2 has been reduced to 2–3 min through the development of sophisticated designs of LH_2 pumps. Equally, rapid LH_2 discharge from the vehicle dewar to the fuel propulsion system is essential. Similar requirements apply to the decanting of LH_2 from the liquefaction plant to transportable dewars for larger industrial applications and hydrogen distribution networks.

Materials

The components of LH_2 storage systems are subjected to frequent load cycles and large temperature differences between ambient and cryogenic conditions (approximately 300 K). Exposure to hydrogen can also accelerate the initiation and propagation of fatigue cracks or ruptures in materials. The materials used for the components must therefore be resistant to thermal contraction and local fatigue to give a maintenance-free lifetime of at least 10 years.

Aluminum plays a major role in the design of LH_2 storage systems due to its low specific weight, high strength modulus, high coefficient of thermal expansion, resistance to hydrogen embrittlement and permeation, good ductility at cryogenic temperatures, and high heat conductivity. The inner shells of dewars are made of aluminum alloys or austenitic stainless steels that at low temperatures are resistant to martensite formation, and therefore hydrogen embrittlement. The shells should also withstand a test pressure of 1.5 times the maximum allowable working pressure.

Dewars are generally covered with perlite or multilayer insulation under high vacuum. The heat exchanger internals, such as coaxial tubes, gas loops and vessel support structures, are made of glass fiber or carbon fiber reinforced plastics that have high mechanical strength and low thermal conductivity. The inner shell and insulation layers are enclosed in a vacuum jacket made of low-carbon, high-strength steel or stainless steel, which experience negligible hydrogen permeation and protect the container and the insulation in case of a fire.

Safety

The recognition of dewars as a practical and safe means of hydrogen storage is essential to generate broad public acceptance of hydrogen-fueled vehicles and other distributed uses of LH_2. Dedicated standards and codes, such as those developed by the International Standards Organization Technical Committees 197 and 220, are

applicable to all dewar and hydrogen liquefaction system components and their use. Dewars should pass both external and seat leakage tests and operate reliably under electrical, mechanical, thermal, and chemical conditions. Liquid hydrogen storage systems require fail-safe design and extensive cryogenic testing of all dewar components.

A working knowledge of the physical properties of LH_2 is fundamental to the technical design of a dewar system and the safe handling and operation of the LH_2 facility. The vapor of LH_2 is colorless, odorless, tasteless, and noncorrosive, but highly flammable. The wide flammability range of hydrogen, namely 4–74 vol% in air, and the small amount of energy required for ignition necessitate special care to prevent the inadvertent mixing of LH_2 vapor with air. Fortunately, the diffusivity of hydrogen gas in air at room temperature is extremely high so that, although its detonation limits are large, it is difficult to ignite hydrogen in air if it is unconfined. Unlike the heavier hydrocarbon molecules of methanol, ethanol, gasoline, or LPG that tend to linger in the presence of a system leak, any LH_2 that is released will evaporate and diffuse rapidly upward and away from the leak or any potential ignition source. Therefore, controlled and systematic venting of LH_2 to the atmosphere poses little safety risk.

The low-pressure operation and cooling of dewars reduces the potential risk of sudden tank rupture and increases the safety factor over CGH_2 storage systems. Onboard LH_2 dewars are designed to withstand the impact of a vehicle accident up to an acceleration of $200\,m\,s^{-2}$ in the direction of travel, and up to $80\,m\,s^{-2}$ perpendicular to the direction of travel.

Liquid hydrogen expands considerably as it warms between 20 K and its critical point, 33 K. Therefore, dewars are filled to between 85% and 95% of full volume capacity, which leaves a vapor space (ullage) to prevent LH_2 losses. Pressure relief valves are fitted to both the inner vessel and the vacuum jacket to protect against overpressurization.

Since LH_2 is one of the coldest liquids known, plant operators and vehicle mechanics should take precautions to avoid severe burns from direct contact with the external walls of the dewar, exposed process lines, or any other cryogenic plant equipment.

Economics

Hydrogen storage systems, whether based on compressed, liquefied, or solid media, are inherently costly. Consequently, considerable efforts are made to reduce the total investment cost of a hydrogen liquefaction plant that can be estimated as capital (65%), power (30–33%), and operating and maintenance costs (2.5–5%). The plant investment cost, Q, is a function of plant capacity, D, and can be estimated with reference to the investment cost of an existing plant (with cost Q_{ref} and capacity D_{ref}, by

$$\frac{Q}{Q_{ref}} = \left(\frac{D}{D_{ref}}\right)^n \qquad [7]$$

where n is the sizing exponent for a given hydrogen liquefaction plant (ranges between 0.6 and 0.7).

Based on a sizing exponent of 0.648, total plant investment cost will range from US$35 million for a 10-tpd capacity plant to US$100 million for a 50-tpd plant. The economic feasibility of an LH_2 delivery system for a distributed application is dependent on the quantities conveyed, transport distance, fuelling frequency, electricity cost, and LH_2 price. For an equivalent mass of hydrogen, dewar capital costs are lower than for CGH_2 vessels, but energy requirements for liquefaction are higher than for compression. For large dewars and long-term storage, the increased LH_2 storage capacity provides greater economic benefits than with CGH_2 storage. The energy savings from efficiency gains of larger and complex plants are offset by high equipment costs; however, the overall plant life cycle costs are lower than for CGH_2 systems. The combined cost of the insulated liquefier, the high boil-off rate, the high energy use, and the degree of automation can be prohibitive, particularly for small-scale plants.

The breakdown of the capital costs for a liquefaction plant with a useful lifetime of 20–30 years are typically 60% for components, 10% for planning, and 30% for construction and erection. The commissioning of a liquefaction plant can last for a period of up to 3 years. The capital cost of the LH_2 storage system components is dominated by those for the insulation and the hydrogen compression system. Depending on the plant design, the capital costs of dewars are estimated to lie between US$20 and 40 per kg of stored LH_2, or, based on plant capacity, between US$25 600 and 118 000 per kg H_2 produced per hour. A liquefaction plant providing $2700\,l\,h^{-1}$ (4.5 tpd) will cost about US$20 million.

The capital cost of an LH_2 refueling station to service 4000 cars lies between US$0.25 and 0.3 million and can be broken down as LH_2 tank (60–65%), LH_2 pump (20–25%), and LH_2 dispenser (15–20%). A CGH_2 station of equivalent hydrogen capacity would cost approximately US$1.25 million. Installation and engineering costs can be as much as 20% of the total investment cost of an LH_2 fueling station.

Applications

Stationary Storage

Industrial hydrogen is commonly stored and transported as either a compressed gas in heavy and bulky cylinders, or more compactly as a cryogenic liquid in either

horizontal or vertical cylindrical dewars. Standard industrial dewars for LH_2 storage can be categorized on the basis of plant capacity, namely small, 130–600 L h^{-1} (0.2–0.9 tpd); medium, 600–3000 L h^{-1} (0.9–5 tpd); or bulk, >3000 L h^{-1} (>5 tpd), vessels.

Large-scale industrial liquefaction plants were first built in the 1950s and have been used extensively in the captive markets of petroleum refining and ammonia production. Larger dewars provide LH_2 at up to 35 000 L h^{-1} (60 tpd), but with the continual improvement in LH_2 storage design and energy efficiency, modern dewars tend to be smaller with capacities between 2000 and 8000 L h^{-1} (3 and 12 tpd). The world's largest dewar is operated by the National Aeronautics and Space Administration (NASA) at the Kennedy Space Center in Florida; it has a capacity of 3800 N m^3 (270 t) to supply hydrogen for the space program. The evaporation rate from this spherical dewar is less than 0.03% per day and thereby enables the economical storage of LH_2 for several years. Taiheiyo Ekika Suiso and Iwatani International have supplied the Japanese Aerospace Exploration Agency with LH_2 for launching vehicle flights. In addition to the United States, Japan, and members of the European Space Agency (e.g., Germany and Austria), other countries engaged in LH_2 production and use as a cryogenic propellant include India, China, and Russia.

Many of the older liquefaction plants were built to produce hydrogen as a premium product for the chemical industry. Smaller dewars with capacities up to 150 L h^{-1} (0.23 tpd) are used to deliver LH_2 for cryogenic research purposes or as a source of high-purity hydrogen for the semiconductor industry. Until 1980, small amounts of LH_2 were used for nuclear and particle physics research performed in 'bubble chambers'. In addition, LH_2 dewars are currently used to retain hydrogen for the cooling of power generator sets and electronic components, as well as for fuel cell plants that deliver combined heat and power. Examples of industrial dewars of various sizes are presented in Figures 9–11.

Transport and Delivery

Liquid hydrogen is relatively easy and safe to store and transport in compact, lightweight, and low-pressure dewars that can be loaded on semitrailers, railway wagons, barges, ships, and even airplanes. The distance between the hydrogen source and the end user is a critical factor in the selection between LH_2, CGH_2, and H_2 pipeline transport modes. Liquid hydrogen is generally the cheapest option, but pipeline delivery of gaseous hydrogen, despite its high capital cost, may be more economical for larger hydrogen flows. For medium- to large-scale quantities, delivery by LH_2 tanker is more practical, energy efficient, and cost effective than conveyance by CGH_2 tube trailer. From a life-cycle perspective, the high energy costs of liquefaction and boil-off are less than the capital cost of additional CGH_2 tube trailers for the delivery of an equivalent quantity of hydrogen.

Figure 9 Small- to medium-scale hydrogen liquefier. Courtesy of Air Liquide.

Figure 10 Medium-scale industrial liquefier. Courtesy of Linde Gas.

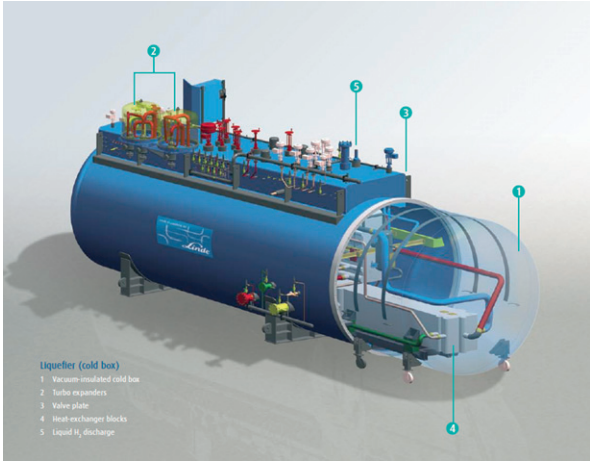

Figure 11 Industrial-scale stationary LH_2 dewar. Courtesy of Linde Kryotechnik AG.

The transport logistics for LH_2 delivery involve

- transfer of LH_2 from the hydrogen liquefaction plant to a portable dewar mounted on a transport vehicle;
- delivery of the portable dewar to a port, terminal, or fueling station, or directly to a large-scale customer;
- transfer from the portable dewar to an on-site stationary dewar, followed by decanting of the LH_2 into vacuum-insulated bottles as dictated by the quantity and frequency of the customer's requirements.

Road

Road transportation of LH_2 by tube tankers could play a significant role in the initial developmental phases of a hydrogen distribution infrastructure. At present, LH_2 is commonly and economically conveyed in 45–65 $N\,m^3$ double-walled insulated tubes on tankers that weigh between 25 and 40 t and have a total LH_2 storage capacity of up to 5000 $N\,m^3$ (4.5 t of LH_2). The higher energy density of LH_2 allows the highest payload of hydrogen to be transported, whereas a standard CGH_2 tube trailer can only carry up to 0.3 t of hydrogen.

Transportable dewars are essentially the same as stationary tanks; they are equipped with automatic shutoff valves and are designed to minimize boil-off, heat leakage, and energy consumption. The rate of hydrogen boil-off from tanker transport lies between 0.3% and 0.6% per day. Some tankers also use liquid nitrogen heat shields to cool the outer wall of the LH_2 vessel to reduce heat transfer to the dewar and minimize evaporative losses. A modern tube tanker for LH_2 road transport is shown in Figure 12.

Rail

Rail transport is also considered a feasible means of LH_2 transportation. Dewar railway wagons have greater LH_2 capacities than tube tankers, with an LH_2 storage of 2.3–9.1 t. Boil-off rates for railway wagons are similar to those of tube tankers, that is, between 0.3% and 0.6% per day.

Figure 12 Tube tanker for LH_2 transport. Courtesy of Air Products.

Pipeline

Hydrogen pipeline networks may require LH_2 storage depending on the quantity of hydrogen to be delivered and the nature of the customer's requirements. There is little or no requirement for hydrogen storage if the hydrogen is continuously delivered to the customer. In pipelines with large variations or intermittency in flow, however, it may be necessary to store hydrogen to meet peak demand. Several hydrogen pipelines with lengths of up to 40 km are operated in the southern states of the United States and in northern Europe. The capital and operating costs are prohibitively high and include the costs of expensive insulation materials and LH_2 compression and cooling at regular intervals along the length of the pipeline.

Although the use of pipelines for long-distance LH_2 delivery is unlikely, a novel design for the simultaneous transport of electricity and hydrogen has recently been proposed. An insulated LH_2 pipeline would house a magnesium diboride conducting wire along its length. The LH_2 ensures that the wire is kept at a supercritical temperature such that it can act as a superconductor of electricity. The benefit of high electrical transmission efficiency could possibly justify the high capital and operating costs of an LH_2 pipeline.

Maritime

Ships, barges, and other maritime vessels have been considered for long-distance and bulk transport of LH_2 in a manner similar to that for liquefied natural gas (LNG). Liquid hydrogen can be transported by sea in standard 12.2-m (40-ft) containers. For instance, LH_2 was transported on board a ship to supply the French space station at Kourou, French Guiana. An example of a

Figure 13 Transportable dewar for bulk LH_2 transport (capacity 300 N m^3). Courtesy of Linde Kryotechnik AG.

portable industrial-scale dewar with capacity of 300-N m^3 LH_2 is presented in Figure 13.

Liquid hydrogen has also been investigated as an emissions-free fuel for passenger ships, submarines, and fishing boats. In such applications, hydrogen boil-off can be recycled to a boiler as an additional combustion fuel. Passenger ships powered by hydrogen fuel cells and supported by fueling stations, LH_2 storage systems, and port facilities are currently being designed.

Novel maritime designs for large-scale LH_2 transportation include a ship of 180 m in length for the conveyance of five small barges, each of which would hold 3000 N m^3 (4.2 t) of LH_2 with no venting over a 50-day trip. On arrival at port, the barges would be separated for delivery to different customers. This avoids the LH_2 losses that would be incurred from multiple transfers from one large dewar. A hydrogen barge is anticipated to cost 3.5–4 times more than an LNG barge. Other proposed vessels include a single-hulled tanker holding 7000 t of LH_2 with an estimated boil-off rate of 0.2–0.4% per day, and a ship supporting four spherical dewars, each with an LH_2 capacity of 350 t.

Onboard Storage

Design imperatives for efficient and practical onboard LH_2 storage and use for transportation applications impose technical performance criteria that are more stringent than those for stationary applications. Considerable investment has been directed to the development of compact and affordable mobile LH2 storage systems that provide a high hydrogen storage capacity and a practical vehicle range to consumers.

Space vehicles

The development of modern LH_2 storage and transport technologies stemmed from the extensive application of LH_2 as a propellant for the launching of space vehicles and nuclear-powered rockets. Liquid hydrogen delivers high levels of power per unit volume and up to 40% more thrust per unit mass than other rocket fuels. In addition, LH_2 stores approximately 3 times more energy than jet-grade kerosene, but the storage system is 4 times larger.

In 1903, just 5 years after the seminal experiments of Dewar, the Russian rocket pioneer Konstantin Tsiolkovsky proposed the use of hydrogen in a space rocket, as did Goddard in 1910, Meyer in 1918, Lewis (Director of Research for the US National Advisory Committee for Aeronautics) in 1939, and Simon (an English physicist) during World War II. The attempts of Walter Theil to use LH_2 in a small rocket engine during the late 1930s were thwarted by numerous leaks. The power plant at Wright Field and the Ohio State University investigated the application of LH_2 to aircraft and rockets from 1945.

Liquid hydrogen and liquid oxygen (LOX) are used by NASA as propellants for the main engines of their space shuttles (SSME). Total hydrogen consumption by the aerospace industry remains relatively stable at approximately 1–1.3 million tonnes per annum (tpa), so an efficient and practical means of storage is essential. Alkaline fuel cells in the Space Shuttle Orbiter also use hydrogen and oxygen to produce electrical power and drinking water for astronauts.

Liquid hydrogen and LOX are stored in separate cryogenic tanks that are positioned within a large external tank (ET) aboard the space shuttle. The first six ETs delivered to NASA were called standard weight tanks (SWTs), each weighing 34.25 t. In 1979, NASA directed that the weight of the ETs be reduced to enable greater payloads to be flown. This resulted in the design and use of a 29.7-t lightweight tank (LWT), which was later replaced in 1998 by the 26.3-t super-lightweight tank (SLWT), made from an aluminum–lithium alloy and having a capacity of 1.497×10^3 L, dimensions of 29.5 m × 8.4 m, and an LH_2 payload of 104 t.

The ET supplies LOX at a rate of 72.3 t min^{-1} (63 600 L min^{-1}) and LH_2 at 12.1 t min^{-1} (171 400 L min^{-1}) to the three SSMEs through 0.43-m-diameter feed lines. The SSME burns the combined LOX–LH_2 fuel via a staged combustion cycle, in which the fuels are first partially burned at high pressure and low temperature and then completely burned at high pressure and high temperature. The ET empties at about 8.5 min after vehicle launch.

Airplanes

The large specific energy of hydrogen, combined with its greatly superior cooling capacity and clean-burn characteristics, makes it a viable and highly efficient future

aviation fuel for long-range flights. At altitudes above 9000 m, LH_2 can be contacted with a working fluid to cool the exterior surfaces of the aircraft to reduce turbulence and drag. This could improve fuel efficiency by up to 30% and reduce operating costs by up to 20%. Additionally, LH_2 can be used directly for turbine cooling, as is undertaken in coal-fired power generation sets, to increase energy efficiency. The LH_2 would be produced and stored on-site at an airfield and consumed during the flight. When compared with maritime LH_2 transport, high-speed aircraft will deliver an equivalent mass of LH_2 more rapidly and thereby reduce boil-off losses.

Investigations of LH_2 as a fuel for airplanes and missiles began during the mid-1940s as the US military pursued superior engine performance for its bomber, reconnaissance, and fighter aircraft. During the early 1950s, the US Air Force developed and tested air-transportable dewars for the storage of up to 750 L of LH_2 or deuterium for their B-36 or B-47 fleet. The basic construction and thermal insulation of the dewars was similar to present-day standard designs. The heat flow to the LH_2 shell was minimal (approximately 4 W), and hydrogen boil-off was about 7.5 L per day, or 1% of rated capacity.

In 1955, Thalne W. Reynolds demonstrated that LH_2 could be handled/jettisoned safely, held in standby condition and made ready for flight in a short time. A lightweight and insulated stainless steel LH_2 tank (6.2 m long, 1.7 N m^3 capacity), designed for a pressure of 0.34 MPa and carrying 94 kg LH_2, was mounted on the left wing of a modified hydrogen-fueled B-57 airplane and extensively tested. The dewar was insulated by a 50-mm coat of plastic foam that was covered with aluminum foil and encased in fiberglass.

Between 1972 and 1984, Daniel Brewer led a team at Lockheed to develop LH_2-fueled aircraft designs and compared their performance and operating costs with those of competing fuels such as synjet (synthetic Jet-A) and methane. Liquid hydrogen demonstrated better performance, greater payloads, lower maintenance costs, reduced noise, higher fuel efficiency, reduced emissions, and greater safety. From 1979, the retrofitting of a small fleet of Lockheed L1011 jets with hydrogen technology and other LH_2 airplane concepts such as the Cryoplane in Russia and Germany, and the National Aerospace Plane in the United States, were pursued with great enthusiasm. All the projects were, however, eventually terminated.

LH_2-fueled, unmanned, aerial vehicles have been flight-tested to assess their suitability for a range of surveillance activities such as hurricane tracking at heights between 20 and 30 km above sea level. These planes can remain in flight mode for approximately 24 h between refueling operations.

Light-duty and commercial road vehicles

Onboard LH_2 storage for road vehicles is carried out in state-of-the-art transportable dewars of up to 200 l capacity. The dewars supply hydrogen for the propulsion system of either a hydrogen fuel cell vehicle (FCV) or a vehicle that is powered by a hydrogen-fueled internal combustion engine (HICE). The dewars occupy 20–25% of the storage volume of an equivalent CGH_2 tank, and therefore provide greater flexibility in the design of FCVs. A dewar of 100-L capacity provides a range of 670 km, compared with 385 and 225 km for a 70-MPa and 35-MPa CGH_2 tank, respectively.

A typical, onboard LH_2 storage system contains the following components: an LH_2 tank with support posts, a refueling connection or receptacle, a pressure relief device, an automatic shutoff valve, a flexible or rigid fuel line, fittings or screwed connection systems, an *o*-H_2-to-*p*-H_2 converter, a safety instrument system, a hydrogen fuel level sensor or flow rate sensor to calculate the LH_2 fuel level, a fuel level indicator, and a boil-off management system. As for stationary LH_2 vessels, the inner supports are designed to keep the isolated LH_2 tank aligned with the outer container.

Dewars for light-duty road vehicles and buses are presently available as individually manufactured items. BMW Group, in conjunction with Linde Gas, has led the development and testing of LH_2 storage systems for hydrogen vehicles and, since 1979, has invested significant resources to improve the performance of HICEs. BMW Group has designed two production-ready 7 Series sedans: model '750 hL', which is a dual-fuel vehicle using either petrol or LH_2, and model '750 h', which is a dedicated LH_2 version. Both vehicles access hydrogen from an onboard LH_2 dewar to power their 150-kW, 12-cylinder combustion engines, and use two independent fuel-induction systems to run on either gasoline or LH_2 at any time. The LH_2 storage vessel used in the 750 h vehicle operates at a maximum pressure of 0.5 MPa, has a capacity of 140 L, weighs 100 kg, and stores 10 kg of LH_2 to provide a driving range of 580 km. The BMW 7 Series LH_2 vehicle and storage tank are shown schematically in **Figures 14 and 15**, respectively. The system performance is anticipated to provide satisfactory capacity, and therefore driving range, for larger classes of vehicle. The BMW Group is currently developing CcH_2 storage technology for application in their HICE vehicle models to improve the thermal endurance of the hydrogen storage system and reduce evaporative losses. Further details of CcH_2 technology are given below.

At present, the specific energy of the best-performing rechargeable batteries is around 200 W h kg^{-1}, which is orders of magnitude less than that for hydrogen, namely 39.47 kW h kg^{-1} (based on higher heating value) and 33.33 kW h kg^{-1} (based on lower heating value). A large

disparity also exists when comparing their respective energy densities: 0.25 MW h m^{-3} for batteries and 2.1 MW h m^{-3} for LH_2. This imposes a severe weight penalty, and therefore limited cruising range, for full-electric or hybrid electric vehicle technologies that rely on batteries for energy storage. Electric vehicles powered by nickel–metal hydride (Ni–MH) batteries are approximately 50% and 230% heavier than FCVs for vehicle ranges of 200 and 400 km, respectively. Lithium-ion batteries provide greater specific energy than other batteries, but electric vehicles powered by them are still about 15%, 60%, and 130% heavier than FCV equivalents for ranges of 200, 400, and 600 km, respectively. At extended ranges, batteries are simply too heavy to be considered practicable, whereas the weight of an FCV remains relatively low at 1.3 t, even for ranges beyond 600 km.

Buses

A full-size, hydrogen-powered, fuel cell bus with regenerative braking operating on a stop–start inner-city service will consume approximately 1.2 kg (7 L) of LH_2 per hour and up to 7 t (100 000 L) of LH_2 per year, based on the assumption that the vehicle operates for 16 h per day for 365 days per year. A typical LH_2 storage system for buses consists of three elliptical cross section LH_2 tanks each with a capacity of 190 L, which corresponds to an energy content of 450 kW h or 150 N m^3 and a specific energy of 4.5 kW h kg^{-1} or an energy density of 2.13 kW h L^{-1}. The tanks are lined with 200–300 layers of insulating foil to reduce evaporation rates to below 1% of the stored LH_2 volume per day.

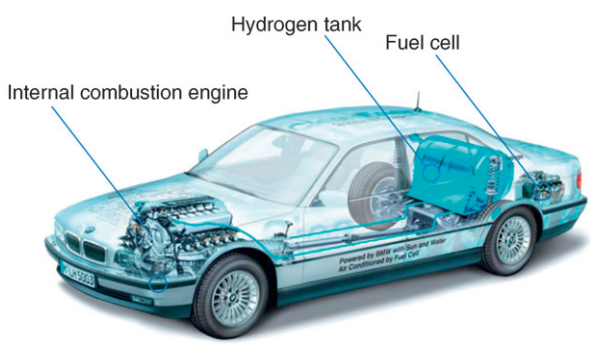

Figure 14 BMW 7 Series LH_2 vehicle with onboard dewar. The latest BMW HICE vehicle designs incorporate cryo-compressed hydrogen storage technology to improve thermal endurance and reduce evaporative losses and boil-off.

Fueling

Stationary fueling stations

Hydrogen fueling stations provide a safe and simple method of hydrogen storage and transfer to support the utilization of hydrogen-powered vehicles. To fuel a vehicle, up to 3000 L h^{-1} of LH_2 supplied from a stationary dewar is vaporized into hydrogen gas and then compressed to 45 MPa via a two-stage hydrogen compressor. The hydrogen can then be dispensed into the fuel tanks of the hydrogen vehicles.

Liquid hydrogen dispensers provide a hydrogen flow rate of up to 3000 L h^{-1} and allow for the fueling of several vehicles in succession. Safe fueling can be accomplished through the use of a clean-break coupling system for connection between the fueling station and vehicle fuel tank. The dispensing system features a steel robotic arm that moves into position at the rear axle of the car. Guided by a programmed optoelectronic system, a jointed arm locates the fuel cap, creates a seal around a rubber plug under vacuum, and opens the fuel cap using a high-precision motor. A nozzle then begins the automated LH_2 fueling process without any concerns regarding icing. The fueling time is similar to that at a conventional petrol or diesel service station, that is, about 2.5–3 min.

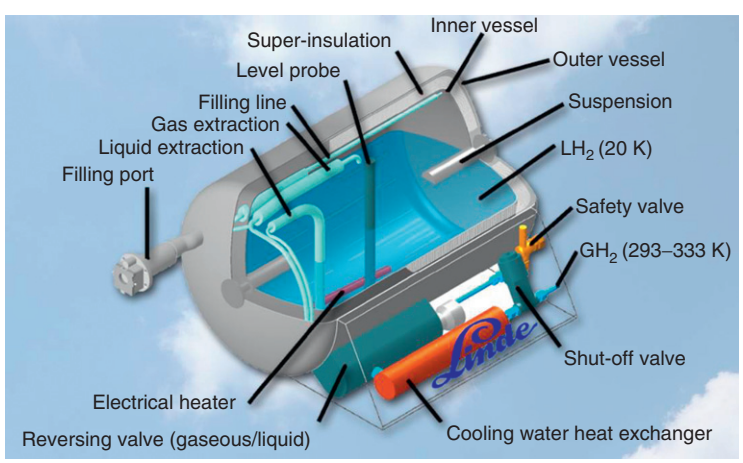

Figure 15 Schematic illustration of an LH_2 dewar for automotive applications. Courtesy of Linde Gas.

The world's first public LH_2 fueling station was opened at Munich airport in 1999. At present, the largest station (ARAL) is based in Berlin since 2004; it can dispense both CGH_2 and LH_2 for the fueling of up to 100 cars per day. Another hydrogen fueling station (Total) was opened in 2006 in Berlin. Both stations have been built as part of the German Clean Energy Partnership (CEP) Program. Similar stations are located in Washington, DC, Oxnard, California, and Yokohama, Japan.

The majority of the 140 stationary hydrogen-fueling stations that currently exist worldwide are primarily serving the needs of public demonstration and testing of hydrogen-powered vehicles. Recent market surveys indicate, however, a strong preference for the use of CGH_2-powered vehicles and fueling stations. Between 2005 and 2006, only 9% of all new hydrogen-fueling stations constructed dispensed LH_2; the remaining 91% stations provided CGH_2. As for HICE vehicles, recent work has focused on the development of CcH_2 technology for application in hydrogen-fueling infrastructure.

Mobile fueling units

Between 1952 and 1954, the US Air Force built and operated a mobile hydrogen liquefaction system with a production capacity of 100 L h^{-1} of 45% liquid p-H_2 at an electrical power consumption of 105 kW. Two trailers carried large horizontal compressors, a gas holder, and auxiliary equipment for the compressors, while a third trailer carried the complete hydrogen purification and liquefaction equipment. These trailers, each with a gross weight of about 25 t, were capable of highway speeds of 89 km h^{-1}.

Gas companies such as Linde Gas, Air Products, and Iwatani International have recently developed trailers and trucks for the mobile fueling of LH_2- and CGH_2-powered vehicles. These vehicles transport up to 1000 L per payload of hydrogen in superinsulated cryostats and, in some cases, carry an onboard fuel cell unit for independent power supply. Mobile fueling improves the flexibility and economics of hydrogen distribution, particularly in the absence of a fully developed hydrogen supply and distribution infrastructure.

Measurement of Liquid Hydrogen

The mass of liquid contained in an LH_2 dewar can be measured by means of a vacuum-insulated turbine flow meter with meter purging and cooldown. The flow meter produces a pulse output that is proportional to the volume flow of LH_2 and corrected for any temperature effects. Alternatively, a mass or 'compressibility' gauge can be used to measure LH_2 flows under cryogenic and high-vacuum conditions.

Technological Advancement

Existing LH_2 storage systems have reached a stage of proven technical feasibility, particularly for large-scale industrial storage and aerospace applications. Nevertheless, there exists great scope for many technological improvements and the commercialization of novel liquefaction processes and dewar designs. Research and demonstration projects on hydrogen storage are focusing on the development of advanced liquefaction techniques and mobile dewars that are compact, lightweight, both mechanically and thermally efficient, durable, safe, and economically viable.

Material and process improvements to existing LH_2 technologies will lead to improved energy efficiency and, therefore, reduce overall energy consumption of the LH_2 system. Lower capital and operation and maintenance costs will translate to the production and widespread distribution of inexpensive LH_2 for an expanding range of market applications.

Performance Targets

Stringent performance targets for onboard hydrogen storage systems have been set by the Hydrogen Implementing Agreement of the International Energy Agency, and by the USDOE. Targets for weight and storage capacity require that performance and cost of dewars are equivalent to those of a conventional gasoline storage system. Performance targets and anticipated advances in transportable dewars, hydrogen liquefaction plants, and delivery infrastructure are presented in **Table 2**. Whether all of these targets will be met is the subject of much conjecture.

Materials Development

As with many other emerging technologies, improvements in LH_2 system performance and reduction of capital costs will be realized through the characterization and investigation of combinations of existing and emerging materials. Much attention is being focused on enhancing the properties and capabilities of LH_2 system components to reduce energy consumption, minimize hydrogen losses, and reduce capital costs. Innovations such as cryosteels for vessel walls and composite materials have the potential to reduce the dewar weight to approach that of a conventional gasoline storage tank. Improved and cheaper forms of insulation such as glass fibers and metallized Mylar, together with LH_2 production systems that employ low-cost high-pressure compressors and expanders, will reduce capital costs by up to 25% while maintaining present levels of energy efficiency. Glass fibers gain strength when operating in the cryogenic temperature range and are a comparatively cheap form of insulation (about US$1.50 per kg).

Table 2 Performance targets for liquid hydrogen (LH_2) systems (target year quoted in parenthesis)

LH_2 fueled light-duty vehicles	
LH_2 storage capacity	> 10.1 kg (at 0.2 Mpa) in a dewar volume of 150 l
Storage system energy density	> 6 wt% (2010) and >9 wt% (2015)
Driving range	> 480 km/300 mi (2015)
System weight	< 11 kg per kg H_2
System volume	< 25 l per kg H_2
Minimum temperature for operability	248 K (− 25 °C)
Durability	> 240 000 km/150 000 mi
Dormancy time	< 30–70 h (starting from a 50% filled storage)
Autonomy time	> 15–30 days (up to 20 km/12.5 mi range)
Evaporative losses (monthly)	< 25% for an infrequent driver
Boil-off rate (monthly)	0% for 8 km/5 mi commuter use < 30% for infrequent driver
Production cost	US$100 $(kW\,h)^{-1}$ (2010); US$15 $(kW\,h)^{-1}$ (2017)
Hydrogen liquefaction plant	
Operating conditions	20–358 K and up to 0.6 MPa
Plant availability	98.5%
Power consumption	0.20 $kW_e\,h\,L^{-1}$ LH_2
Boil-off rate (daily)	0.03%
Energy efficiency(Carnot)	25% for small-scale plants 30 tpd
Energy efficiency (Carnot)	40% for large-scale plants 300 tpd
Energy efficiency (overall)	84% for small-scale plants 30 tpd (2017)
Energy efficiency (overall)	88% for large-scale plants 300 tpd (2017)
Production cost	US$4 $(kW\,h)^{-1}$ (2010); US$2 $(kW\,h)^{-1}$ (2015)
Capital cost	US$35 million for small-scale plants 30 tpd (2017)
Capital cost	US$120 million for large-scale plants 300 tpd (2017)
Hydrogen delivery	
Delivery cost (by tanker)	Additional US$1.40–2.42 kg^{-1} LH_2 to production costs US$1.80 kg^{-1} LH_2 for small-scale transport; US$0.75 kg^{-1} LH_2 for large-scale transport
Delivery cost (from central and semi-central production facilities to refueling station gate and other end users)	< US$0.90 kg^{-1} LH_2 (2010)
Delivery cost (from production site to the point of use in vehicles or stationary power)	< US$1.00 kg^{-1} LH_2 (2017)
Cost of compression, storage, and dispensing at refueling stations and stationary power sites	< US$0.80 kg^{-1} LH_2 (2010)

Thermal Management and Energy Efficiency

Current hydrogen liquefaction plants operate with a relatively modest thermodynamic energy efficiency of 30 to 35%. There is great scope to increase the thermodynamic energy efficiency and reduce the total work input of the compression system to lower hydrogen liquefaction costs. Costs can be significantly lowered if the electrical power required by the liquefaction plant is provided from an inexpensive source such as a gas or a steam turbine. Further gains will be realised with advanced thermal management systems, integration of *o*-H_2 to *p*-H_2 converters and inter-cooling processes, improved insulation technology, and the automation of boil-off control and re-liquefaction.

The USDOE is supporting the development of new high-efficiency liquefaction plants based on the combined reverse-Brayton Joule–Thompson (CRBJT) hydrogen liquefaction cycle that combines the benefits of highly efficient isentropic expansion and the highly reliable Joule–Thompson expansion cycle. Energy released in the expansion of hydrogen by a turbo-expander is recovered as useful work and used for compression. The flow through the turbo-expander provides initial cooling of the system and enables the hydrogen temperature to fall below the inversion temperature. The CRBJT cycle minimizes the contribution of the less efficient isenthalpic (8–12 $kW\,h\,kg^{-1}$) expansion and reduces energy consumption to 3.6–5.0 $kW_e\,h$ per kg of LH_2. The demonstration of a small-scale ($\sim$200 kg per day) hydrogen liquefaction plant based on the CRBJT cycle has indicated that an overall thermodynamic energy efficiency of 90% is possible. A more complex but efficient CRBJT cycle involving twin sets of turbo-expanders and compressors with optimization of pressures, temperatures, and flow rates is anticipated to increase the overall thermodynamic energy efficiency of current technology by up to 50% with an energy consumption approaching the ideal work of liquefaction (3.228 $kW\,h\,kg^{-1}$).

The use of highly efficient compressors, expanders, and refrigeration processes will lower electricity costs significantly; turbo-expanders alone will reduce power

costs by approximately US\$0.50 kg^{-1} LH_2 with a capital cost increase of only US\$0.05–0.08 kg^{-1} LH_2. Plant energy consumption is expected to decrease to approximately 0.8 $kW_e h L^{-1}$ LH_2 over the medium term. Further developments in cooling techniques could result in a 40–60% reduction in energy consumption. Values as low as 0.35 $kW_e h L^{-1}$ LH_2 are considered achievable for commercial plants over the long term.

New Technology and Processes

Increased customer demand for LH_2 will prompt the design of less expensive and more efficient LH_2 dewar technology and improved liquefaction plant processes. Many opportunities exist for the integration of LH_2 systems with other hydrogen-based technologies to improve the system efficiency and reduce costs of a hydrogen plant. For example, the heat required to vaporize LH_2 could be sourced from the waste heat generated from the operation of a fuel cell or a metal hydride system. Energy requirements and capital costs of hydrogen liquefaction plants can be reduced by integration with evaporation and warming processes at LNG import terminals.

Other technological improvements include new compression and expansion technology such as high-speed centrifugal compressors and expanders; new cooling techniques for low-temperature refrigeration such as magnetic and acoustic liquefaction and multicomponent refrigerant cycles for LH_2 precooling; use of metal hydride compressors; and the promising development of cryo-compressed and conformable vessels.

Multicomponent refrigerants such as helium–neon mixtures allow for improved integration between the precooling and hydrogen liquefaction loops and present opportunities for precooling hydrogen to a temperature well below the NBP of the working fluid. The use of multicomponent refrigerants for the low-temperature cycle will reduce the specific energy consumption to 25.2 MJ kg^{-1} (7 kW h kg^{-1}) for a 7200 kg h^{-1} (173 tpd) capacity plant.

Magnetic refrigerators offer a marked improvement in cooling performance in comparison with conventional mechanical coolers. Magnetic liquefaction units consist of a superconducting magnet, heat switches, and a magnetic material such as polycrystal gadolinium-doped dysprosium aluminum that exhibits the magneto-caloric effect. The refrigeration liquefies hydrogen directly on the surface of the magnetic material and thereby reduces the work of liquefaction. Small-scale units with production capacities of 5 kg of LH_2 per day have demonstrated an increase in the thermodynamic efficiency from 35% to 50%. The research groups developing these systems, led by the National Institute for Materials Science of Japan, anticipate further improvements through the investigation of other magnetic materials, with a system scale-up to production capacities of up to 1 t of LH_2 per day.

Conventional cryogenic hydrogen storage vessels are limited to the storage of low-pressure LH_2 but a team from the Lawrence Livermore National Laboratory (LLNL) has designed and tested an insulated CGH_2 vessel that can operate at both cryogenic temperatures as low as 20 K and high pressures up to 35 MPa. This Cryo-compressed hydrogen (CcH_2) storage technology provides flexibility for the interchange between multiple fueling modes of LH_2 and gaseous hydrogen at either cryogenic or ambient temperature. Advantages of cryo-compressed vessels over conventional storage dewars include

- 2–3 times higher storage system energy density than CGH_2 tanks at room temperature;
- elimination of evaporative losses in routine use;
- improved thermal endurance, that is, 5–10 times longer than conventional LH_2 tanks;
- no overpressurization during hydrogen fill;
- reduction in the capital cost of CGH_2 vessels by up to 25%.

Research at LLNL has identified an ideal operating regime for cryo-compressed vessels (200 K, 48.3 MPa) and has verified the safety and reliability performance of these vessels after extensive durability testing. The BMW Group is also committed to the further development of cryo-compressed vessels for application across their LH_2 vehicle range and for hydrogen fueling infrastructure.

Various conformable tank designs that can be shaped to maximize the limited space available in automotive vehicles for hydrogen storage are also under development at LLNL. These flexible designs are only suitable for systems that operate at low pressure, such as cryogenic LH_2 storage. Conformable pressure vessels will minimize cargo space intrusion and extend the range of hydrogen vehicles by 20–40% without dramatic changes to current vehicle designs.

The LLNL has investigated three concepts for filament-wound conformable pressure vessels: the sandwich construction, the ribbed construction, and the pillow construction. The last mentioned is characterized by a series of flat-sided segments with ellipsoidal edges (or 'pillows') and presents the best development potential of the three designs. Analysis, experiments, and validation have included evaluation of filament-winding techniques, winding patterns, reinforcement of vessel corners, stress distributions, and manufacturing defects.

Macro-lattice conformable vessels use an internal structure to provide structural support of the vessel that lowers the bending stresses on the outer skin of the vessel and, in turn, reduces the outer wall thickness and hence the capital cost. The internal structure consists of steel or

composite material struts that provide optimum structural efficiency. The cubic container with polycarbonate surfaces is held together by metallic struts – a design that is amenable to high-volume manufacturing.

Replicant conformable vessels also use an internal structure to withstand the internal vessel pressure, along with a thin outer shell to contain the hydrogen. The internal structure is made of 'replicants', which are small structural members that fill the interior of the vessel. Replicant vessels are considered to have a mass production advantage over large sizes, in which the individual macro-lattice struts would be very large. Mass production of the replicants and robotic assembly could result in the production of large-scale conformable vessels with significant reductions in manufacturing time.

Nomenclature

Symbols and Units

D	liquefaction plant capacity (tpa)
D_{ref}	capacity of an existing plant
K	reaction rate constant
m_c	constant addition rate of liquid hydrogen (kg)
m_L	mass of liquid hydrogen in dewar (kg)
m_o	mass of liquid *ortho*-H_2 mass in dewar (kg)
m_v	mass of vapor hydrogen mass dewar (kg)
n	sizing exponent for LH_2 plants (ranges between 0.6 and 0.7)
o-H_2	*ortho*-hydrogen
p-H_2	*para*-hydrogen
$\mathcal{Q}$	investment cost ($)
$\mathcal{Q}_{ref}$	investment cost for an existing plant
S	entropy ($JK^{-1}mol^{-1}$)
T	temperature (K)
t	time (s)
T_a	ambient (or heat sink) temperature (K)
T_e	equilibrium temperature of the o-H_2-to-p-H_2 conversion (K)
$W_{condensation}$	work required for gas-to-liquid conversion (J)
$W_{conversion}$	work required to convert *ortho*-H_2 to *para*-H_2 (J)
$W_{cooling}$	work required to reduce hydrogen gas temperature (J)
W_L	ideal work of liquefaction $= 11.621 MJ\,kg^{-1}$ ($3.228\,kW\,h\,kg^{-1}$) for hydrogen
x_o	*ortho*-H_2 concentration in dewar
x_{oc}	*ortho*-H_2 concentration in added liquid hydrogen
ΔH	change in enthalpy between initial (gaseous) state and final (liquid) state ($J\,mol^{-1}$)
ΔH_c	heat of transformation or conversion ($J\,mol^{-1}$)
ΔH_v	heat of vaporization ($J\,mol^{-1}$)

Abbreviations and Acronyms

CcH_2	cryo-compressed hydrogen
CEP	Clean Energy Partnership
CGH_2	compressed gaseous hydrogen
CRBJT	combined reverse-Brayton Joule–Thompson hydrogen liquefaction cycle
ET	external tank
FCV	fuel cell vehicle
GH_2	gaseous hydrogen
GN_2	gaseous nitrogen
HE	heat exchanger
HHV	higher heating value
HICE	hydrogen-fueled internal combustion engine
LH_2	liquid hydrogen
LHV	lower heating value
LLNL	Lawrence Livermore National Laboratory
LN_2	liquid nitrogen
LNG	liquefied natural gas
LOX	liquid oxygen
LPG	liquefied petroleum gas
LSU	liquid separation unit
LWT	lightweight tank
NASA	National Aeronautics and Space Administration
NBP	normal boiling point
Ni–MH	nickel–metal hydride
SLWT	super lightweight tank
SSME	space shuttle main engine
SWT	standard weight tank
USDOE	United States Department of Energy

See also: **Applications – Stationary:** Fuel Cells; Residential Energy Supply: Fuel Cells; Uninterruptible and Back-up Power: Fuel Cells; **Applications – Transportation:** Aviation: Fuel Cells; Buses: Fuel Cells; Electric Vehicles: Fuel Cells; Light Traction: Fuel Cells; Ships: Fuel Cells; **Energy:** Energy Storage; Hydrogen

Economy; **Fuels – Hydrogen Production:** Autothermal Reforming; Biomass: Fermentation; Biomass: Thermochemical Processes; Coal Gasification; Natural Gas: Conventional Steam-Reforming; Natural Gas: Solar-Thermal Steam Reforming; Natural Gas: Solar-Thermal Steam Reforming; Photoelectrolysis; Photothermally and Thermally-Assisted Photovoltaic; Thermochemical Cycles; Water Electrolysis; **Fuels – Hydrogen Storage:** Carbon Materials; Chemical Carriers; Complex Hydrides; Compressed; Glass Microspheres; High Temperature Hydrides; Hydrides; Metal–Organic Frameworks; Zeolites; **Fuels – Safety:** Hydrogen: Overview; Hydrogen: Transportation; **Photoelectrochemical Cells:** Dye-Sensitized Cells.

Further Reading

Bonhoff K (2008) The clean energy partnership Berlin – CEP. *Journal of Power Sources* 181: 350–352.

Brewer DG (1991) *Hydrogen Aircraft Technology*. Boca Raton, FL: CRC Press.

Dewar J (1927) In: Lady Dewar (ed.) *Collected Papers of Sir James Dewar*, pp. 678–691. Cambridge UK: Cambridge University Press.

Sloop JL (1977) *Liquid Hydrogen as a Propulsion Fuel, 1945–1959*. In the NASA History Series. Washington, USA: National Aeronautics and Space Administration. NASA SP; 4404, TI-785.S58 629.47'522 77-26960.

Hoffmann P (2001) *Tomorrow's Energy: Hydrogen, Fuel Cells and the Prospects for a Cleaner Planet*. Cambridge, MA: MIT Press.

Rand DAJ and Dell RM (2008) *Hydrogen Energy: Challenges and Prospects*. Cambridge, UK: The Royal Society of Chemistry.