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Hydrogen Energy Technologies

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27.1 Introduction

Energy carriers are a convenient form of stored energy. Electricity is one type of carrier that can be produced from various sources, transported over large distances, and distributed to the end user. Hydrogen is another type of energy carrier. If produced from clean sources, it constitutes a clean and versatile carrier. Liquid hydrogen is already used for space shuttles and rockets and is also proposed for the future hypersonic or supersonic space vehicles. However, at present there is increased interest from governments in the development of hydrogen as a fuel for other applications such as transportation and stationary power from off-peak storage. This chapter provides the information about hydrogen and the status of hydrogen technologies. The topics covered include hydrogen production, storage, distribution, conversion, and safety.

27.2 Properties of Hydrogen

Hydrogen is an odorless, colorless gas. With a molecular weight of 2.016 g/mol, hydrogen is the lightest element. Its density is about 14 times less than air (0.08376 kg/m^3 at standard temperature and pressure). Hydrogen is liquid at temperatures below 20.3 K (at atmospheric pressure). Hydrogen has the highest energy content per unit mass of all fuels—its higher heating value is 141.9 MJ/kg, almost three times

TABLE 27.1 Properties of Hydrogen (at Standard Temperature and Pressure)

Molecular weight		2.016
Density	kg/m^3	0.0838
Higher heating value	MJ/kg	141.90
	MJ/m^3	11.89
Lower heating value	MJ/kg	119.90
	MJ/m^3	10.05
Boiling temperature	K	20.3
Density as liquid	kg/m^3	70.8
Critical point		
Temperature	K	32.94
Pressure	Bar	12.84
Density	kg/m^3	31.40
Self-ignition temperature	K	858
Ignition limits in air	(vol. %)	4–75
Stoichiometric mixture in air	(vol. %)	29.53
Flame temperature in air	K	2,318
Diffusion coefficient	cm^2/s	0.61
Specific heat (c_p)	$kJ/(kg \cdot K)$	14.89

higher than that of gasoline. However, because of its low density, its heating value on volumetric basis is almost one third that of natural gas. Some important properties of hydrogen are compiled in Table 27.1. It exists in three isotopes: protium, deuterium, and tritium. A standard hydrogen atom (protium) is the simplest of all the elements and consists of one proton and one electron. Molecular hydrogen (H_2) exists in two forms: ortho- and para-hydrogen. Both forms have identical chemical properties, but due to different spin orientations have somewhat different physical properties. At room temperature hydrogen consists of approximately 75% ortho- and 25% para-hydrogen. Because para-hydrogen is more stable at lower temperatures its concentration increases at lower temperatures, reaching virtually 100% at liquid hydrogen temperatures.

27.3 Hydrogen Production Methods

Although hydrogen is the most plentiful element in the universe, making up about three quarters of all matter, free hydrogen is scarce. The atmosphere contains trace amounts of it (0.07%), and it is usually found in small amounts mixed with natural gas in crustal reservoirs. A few wells, however, have been found to contain large amounts of hydrogen, such as some wells in Kansas that contain 40% hydrogen, 60% nitrogen, and trace amounts of hydrocarbons [1]. The Earth's surface contains about 0.14% hydrogen (the tenth most abundant element), most of which resides in chemical combination with oxygen as water. Hydrogen, therefore, must be produced. Logical sources of hydrogen are hydrocarbon (fossil) fuels (C_xH_y) and water (H_2O). Presently, hydrogen is mostly being produced from fossil fuels (natural gas, oil, and coal). However, except for the space program, hydrogen is not being used directly as a fuel or as an energy carrier. It is being used in refineries to upgrade crude oil (hydrotreating and hydrocracking), in the chemical industry to synthesize various chemical compounds (such as ammonia, methanol, etc.), and in metallurgical processes (as a reduction or protection gas). The total annual hydrogen production worldwide in 1996 was about 40 million tons (5.6 EJ) [2]. Less than 10% of that amount was supplied by industrial gas companies; the rest was produced at consumer-owned and operated plants (so-called *captive production*) such as refineries and at ammonia and methanol production facilities. Production of hydrogen as an energy carrier would require an increase in production rates by several orders of magnitude.

A logical source for large-scale hydrogen production is water, which is abundant on Earth. Different methods of hydrogen production from water have been, or are being developed. They include

TABLE 27.2 Hydrogen Production Cost

Technology	Cost of H_2 (\$/GJ)	Cost of H_2 (\$/kg)
Direct biomass gasification	12.5–21.6	1.51–2.59
Steam reforming of bio-oil	10.3–19.9	1.24–2.38

Source: From Spath, P. L., Mann, M. K. and Amos, W. A. 2000. *Update of Hydrogen from Biomass—Determination of the Delivered Cost of Hydrogen, NREL/MP-510-33112*, National Renewable Energy Laboratory, Golden, CO; Craig, K. R. and Mann, M. K. 1996. Cost and Performance Analysis of Biomass Based Integrated Gasification Combined Cycle BIGCC Power Systems, NREL/TP-430-21657, National Renewable Energy Laboratory, Golden, CO.

electrolysis, thermochemical processes, photolysis, photoelectrochemical processes, and photocatalysis. Biomass is another important renewable resource for producing hydrogen. Some of these methods are described below (Table 27.2).

27.3.1 Electrolysis

Electrolysis appears to be the only method developed to date that can be used for large-scale hydrogen production in a post-fossil-fuel era. Production of hydrogen by water electrolysis is a mature technology, based on a fundamentally simple process; it is very efficient, and does not involve moving parts.

The following reactions take place at the electrodes of an electrolysis cell filled with a suitable electrolyte (aqueous solution of KOH, NaOH, or NaCl) upon the application of a potential:

$$\text{Cathode reaction: } 2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq) \tag{27.1}$$

$$\text{Anode reaction: } 2OH^-(aq) \rightarrow \frac{1}{2}O_2(g) + H_2O(l) \tag{27.2}$$

$$\text{Overall cell reaction: } H_2O(l) \rightarrow H_2(g) + O_2(g) \tag{27.3}$$

The reversible decomposition potential ($E_{\text{rev}} = \Delta G/nF$) of the above reaction is 1.229 V at standard conditions. The total theoretical water decomposition potential is 1.480 V corresponding to hydrogen's enthalpy (because $\Delta H = \Delta G + T\Delta S$). Due to irreversible processes occurring at the anode and cathode, including the electrical resistance of the cell, the actual potentials are always higher, typically between 1.75 and 2.05 V. This corresponds to the efficiencies of 72% to 82%.

Several advanced electrolyzer technologies are being developed, such as:

- Advanced alkaline electrolysis, which employs new materials for membranes and electrodes that allow further improvement in efficiency—up to 90% [3,4].
- Solid polymer electrolytic (SPE) process, which employs a proton-conducting ion-exchange membrane as electrolyte and as a membrane that separates the electrolysis cell. This type of electrolyzer can operate at high current densities (up to 2 A/cm^2 which is about one order of magnitude higher than standard electrolyzers with alkaline liquid electrolytes). The water to be dissociated does not require dissolved electrolytes to increase its conductivity and is added solely to the anode side [4,5].
- High-temperature steam electrolysis operates between 700°C and 1000°C and employs oxygen ion-conducting ceramics as an electrolyte. Electrical energy consumption is reduced because part of the energy required for water dissociation is supplied in the form of heat. The water to be dissociated is entered on the cathode side as steam, which forms a steam–hydrogen mixture during electrolytic dissociation. The O_2^- ions are transported through the ceramic material to the anode, where they are discharged as oxygen [6].

An electrolysis plant can operate over a wide range of capacity factors and is convenient for wide range of operating capacities, which makes this process interesting for coupling with renewable energy sources, particularly with photovoltaics (PV). Photovoltaics generate low-voltage direct current that is required for the electrolysis process.

The performance of photovoltaic-electrolyzer systems has been studied extensively both in theory and in practice [7–10]. Several experimental PV-electrolysis plants are currently operating all over the world, including:

- Solar–Wasserstoff–Bayern pilot plant in Neunburg vorm Wald in Germany [11]
- HYSOLAR project in Saudi Arabia [12]
- Schatz Energy Center, Humboldt State University, Arcata, California [13]
- Helsinki University of Technology, Helsinki, Finland [14]
- INTA Energy Laboratory, Huelva, Spain, [15]

27.3.2 Thermochemical Processes

Thermochemical hydrogen production is a means of splitting water via a series of chemical reactions. All chemical intermediates are recycled internally within the process so that water is the only raw material and hydrogen and oxygen are the only products. The maximum temperature requirements for most thermochemical cycles lie within a temperature range of 650°C–1100°C [16], thus eliminating the use of lower-temperature heat sources. High-concentration solar collectors and nuclear reactors are the possible sources of heat for these cycles. According to Wendt [17] 2000–3000 different theoretical cycles have been proposed and evaluated. However, out of all the possible thermochemical cycles, Mark 1, Mark 15, ZnO/Zn, UT-3, Fe_3O_4/FeO, and iodine–sulfur processes are the only few that have been studied extensively.

Although theoretical efficiencies of hydrogen production by thermochemical cycles are as high as 50%, practical achieved efficiencies are extremely low. Material problems at the high temperatures have also hindered the development of efficient, scaleable reactor concepts. The problems associated with the separation of hydrogen and oxygen, the depletion of intermediate products, and matching the reaction rates of the individual steps have further limited the practical implementation of thermochemical cycles. Thus far, only one cycle has been demonstrated on a bench scale and none of them have been demonstrated at a larger scale.

27.3.3 Photoelectrochemical Hydrogen Production

Photoelectrochemical (PEC) systems combine both photovoltaics and electrolysis into a one-step water-splitting process. These systems use a semiconductor electrode exposed to sunlight in combination with a metallic or semiconductor electrode to form a PEC cell. A schematic illustration of a PEC hydrogen production cell driven by solar energy is shown in Figure 27.1. In general, the semiconductor electrode (photoanode) is activated by solar radiation that drives the reaction in aqueous solution. Due to bandgap illumination, electrons and holes are formed in the conduction and valence bands, respectively, at the photoanode.

The photogenerated holes at the anode split the water molecules into hydrogen ions and oxygen. Released hydrogen ions migrate to the cathode through the aqueous electrolyte.

$$2h^+ + H_2O \rightarrow \frac{1}{2}O_2 + 2H^+. \tag{27.4}$$

Electrons generated at the photoanode are transferred over the external circuit to the cathode, where they reduce hydrogen ions into gaseous hydrogen:

$$2H^+ + 2e^- \rightarrow H_2. \tag{27.5}$$

Ideally, electrochemical decomposition of water takes place when the electromotive force of the cell is equal to 1.23 eV. If one considers internal losses in the PEC, a minimum bandgap of 1.8 eV is required to run the reaction [19]. Photoelectrochemically stable semiconductors such as TiO_2 and $SrTiO_3$ have a wide bandgap and hence are limited in the UV region of the solar spectrum, whereas narrow-bandgap

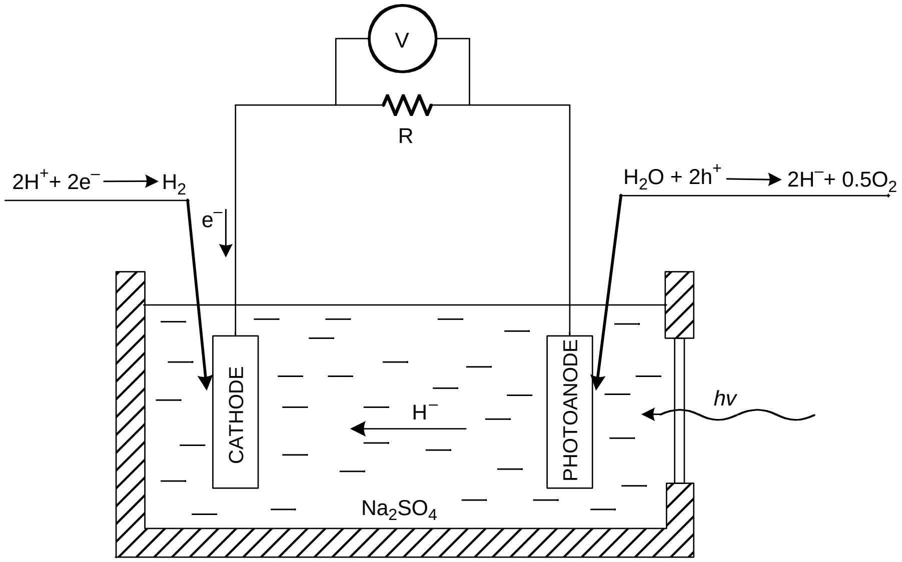

FIGURE 27.1 Schematic representation of photoelectrochemical cell (PEC). (Adapted from Bak, T., Nowotny, J., Rekas, M. and Sorrell, C. C., 2002. *International Journal of Hydrogen Energy*, 27, 991–1022.)

semiconductors such as GaP and GaAs are often photoelectrochemically unstable [20]. The problem of low light absorption is addressed by enlarging the spectral response of the PEC cells. The techniques used to solve the problem are dye adsorption, metal incorporation, and use of multijunction cells.

27.3.4 Photochemical Hydrogen Production

Photochemical systems differ from PEC systems in that they use a semiconductor suspension instead of individual electrodes to induce the reactions. Photochemical systems have photosensitizer particles suspended in an aqueous solution where a photosensitizer is an organic or semiconductor molecule that can absorb sunlight and induce photochemical reactions for the hydrogen production. The reduction and oxidation reactions occur simultaneously at the surface of the suspended photosensitizer particles. Because absorption of a single photon can cause the transfer of at most one electron, a catalyst is required along with light to induce the redox reaction.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-, \tag{27.6}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-. \tag{27.7}$$

Figure 27.2 illustrates the schematic of a general photochemical reaction to generate hydrogen. No photochemical system has been able to reach an efficiency of 10%.

27.3.5 Hydrogen Production from Biomass

Biomass represents a large potential feedstock resource for environmentally clean hydrogen production. It lends itself to both biological and thermal conversion processes. In the thermal path, hydrogen can be produced in two ways: direct gasification and pyrolysis to produce liquid bio-oil followed by steam reforming.

Direct gasification of biomass is in many ways similar to coal gasification. The process occurs broadly in three steps: biomass is first gasified (using steam or air) to produce an impure syngas mixture composed of hydrogen, CO, CO_2, CH_4, small amounts of higher hydrocarbons, tar, and water vapor. The gas may also contain particulate matter that is removed using cyclones and scrubbers. The particulate-free gas is

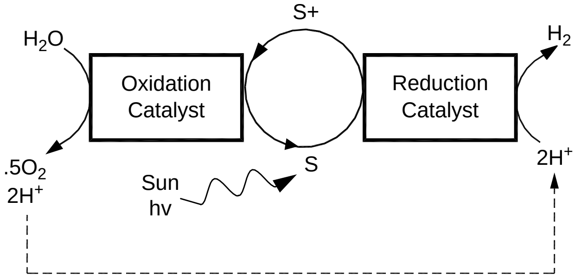

FIGURE 27.2 Minimal scheme for the photochemical splitting of water. S is a photochemical sensitizer. (Adapted from Bolton, J. R., 1996. Solar photoproduction of hydrogen, *International Energy Agency Technical Report*, IEA/H2/TR-96, International Energy Agency, Paris, France.)

compressed and then catalytically steam reformed to eliminate the tars and higher hydrocarbons. This is followed by high- and low-temperature shift conversions to convert the CO to CO_2 and thereby produce additional hydrogen. Finally, the hydrogen is separated from other products by pressure swing adsorption (PSA) [22]. Figure 27.3 illustrates the sequence of processes. The main reactions taking place in biomass gasification are as follows:

$$CH_{1.5}O_{0.7} + 0.3H_2O \rightarrow CO + 1.05H_2 \quad \Delta H_R = +74.4\ \text{kJ/mol} \quad \text{(biomass gasification)}, \tag{27.8}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_R = -41.2\ \text{kJ/mol} \quad \text{(water}-\text{gas shift)}. \tag{27.9}$$

Biomass typically contains about 6% hydrogen by weight. However, in presence of hydrogen-bearing species (steam), the hydrogen yield can be considerably improved above the 6% minimum [23]. Gasification temperatures encountered are typically in the range 600–850°C, which is lower than many thermochemical water-splitting cycles, thereby making biomass gasification an attractive technology to produce hydrogen. Steam gasification of biomass is endothermic and the energy required for the process is supplied by burning part of the biomass feedstock or uncombusted char. Tars are polyaromatic hydrocarbons produced during gasification of biomass. Tars are undesirable coproducts as they clog filters, pipes, and valves and damage downstream equipments such as engines and turbines. Efforts are being made to minimize or reform the tars to additional product hydrogen [24,25].

Hydrogen can be alternately produced by reforming the biomass to a liquid bio-oil in a process called *pyrolysis*. Pyrolysis is an endothermic thermal decomposition of biomass carried out in an inert

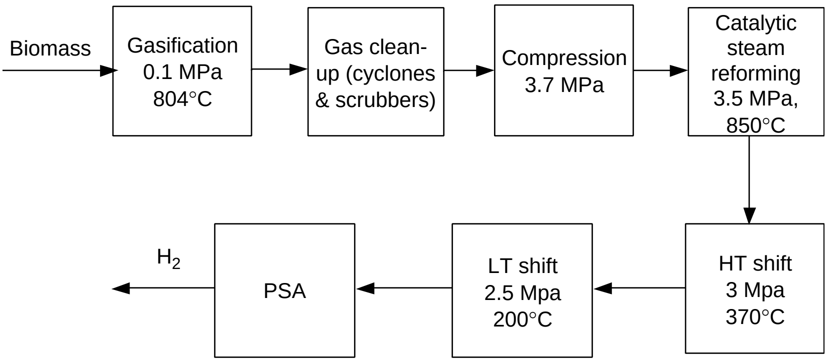

FIGURE 27.3 Gasification followed by steam reforming. (From Spath, P. L., Mann, M. K. and Amos, W. A., 2000. Update of hydrogen from biomass—Determination of the delivered cost of hydrogen, NREL/MP-510-33112, National Renewable Energy Laboratory, Golden, CO.)

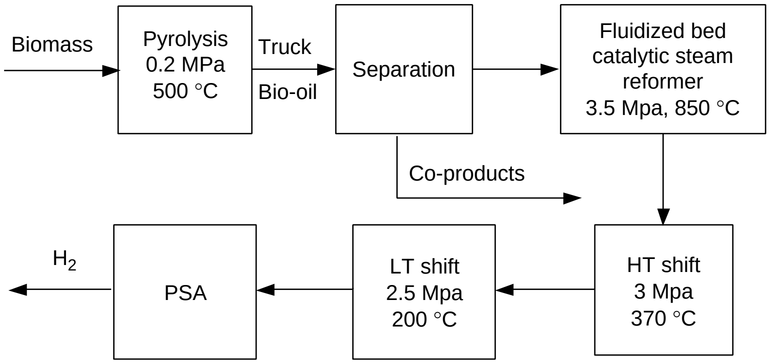

FIGURE 27.4 Pyrolysis followed by steam reforming. (From Spath, P. L., Mann, M. K. and Amos, W. A., 2000. Update of hydrogen from biomass—Determination of the delivered cost of hydrogen, NREL/MP-510-33112, National Renewable Energy Laboratory, Golden, CO.)

atmosphere at 450–550°C [26].The bio-oil so produced is a liquid composed of 85% oxygenated organics and 15% water. The bio-oil is then steam-reformed in the presence of a nickel-based catalyst at 750–850°C followed by shift conversion to convert CO to CO_2 which produces additional hydrogen [27]. Figure 27.4 illustrates the sequence of processes. The reactions can be written as:

$$\text{Biomass} \rightarrow \text{Bio}-\text{oil} + \text{char} + \text{gas} \quad (\text{pyrolysis}), \tag{27.10}$$

$$\text{Bio}-\text{oil} + H_2O \rightarrow CO + H_2 \quad (\text{reforming}), \tag{27.11}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (\text{shift}). \tag{27.12}$$

A number of research groups around the world are involved in research on hydrogen production from a variety of biomass resources, including wood, municipal solid waste, and residues from industries [25,28–35]. There are currently no commercial biomass gasification processes for hydrogen production but there are several demonstration plants of biomass gasifiers for producing electricity or chemicals [45]. Biomass resources have the advantage of being renewable and can therefore make an important contribution to renewable hydrogen production. However, an important factor that prohibits commercialization is the difficulty of transporting large amounts of low energy density biomass feed stocks over long distances. The cost associated with growing, harvesting, and transporting biomass may be up to 40% of the total biomass plant operating cost [22,37].

Additional technical and economic considerations for capture and storage of CO_2 may also be necessary as both gasification and pyrolysis produce carbon dioxide.

27.3.6 Biological Methods

Hydrogen may also be produced from biological processes involving organic compounds. The two fundamental ways of biological hydrogen production are: (1) fermentation of the bacteria, which is an anaerobic process that converts organic substances like, starch, cellobiose, sucrose, and xylose to H_2 and CO_2 without the need of sunlight and oxygen, and (2) biophotolysis, a process that uses microalgae-cynobacteria and green algae to produce hydrogen in the presence of sunlight and water [38]. Both of these processes are being researched. However, the efficiencies of these processes are so low that they are not an option in the near term.

27.4 Hydrogen Storage

27.4.1 Gaseous Hydrogen Storage

Because of hydrogen's low density, its storage always requires relatively large volumes and is associated with either high pressures (thus requiring heavy vessels), or extremely low temperatures, and/or combination with other materials (much heavier than hydrogen itself). Table 27.3 shows achievable storage densities with different types of hydrogen storage methods. Some novel hydrogen storage methods may achieve even higher storage densities, but have yet to be proven in terms of practicality, cost, and safety.

Depending on storage size and application, several types of hydrogen storage may be differentiated:

1. Stationary large storage systems: these are typically storage devices at the production site or at the start or end of pipelines and other transportation pathways.
2. Stationary small storage systems: at the distribution or final user level, for example, a storage system to meet the demand of an industrial plant.
3. Mobile storage systems for transport and distribution: these include both large-capacity devices, such as a liquid hydrogen tanker–bulk carrier, and small systems, such as a gaseous or liquid hydrogen truck trailer.
4. Vehicle tanks: to store hydrogen used as fuel for road vehicles.

27.4.1.1 Large Underground Hydrogen Storage

Underground storage of hydrogen in caverns, aquifers, depleted petroleum and natural gas fields, and man-made caverns resulting from mining and other activities may be technologically feasible [39]. But hydrogen storage systems of the same type and the same energy content will be more expensive by approximately a factor of 3 than natural gas storage systems due to hydrogen's lower volumetric heating value. Technical problems, specifically for the underground storage of hydrogen other than expected losses of the working gas in the amount of 1–3% per year are not anticipated. The city of Kiel's public utility has been storing town gas with a hydrogen content of 60–65% in a gas cavern with a geometric volume of about 32,000 m^3 and a pressure of 80–160 bar at a depth of 1,330 m since 1971 [40]. Gaz de France (the French national gas company) has stored hydrogen-rich refinery byproduct gases in an aquifer structure near Beynes, France. Imperial Chemical Industries of Great Britain stores hydrogen in the salt mine caverns near Teeside, United Kingdom [41].

27.4.1.2 Aboveground Pressurized Gas Storage Systems

Today, pressurized gas storage systems are used in natural gas business in various sizes and pressure ranges from standard pressure cylinders (50 L, 200 bar) to stationary high-pressure containers (over 200

TABLE 27.3 Hydrogen Storage Types and Densities

	kg H_2/kg	kg H_2/m^3
Large volume storage (10^2–10^4 m^3 geometric volume)		
Underground storage		5–10
Pressurized gas storage (aboveground)	0.01–0.014	2–16
Metal hydride	0.013–0.015	50–55
Liquid hydrogen	~1	65–69
Stationary small storage (1–100 m^3 geometric volume)		
Pressurized gas cylinder	0.012	~15
Metal hydride	0.012–0.014	50–53
Liquid hydrogen tank	0.15–0.50	~65
Vehicle tanks (0.1–0.5 m^3 geometric volume)		
Pressurized gas cylinder	0.05	15
Metal hydride	0.02	55
Liquid hydrogen tank	0.09–0.13	50–60

TABLE 27.4 Theoretical Capacities of Hydriding Substances as Hydrogen Storage Media

Medium	Hydrogen Content (kg/kg)	Hydrogen Storage Capacity (kg/L of vol.)	Energy Density (kJ/kg)	Energy Density (kJ/L of vol.)
MgH_2	0.070	0.101	9,933	14,330
Mg_2NiH_4	0.0316	0.081	4,484	11,494
VH_2	0.0207		3,831	
$FeTiH_{1.95}$	0.0175	0.096	2,483	13,620
$TiFe_{0.7}Mn_{0.2}H_{1.9}$	0.0172	0.090	2,440	12,770
$LaNi_5H_{7.0}$	0.0137	0.089	1,944	12,630
$R.E.Ni_5H_{6.5}$	0.0135	0.090	1,915	12,770
Liquid H_2	1.00	0.071	141,900	10,075
Gaseous H_2 (100 bar)	1.00	0.0083	141,900	1,170
Gaseous H_2 (200 bar)	1.00	0.0166	141,900	2,340
Gasoline	–	–	47,300	35,500

bar) or low-pressure spherical containers (greater than 30,000 m^3, 12–16 bar). This application range will be similar for hydrogen storage.

27.4.1.3 Vehicular Pressurized Hydrogen Tanks

Storage of hydrogen in automobiles is possible using ultra-light but strong new composite materials. Pressure vessels that allow hydrogen storage at pressures greater than 200 bar have been developed and used in automobiles (such as Daimler–Benz NECAR II). A storage density higher than 0.05 kg of hydrogen per 1 kg of total weight is easily achievable [42].

27.4.1.4 Metal-Hydride Storage

Hydrogen can be stored in a solid state by forming metal hydride. During the formation of the metal hydride, hydrogen molecules are dissociated into H atoms that are inserted in interstitial spaces inside the lattice of intermetallic compounds and/or alloys. In such a way, effective storage comparable with the density of liquid hydrogen is created. However, when the mass of the metal or alloy is taken into account, the metal hydride gravimetric storage density is comparable with storage of pressurized hydrogen. The best theoretically achievable gravimetric storage density is about 0.07 kg of H_2/kg of metal for a high-temperature hydride such as MgH_2, as shown in Table 27.4 that gives a comparison of some hydriding substances with liquid hydrogen, gaseous hydrogen, and gasoline [43].

An overview of hydrogen storage alloys has been discussed by Sandrock [44] from the solid–gas reaction point of view. There are a number of important properties that must be considered in metal hydride storage. Some of the most important ones are: (1) ease of activation, (2) heat transfer rate, (3) kinetics of hydriding and dehydriding, (4) resistance to gaseous impurities, (5) cyclic stability, (6) safety, and (7) weight and cost. Although metal hydrides can theoretically store large amounts of hydrogen, the practical gravimetric hydrogen density is limited to less than 3%. Another stumbling block for this storage method is the low practical cyclic stability achieved thus far.

27.5 Liquid Hydrogen

At present, liquid hydrogen is primarily used as a rocket fuel because it has the lowest boiling point density and the highest specific thrust of any known fuel. Its favorable characteristics include its high heating value per unit mass, its wide ignition range in hydrogen/oxygen or air mixtures, as well as its large flame speed and cooling capacity due to its high specific heat which permits very effective engine cooling and cooling the critical parts of the outer skin [45,46]. Liquid hydrogen has some other important uses, such as in high-energy nuclear physics and bubble chambers. For the transport of hydrogen in liquid form, cryogenic refrigeration and special dewar vessels are required. Although liquid hydrogen can provide a lot of advantages, its uses are restricted in part because liquefying hydrogen consumes a large amount of energy (around 30% of its heating value). Liquefying 1 kg of hydrogen in a medium-size plant requires 10–13 kWh of electricity [46]. In addition, boil-off losses associated with the storage, transportation, and handling of liquid hydrogen can consume up to 40% of its available combustion energy. It is therefore important to search for ways that can improve the efficiency of the liquefiers and diminish the boil-off losses.

27.5.1 Hydrogen Liquefaction

Production of liquid hydrogen requires the use of liquefiers that utilize different principles of cooling. In general, hydrogen liquefiers may be classified as conventional, magnetic, or hybrid. Many types of conventional liquefiers exist, such as the Linde–Hampson liquefiers, the Linde Dual-Pressure liquefiers, the Claude liquefiers, the Kapitza liquefiers, the Heylandt liquefiers, and those liquefiers utilizing the Collins cycle, to name a few. Conventional liquefiers generally comprise compressors, expanders, heat exchangers, and Joule–Thomson valves. Magnetic liquefiers, on the other hand, utilize the magnetocaloric effect. This effect is based upon the principle that some magnetic materials experience a temperature increase upon the application of a magnetic field and a temperature drop upon lifting the magnetic field. The magnetic analog of several conventional liquefiers includes the Brayton liquefiers, the Stirling liquefiers, and the active magnetic regenerative (AMR) liquefier. Additional information on liquid hydrogen production methods can be found in Sherif et al. [47].

27.5.2 Liquid Hydrogen Storage

Hydrogen is usually transported in large quantities by truck tankers of 30–60 m^3 capacity, by rail tank cars of 115 m^3 capacity, and by barge containers of 950 m^3 capacity [48]. Liquid-hydrogen storage vessels are usually available in sizes ranging from 1-L dewar flasks used in laboratory applications to large tanks of 5000 m^3 capacity. The National Aeronautics and Space Administration (NASA) typically uses large tanks of 3,800 m^3 capacity (25 m in diameter) [39]. The total boil-off rate from such dewars is approximately 600,000 LPY (liters per year) which is vented to a burn pond.

The contributing mechanisms to boil-off losses in cryogenic hydrogen storage systems are: (1) ortho–para conversion; (2) heat leak (shape and size effect, thermal stratification, thermal overfill, insulation, conduction, radiation, cool-down), (3) sloshing, and (4) flashing.

27.6 Hydrogen Transport and Distribution

Hydrogen can be transported by means of underground pipelines (gaseous hydrogen) and/or supertankers (liquid hydrogen). Presently, hydrogen transportation through pipelines is used either in links between nearby production and utilization sites (up to 10 km) or in more extensive networks (roughly 200 km). Table 27.5 lists the principal existing hydrogen pipelines [49]. For hydrogen pipelines, it is necessary to use steel that is resistant to embrittlement by hydrogen under pressure, particularly for very pure hydrogen (greater than 99.5% purity). Reciprocating compressors used for natural gas can be used for hydrogen without major design modifications. However, special attention must be given to sealing (to avoid hydrogen leaks) and to materials selection for the parts subject to fatigue stress. Use of centrifugal compressors for hydrogen creates more problems due to hydrogen's exceptional lightness.

As a rule, hydrogen transmission through pipelines requires larger diameter piping and more compression power than natural gas for the same energy throughput. However, due to lower pressure losses in the case of hydrogen, the recompression stations would need to be spaced twice as far apart. In economic terms, most of the studies found that the cost of large-scale transmission of hydrogen is about 1.5–1.8 times that of natural gas transmission.

To match the consumption demand, hydrogen can be regionally transported and distributed, either as a gas or as a liquid, by pipelines or in special cases in containers by road and rail transportation. Gaseous (and liquid) hydrogen carriage is subject to strict regulations ensuring public safety, which in some

TABLE 27.5 Some Major Hydrogen Pipelines

Location	Years of Operation	Diameter (mm)	Length (km)	Pressure (MPa)	Purity
AGEC, Alberta, Canada	Since 1987	273	3.7	3.79	99.9%
Air Liquide, France	Since 1966	various	290	6.48–10	Pure and raw
Air Products, Houston, TX	Since 1969	114–324	100	0.35–5.5	Pure
Air Products, Louisiana	Since 1990	102–305	48	3.45	
Chemische Werke Huls	Since 1938	168–273	215	to 2.5	Raw gas
Cominco, B.C., Canada	Since 1964	5	0.6	>30	62–100%
Gulf Petroleum Canada		168.3	16		93.5%
Hawkeye Chemical, Iowa	Since 1987	152	3.2	2.75	
ICI Bilingham, U.K.			15	30	Pure
Philips Petroleum	Since 1986	203	20.9	12	

countries is very constraining. Transportation of gaseous or liquid hydrogen in a discontinuous mode is currently employed by occasional or low-volume users. The cost of discontinuous transport is very high (it can be as high as 2–5 times the production cost).

27.7 Hydrogen Conversion Technologies

Hydrogen as an energy carrier can be converted into useful forms of energy in several ways, specifically:

- Combustion in internal combustion engines [50]
- Combustion with pure oxygen to generate steam
- Catalytic combustion to generate heat
- Electrochemical conversion to electricity
- Metal hydride conversions

27.7.1 Steam Generation by Hydrogen/Oxygen Combustion

Hydrogen combusted with pure oxygen results in pure steam, i.e.,

$$2H_2 + O_2 \rightarrow 2H_2O. \tag{27.13}$$

The above reaction creates temperatures in the flame zone above 3,000°C, therefore additional water must be injected so that the steam temperature can be regulated at a desired level. Both saturated and superheated vapor can be produced.

The German Aerospace Research Establishment has developed a compact hydrogen/oxygen steam generator [51]. The steam generator consists of the ignition, combustion, and evaporation chambers. In the ignition chamber, a combustible mixture of hydrogen and oxygen at a low oxidant/fuel ratio is ignited by means of a spark plug. The rest of the oxygen is added in the combustion chamber to adjust the oxidant/fuel ratio exactly to the stoichiometric one. Water is also injected in the combustion chamber after it has passed through the double walls of the combustion chamber. The evaporation chamber serves to homogenize the steam. The steam's temperature is monitored and controlled. Such a device is very efficient because there are no emissions other than steam and very little thermal losses.

The hydrogen steam generator can be used to generate steam for spinning reserve in power plants, for peak load electricity generation, for industrial steam supply networks, and as a micro steam generator in medical technology and biotechnology [51].

27.7.1.1 Catalytic Combustion of Hydrogen

Hydrogen and oxygen in the presence of a suitable catalyst may be combined at temperatures significantly lower than flame combustion (from ambient to 500°C). This principle can be used to design catalytic burners and heaters. Catalytic burners require considerably more surface area than conventional flame burners. Therefore, the catalyst is typically dispersed in a porous structure. The reaction rate and resulting temperature are easily controlled, by controlling the hydrogen flow rate. The reaction takes place in a reaction zone of the porous catalytic sintered metal cylinders or plates in which hydrogen and oxygen are mixed by diffusion from opposite sides. A combustible mixture is formed only in the reaction zone and assisted with a (platinum) catalyst to burn at low temperatures (Figure 27.2). The only product of catalytic combustion of hydrogen is water vapor. Due to low temperatures there are no nitrogen oxides formed. The reaction cannot migrate into the hydrogen supply because there is no flame and hydrogen concentration is above the higher flammable limit (75%). Possible applications of catalytic burners are in household appliances such as cooking ranges and space heaters. The same principle is also used in hydrogen sensors.

27.7.1.2 Electrochemical Conversion (Fuel Cells)

Hydrogen can be combined with oxygen without combustion in an electrochemical reaction (reverse of electrolysis) and produce electricity (DC). The device where such a reaction takes place is called the *electrochemical fuel cell* or just *fuel cell* [52,53]. Fuel cells are described in more detail in the next chapter and will not be covered here.

27.8 Hydrogen Safety

Like any other fuel or energy carrier, hydrogen poses risks if not properly handled or controlled. The risk of hydrogen, therefore, must be considered relative to the common fuels such as gasoline, propane, or natural gas. The specific physical characteristics of hydrogen are quite different from those common fuels. Some of those properties make hydrogen potentially less hazardous, whereas other hydrogen characteristics could make it more dangerous in certain situations.

Because hydrogen has the smallest molecule, it has a greater tendency to escape through small openings than other liquid or gaseous fuels. Based on properties of hydrogen such as density, viscosity, and diffusion coefficient in air, the propensity of hydrogen to leak through holes or joints of low pressure fuel lines may be only 1.26–2.8 times faster than a natural gas leak through the same hole (and not 3.8 times faster as frequently assumed based solely on diffusion coefficients). Experiments have indicated that most leaks from residential natural gas lines are laminar [54]. Because natural gas has over three times the energy density per unit volume, a natural gas leak would result in more energy release than a hydrogen leak.

For very large leaks from high-pressure storage tanks, the leak rate is limited by the sonic speed. Due to higher sonic velocity (1,308 m/s) hydrogen would initially escape much faster than natural gas (sonic velocity of natural gas is 449 m/s). Again, because natural gas has more than three times the energy density than hydrogen, a natural gas leak will always contain more energy.

Some high strength steels are prone to hydrogen embrittlement. Prolonged exposure to hydrogen, particularly at high temperatures and pressures, can cause the steel to lose strength, eventually leading to failure. However, most other construction, tank, and pipe materials are not prone to hydrogen embrittlement. Therefore, with proper choice of materials, hydrogen embrittlement safety risks could be avoided.

If a leak should occur for whatever reason, hydrogen will disperse much faster than any other fuel, thus reducing the hazard levels. Hydrogen is both more buoyant and more diffusive than gasoline, propane, or natural gas. Table 27.6 compares some properties and leak rates for hydrogen and natural gas.

Hydrogen/air mixture can burn in relatively wide volume ratios, between 4% and 75% of hydrogen in air. The other fuels have much lower flammability ranges: natural gas 5.3–15%, propane 2.1–10%, and gasoline 1–7.8%. However, the range has little practical value. In many actual leak situations, the key

TABLE 27.6 Properties and Leak Rates of Hydrogen and Natural Gas

	Hydrogen	Natural gas
Flow parameters		
Diffusion coefficient (cm^2/s)	0.61	0.16
Viscosity (μ-poise)	87.5	100
Density (kg/m^3)	0.0838	0.651
Sonic velocity (m/s)	1308	449
Relative leak rates		
Diffusion	3.80	1
Laminar flow	1.23	1
Turbulent flow	2.83	1
Sonic flow	2.91	1

parameter that determines if a leak would ignite is the lower flammability limit, and hydrogen's lower flammability limit is 4 times higher than that of gasoline, 1.9 times higher than that of propane, and slightly lower than that of natural gas.

Hydrogen has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The ignition energy is a function of fuel/air ratio, and for hydrogen it reaches a minimum at about 25–30%. At the lower flammability limit, hydrogen ignition energy is comparable with that of natural gas [55]. Hydrogen has a flame velocity seven times faster than that of natural gas or gasoline. A hydrogen flame would therefore be more likely to progress to a deflagration or even a detonation than other fuels. However, the likelihood of a detonation depends in a complex manner on the exact fuel/air ratio, the temperature and particularly the geometry of the confined space. Hydrogen detonation in the open atmosphere is highly unlikely.

The lower detonability fuel/air ratio for hydrogen is 13–18%, which is two times higher than that of natural gas and 12 times higher than that of gasoline. Because the lower flammability limit is 4%, an explosion is possible only under the most unusual scenarios, e.g., hydrogen would first have to accumulate and reach 13% concentration in a closed space without ignition, and only then an ignition source would have to be triggered. Should an explosion occur, hydrogen has the lowest explosive energy per unit stored energy in the fuel, and a given volume of hydrogen would have 22 times less explosive energy than the same volume filled with gasoline vapor.

Hydrogen flame is nearly invisible, which may be dangerous because people in the vicinity of a hydrogen flame may not even know there is a fire. This may be remedied by adding chemicals that will provide the necessary luminosity. The low emissivity of hydrogen flames means that nearby materials and people will be much less likely to ignite and/or be hurt by radiant heat transfer. The fumes and soot from a gasoline fire pose a risk to anyone inhaling the smoke, whereas hydrogen fires produce only water vapor (unless secondary materials begin to burn).

Liquid hydrogen presents another set of safety issues, such as risk of cold burns, and the increased duration of leaked cryogenic fuel. A large spill of liquid hydrogen has some characteristics of a gasoline spill; however, it will dissipate much faster. Another potential danger is a violent explosion of a boiling liquid expanding vapor in case of a pressure-relief-valve failure.

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