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Hydrogen Economy

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This chapter presents an overview of how a hydrogen economy can be realized. We will give an overview of the principles of hydrogen energy production, storage, and utilization. We will also discuss different aspects of hydrogen safety. Hydrogen production will cover a whole array of methods including electrolysis, thermolysis, photolysis, thermochemical cycles, and production from biomass. Hydrogen storage will cover all modes of gaseous, liquid, slush, and metal hydride storage. Hydrogen utilization will focus on a large cross section of applications such as fuel cells and catalytic combustion of hydrogen. Details of many of these topics will be presented in the rest of the handbook.

1.1 Introduction

A hydrogen economy is one in which hydrogen is the main energy carrier along with electricity. Hydrogen would be produced from renewable energy sources such as solar or wind energy through water electrolysis. While this is considered an ideal scenario for a hydrogen economy, other possibilities exist. In theory, hydrogen and electricity can satisfy all the energy needs of humankind and form an energy system that would be permanent and independent of energy sources [1–3]. Hydrogen has unique characteristics that make it an ideal energy carrier [4]. These include the fact that (1) it can be produced from and converted into electricity at relatively high efficiencies; (2) its raw material for production is water, which is available in abundance; (3) it is a completely renewable fuel; (4) it can be stored in gaseous form (convenient for large-scale storage), in liquid form (convenient for air and space transportation), or in the form of metal hydrides (convenient for surface vehicles and other relatively small-scale storage requirements); (5) it can be transported over large distances through pipelines or via tankers; (6) it can be converted into other forms of energy in more ways and more efficiently than any other fuel (such as catalytic combustion, electrochemical conversion, and hydriding); and (7) it is environmentally compatible since its production, storage, transportation, and end use do not produce any pollutants (except for small amounts of nitrogen oxides), greenhouse gases, or any other harmful effects on the environment.

In a hydrogen economy, electricity and hydrogen would be produced in large quantities from available energy sources and used in every application where fossil fuels are being used today. This includes large industrial plants as well as small, decentralized units, wherever the primary energy source (solar, nuclear, and even fossil) is available. Electricity would be used directly or transformed into hydrogen. For large-scale storage, hydrogen can be stored underground in ex-mines, caverns, and/or aquifers. Energy transport to the end users, depending on distance and overall economics, would either be in the form of electricity or in the form of hydrogen. Hydrogen would be transported by means of pipelines or supertankers. It would then be used in transportation and industrial, residential, and commercial sectors as a fuel. Some of it would be used to generate electricity (via fuel cells), depending on demand, geographical location, or time of the day.
1.2 Hydrogen Production

Hydrogen is usually found in small amounts mixed with natural gas in crustal reservoirs. However, a few wells 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 [5]. Logical sources of hydrogen are hydrocarbon (fossil) fuels (C\textsubscript{x}H\textsubscript{y}) and water (H\textsubscript{2}O). 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 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 and methanol), 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) [6]. Less than 10% of that amount was supplied by industrial gas companies; the rest is being produced at consumer-owned and consumer-operated plants (the so-called captive production), such as refineries, and by ammonia and methanol producers. Production of hydrogen as an energy carrier would require an increase in production rates by several orders of magnitude.

To help speed up the introduction of fuel cell–powered vehicles, car manufacturers in collaboration with oil- and fuel-processing companies are intensively working on the development of onboard fuel processors. These devices would enable the use of conventional fuels such as gasoline and diesel, as well as methanol. This would allow the car companies to plan to overcome nonexistence of a hydrogen refueling infrastructure and the difficulties of onboard hydrogen storage. However, development of such compact fuel processors poses several engineering challenges, such as rapid start-up, high efficiency, and very high purity of the produced gas (<100 ppm CO).

The most logical source for large-scale hydrogen production is water. Methods of hydrogen production from water include electrolysis, direct thermal decomposition or thermolysis, thermochemical processes, and photolysis.

1.2.1 Electrolysis

The production of hydrogen by water electrolysis is a mature technology, based on a fundamentally simple process, is very efficient, and does not involve moving parts. It is suitable for large-scale hydrogen production. Typical efficiencies are 72%–82%. Several advanced electrolyzer technologies are being developed such as the advanced alkaline electrolysis (which employs new materials for membranes and electrodes that allow further improvement in efficiency—up to 90% [7, 8]), the solid polymer electrolytic (SPE) process (which employs a proton-conducting ion exchange membrane as an electrolyte and as a membrane that separates the electrolysis cell [8, 9]), and high-temperature steam electrolysis (which operates between 700°C and 1000°C and which employs oxygen ion–conducting ceramics as electrolyte [10]). An electrolysis plant can operate over a wide range of capacity factors and is convenient for a wide range of operating capacities, which makes this process interesting for coupling with renewable energy sources, particularly with photovoltaics (PVs). The latter generate low-voltage direct current, which is exactly what is required for the electrolysis process. Theoretical and experimental studies on the performance of PV-electrolyzer systems have been performed [11–14]. Examples of experimental PV-electrolysis plants
that are currently in operation worldwide include the Solar-Wasserstoff-Bayern pilot plant (Neunburg vorm Wald, Germany) [15], the HYSOLAR project (Saudi Arabia) [16], Schatz Energy Center (Humboldt State University, Arcata, California) [17], Helsinki University of Technology (Helsinki, Finland) [18], and INTA Energy Laboratory (Huelva, Spain) [19].

1.2.2 Direct Thermal Decomposition of Water (Thermolysis)

Water can be split thermally at temperatures above 2000 K [20]. The degree of dissociation is a function of temperature: only 1% at 2000 K, 8.5% at 2500 K, and 34% at 3000 K. The product is a mixture of gases at extremely high temperatures. The main problems in connection with this method are related to materials required for extremely high temperatures, recombination of the reaction products at high temperatures, and separation of hydrogen from the mixture.

1.2.3 Thermochemical Cycles

Production of hydrogen employing thermochemical cycles involves the chemical splitting of water at temperatures lower than those needed for thermolysis, through a series of cyclical chemical reactions that ultimately release hydrogen. Some of the more thoroughly investigated thermochemical process cycles include the following [9,21,22]: sulfuric acid–iodine cycle, hybrid sulfuric acid cycle, hybrid sulfuric acid–hydrogen bromide cycle, calcium bromide–iron oxide cycle (UT-3), and iron–chlorine cycle. Depending on the temperatures at which these processes are occurring, relatively high efficiencies are achievable (40%–50%). However, the problems related to movement of a large mass of materials in chemical reactions, toxicity of some of the chemicals involved, and corrosion at high temperatures remain to be solved in order for these methods to become practical.

1.2.4 Photolysis

Photolysis (or direct extraction of hydrogen from water using only sunlight as an energy source) can be accomplished by employing photobiological systems, photochemical assemblies, or photoelectrochemical cells [23,24]. Intensive research activities are opening new perspectives for photoconversion, where new redox catalysts, colloidal semiconductors, immobilized enzymes, and selected microorganisms could provide means of large-scale solar energy harvesting and conversion into hydrogen.

1.2.5 Hydrogen Production from Biomass

Hydrogen can be obtained from biomass by a pyrolysis/gasification process [25]. The biomass preparation step involves heating of the biomass/water slurry to high temperatures under pressure in a reactor. This process decomposes and partially oxidizes the biomass, producing a gas product consisting of hydrogen, methane, CO2, CO, and nitrogen. Mineral matter is removed from the bottom of the reactor. The gas stream goes to a high-temperature shift reactor where the hydrogen content is increased. Relatively high-purity hydrogen is produced in the subsequent pressure swing adsorption unit. The whole system is very much similar to a coal gasification plant, with the exception of the unit for pretreatment of the biomass and the design of the reactor. Because of the lower calorific value per unit mass of biomass as compared to coal, the processing facility is larger than that of a comparably sized coal gasification plant.
1.3 Hydrogen Storage

Once hydrogen is produced, it needs to be stored in order to overcome daily and seasonal discrepancies between energy source availability and demand. Several forms of storage are discussed briefly in the following.

1.3.1 Gaseous Hydrogen Storage

Depending on storage size and application, several types of hydrogen storage systems may be available. This includes stationary large storage systems and stationary small storage systems at the distribution, or final user level; mobile storage systems for transport and distribution including both large-capacity devices (such as a liquid hydrogen tanker—bulk carrier) and small systems (such as a gaseous or liquid hydrogen truck trailer); and vehicle tanks to store hydrogen used as fuel for road vehicles. 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). Studies dealing with large underground storage of hydrogen include those reported in Refs. [26–28]. Pressurized gas storage systems are used today in the natural gas business in various sizes and pressure ranges from standard pressure cylinders (50 L, 200 bar) to stationary high-pressure containers (over 200 bar) or low-pressure spherical containers (>30,000 m³, 12–16 bar). This application range will be similar for hydrogen storage. Storage in vehicular pressurized hydrogen tanks are discussed in Ref. [29].

1.3.2 Metal Hydride Storage

In the presence of some metals and alloys, hydrogen can form metal hydrides. During that process, hydrogen molecules are split and hydrogen atoms are inserted in spaces inside the lattice of the metal or alloy. This creates effective storage comparable to the density of liquid hydrogen. However, when the mass of the metal or alloy is taken into account, then the metal hydride gravimetric storage density becomes comparable to storage of pressurized hydrogen. The best achievable gravimetric storage density is about 0.07 kg of H₂/kg of metal, for a high-temperature hydride such as MgH₂ [30]. During the storage process (charging or absorption), heat is released, which must be removed in order to achieve the continuity of the reaction. During the hydrogen release process (discharging or desorption), heat must be supplied to the storage tank. An advantage of storing hydrogen in hydriding substances is the safety aspect. A serious damage to a hydride tank (such as one that could be caused by a collision) would not pose a fire hazard since hydrogen would remain in the metal structure.

1.3.3 Novel Hydrogen Storage Methods

There are several emerging methods of storing hydrogen that are still under investigation. For example, hydrogen can be physically adsorbed on activated carbon and be packed on the surface and inside the carbon structure more densely than if it has been just compressed. Amounts of up to 48 g H₂ per kg of carbon have been reported at 6.0 MPa and 87 K [31]. The adsorption capacity is a function of pressure and temperature; therefore, at higher pressures and/or lower temperatures, even larger amounts of hydrogen can be adsorbed.
For any practical use, relatively low temperatures are needed (less than 100 K). Since the adsorption is a surface process, the adsorption capacity of hydrogen on activated carbon is largely due to the high surface area of the activated carbon, although there are some other carbon properties that affect the ability of activated carbon to adsorb hydrogen. Researchers at the Northeastern University developed a carbon nanotube capable of storing up to 75% of hydrogen by weight [32]. This material is being researched in several laboratories including the National Renewable Energy Laboratory, which is claiming a storage density corresponding to about 10% of the nanotube weight [33]. Hydrogen can also be stored in glass microspheres of approximately 50 μm diameter. The microspheres can be filled with hydrogen by heating them to increase the glass permeability to hydrogen. At room temperature, a pressure of approximately 25 MPa is achieved resulting in storage density of 14% mass fraction and 10 kg H₂/m³ [34]. At 62 MPa, a bed of glass microspheres can store 20 kg H₂/m³. The release of hydrogen occurs by reheating the spheres to again increase the permeability. Researchers at the University of Hawaii are investigating hydrogen storage via polyhydride complexes. Complexes have been found that catalyze the reversible hydrogenation of unsaturated hydrocarbons. This catalytic reaction could be the basis for a low-temperature hydrogen storage system with an available hydrogen density greater than 7% [35].

1.3.4 Liquid Hydrogen Storage

Liquid hydrogen’s favorable characteristics include its high heating value per unit mass and large cooling capacity due to its high specific heat [36,37]. Liquid hydrogen has some important uses such as in the space program, in high-energy nuclear physics, and in bubble chambers. The transport of hydrogen is vastly more economical when it is in liquid form even though 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 by existing conventional methods 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 energy (electricity) [37]. 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.

1.3.4.1 Hydrogen Liquefaction

The 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 the Collins liquefiers. 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 on 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. [39].
1.3.4.2 Liquid Hydrogen Storage

The need for liquid hydrogen is highest in the transportation sector and the space program. Transport of large quantities of hydrogen is usually accomplished by truck tankers of 30–60 m³ capacity, by rail tank cars of 115 m³ capacity, and by barge containers of 950 m³ capacity [39]. Liquid hydrogen storage vessels are usually available in sizes ranging from 1 L Dewar flasks used in laboratory applications to large tanks of 5000 m³ capacity. The National Aeronautics and Space Administration (NASA) typically uses large tanks of 3800 m³ capacity (25 m in diameter) [26]. 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 as follows: (1) ortho–para conversion, (2) heat leak (shape and size effect, thermal stratification, thermal overfill, insulation, conduction, radiation, cooldown), (3) sloshing, and (4) flashing. In order to minimize the storage boil-off losses, the conversion rate of ortho-to-para hydrogen should be accelerated with a catalyst that converts the hydrogen during the liquefaction process [40–43]. The use of a catalyst usually results in a larger refrigeration load and consequently in an efficiency penalty primarily because the heat of conversion must be removed. The time for which hydrogen is to be stored usually determines the optimum amount of conversion. For use within a few hours, no conversion is necessary. For example, large-scale use of liquid hydrogen as a fuel for jet aircraft is one of those cases where conversion is not necessary since utilization of the liquid is almost a continuous process and long-term storage is therefore not needed [43]. For some other uses, a partial conversion might be required to create more favorable conditions. It should be noted that for every initial ortho concentration, there exists a unique curve for boil-off of hydrogen with respect to time.

The heat leakage losses are generally proportional to the ratio of surface area to the volume (S/V) of the storage vessel. The most favorable shape is therefore spherical since it has the least S/V ratio. Spherical shape containers have another advantage. They have good mechanical strength since stresses and strains are distributed uniformly. Storage vessels may also be constructed in other shapes such as cylindrical, conical, or any combination of these shapes. Cylindrical vessels are usually required for transportation of liquid hydrogen by trailers or railway cars because of limitations imposed on the maximum allowable diameter of the vessel. For normal highway transportation, the outside diameter of the vessel cannot exceed 2.44 m. From an economics standpoint, cylindrical vessels with either dish, elliptical, or hemispherical heads are very good, and their S/V ratios are only about 10% greater than that of the sphere [44]. Since boil-off losses due to heat leak are proportional to the S/V ratio, the evaporation rate will diminish drastically as the storage tank size is increased. For double-walled, vacuum-insulated, spherical Dewars, boil-off losses are typically 0.3%–0.5% per day for containers having a storage volume of 50 m³, 0.2% for 103 m³ tanks, and about 0.06% for 19,000 m³ tanks [45].

Additional boil-off may be caused by thermal stratification in liquid hydrogen in which case the warmer upper layers evaporate much faster than the bulk liquid [44]. One way of decreasing boil-off losses due to stratification and thermal overfill is by employing high-conductivity plates (conductors) installed vertically in the vessel. The plates produce heat paths of low resistance between the bottom and top of the vessel and can operate most satisfactorily in eliminating temperature gradients and excessive pressures. Another way is to pump the heat out and maintain the liquid at subcooled or saturated conditions. An ideal refrigeration system to perform this task can be an efficient magnetic refrigerator.
The magnetic refrigerator is very suitable for this job because of its relatively higher efficiency, compactness, lower price, and reliability [46–53].

Liquid hydrogen containers are usually of three types: double-jacketed vessels with liquid nitrogen in the outer jacket, superinsulated vessels with either a reflecting powder or multilayer insulation (MLI), and containers with vapor-cooled shields (VCSs) employing superinsulation. Although MLI provides for a low boil-off rate, the addition of a VCS will lower the boil-off losses even further. A VCS is a type of insulation that takes the vapor boil-off and passes it past the tank before being reliquefied or vented. Published data indicate that a reduction of more than 50% in boil-off losses may be achieved for a 100,000 lb liquid hydrogen cryogenic facility with a VCS than without one. Brown [54] showed that locating the VCS at half the distance from the tank to the outer surface of a 4 in. MLI of a 100,000 lb facility would reduce the boil-off by 10%. A dual VCS system on the tank would improve the performance by 40% over a single VCS. Brown [54] also showed that the preferred locations for the inner and outer shields in a dual VCS system are 30% and 66% of the distance from the tank to the outer surface of the MLI.

Another process that leads to boil-off during liquid hydrogen transportation by tankers is sloshing. Sloshing is the motion of liquid in a vessel due to acceleration or deceleration. Due to different types of acceleration and deceleration, there exist different types of sloshing. Acceleration causes the liquid to move to one end and then reflect from that end, thus producing a hydraulic jump. The latter then travels to the other end, thus transforming some of its impact energy to thermal energy. The thermal energy dissipated eventually leads to an increase in the evaporation rate of the liquid [40,44]. The insertion of traverse or antislosh baffles not only restrains the motion of the liquid, thus reducing the impact forces, but also increases the frequency above the natural frequency of the tanker [40,55].

Another source of boil-off is flashing. This problem occurs when liquid hydrogen, at a high pressure (2.4–2.7 atm), is transferred from trucks and railcars to a low-pressure Dewar (1.17 atm). This problem can be reduced if transportation of liquid hydrogen is carried out at atmospheric pressures. Furthermore, some of the low-pressure hydrogen can be captured and reliquefied.

1.3.5 Slush Hydrogen Storage

Slush hydrogen is a mixture of liquid and frozen hydrogen in equilibrium with the gas at the triple point, 13.8 K. The density of the icelike form is about 20% higher than that of the boiling liquid. To obtain the icelike form, one has to remove the heat content of the liquid at 20.3 K until the triple point is reached and then remove the latent heat of fusion. The cold content of the icelike form of hydrogen is some 25% higher than that of the saturated vapor at 20.3 K.

Slush hydrogen is of great interest for the space program because of its potential in reducing its physical size and significantly cutting the projected gross liftoff weight [56]. Some of the problems related to liquid hydrogen storage, such as low density, temperature stratification, short holding time due to its low latent heat, hazards associated with high vent rates, and unstable flight conditions caused by sloshing of the liquid in the fuel tank, may be eliminated or reduced if slush hydrogen is used. It is apparent that the use of slush hydrogen should be considered only for cases in which higher density and greater solid content are really needed. This is mainly because the production costs of slush hydrogen now and in the near future are greater than the liquefaction costs of hydrogen due to the larger energy use involved. For additional information on slush hydrogen properties, its production methods, and its applications, the reader is referred to Baker and Matsch [57], Sindt [58], and Voth [59].
1.4 Hydrogen Transport

In a hydrogen economy, it is envisaged that from the production plants and/or storage, hydrogen will be transmitted to consumers 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) [60]. Future developments will certainly entail greater flow rates and distances. However, it would be possible to use the existing natural gas pipelines with some modifications. For hydrogen pipelines, it is necessary to use steel less prone to embrittlement by hydrogen under pressure (particularly for very pure hydrogen [>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. The 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. However, transportation of hydrogen over distances greater than 1000 km is more economical than transmission of electricity [61]. Hydrogen in the gas phase is generally transported in pressurized cylindrical vessels (typically at 200 bar) arranged in frames adapted to road transport. The unit capacity of these frames or skids can be as great as 3000 m$^3$. Hydrogen gas distribution companies also install such frames at the user site to serve as a stationary storage.

1.5 Hydrogen Conversion

Hydrogen as an energy carrier can be converted into useful forms of energy in several ways including combustion in internal combustion engines and jet and rocket engines, combustion with pure oxygen to generate steam, catalytic combustion to generate heat, electrochemical conversion to electricity, and metal hydride conversions.

1.5.1 Combustion in Internal Combustion, Jet, and Rocket Engines

Hydrogen-powered internal combustion engines are on average about 20% more efficient than comparable gasoline engines. The thermal efficiency of an internal combustion engine can be improved by increasing either the compression ratio or the specific heat ratio or both. In hydrogen engines, both ratios are higher than in a comparable gasoline engine due to hydrogen’s lower self-ignition temperature and ability to burn in lean mixtures. However, the use of hydrogen in internal combustion engines results in loss of power due to the lower energy content in a stoichiometric mixture in the engine’s cylinder. A stoichiometric mixture of gasoline and air, and gaseous hydrogen and air, premixed externally, occupies ~2% and 30% of the cylinder volume, respectively. Under these conditions, the energy of
the hydrogen mixture is only 85% of the gasoline mixture, thus resulting in about 15% reduction in power. The power output of a hydrogen engine can be improved by using more advanced fuel injection techniques or liquid hydrogen. For example, if liquid hydrogen is premixed with air, the amount of hydrogen that can be introduced into the combustion chamber can be increased by approximately one-third [62]. One major advantage of hydrogen-powered engines is that they emit far fewer pollutants than comparable gasoline engines. Basically, the only products of hydrogen combustion in air are water vapor and small amounts of nitrogen oxides. Hydrogen has a wide flammability range in air (4%–75% vol.), and therefore high excess air can be utilized more effectively. The formation of nitrogen oxides in hydrogen/air combustion can be minimized with excess air. NOx emissions can also be lowered by cooling the combustion environment using techniques such as water injection, exhaust gas recirculation, or using liquid hydrogen. The emissions of NOx in hydrogen engines are typically one order of magnitude smaller than the emissions from comparable gasoline engines primarily because the former run leaner than the latter. Small amounts of unburned hydrocarbons, CO2, and CO have been detected in hydrogen engines due to lubrication oil [62].

1.5.2 Steam Generation by Hydrogen/Oxygen Combustion

Hydrogen combusted with pure oxygen results in pure steam. This creates temperatures in the flame zone above 3000°C; therefore, additional water has to be injected so that the steam temperature can be regulated at a desired level. Both saturated and superheated vapor can be produced.

A compact hydrogen/oxygen steam generator has been commercially developed by the German Aerospace Research Establishment (DLR) [63]. This 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 close to 100% efficient, since there are no emissions other than steam and little or no thermal losses. Hydrogen steam generators 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 [63].

1.5.3 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 catalyst (platinum) to burn at low temperatures. 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, since 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.

### 1.5.4 Electrochemical Conversion (Fuel Cells)

Hydrogen can be combined with oxygen without combustion in an electrochemical reaction (reverse electrolysis) and produce direct-current electricity. The device where such a reaction takes place is called a fuel cell. Depending on the type of electrolyte used, there are several types of fuel cells:

- **Alkaline fuel cells (AFCs)** use concentrated (85 wt.%) KOH as the electrolyte for high-temperature operation (250°C) and less concentrated (35–50 wt.%) for low-temperature operation (<120°C). The electrolyte is retained in a matrix (usually asbestos), and a wide range of electrocatalysts can be used (such as Ni, Ag, metal oxides, and noble metals). This fuel cell is intolerant to CO₂ present in either the fuel or the oxidant [64].

- **Polymer electrolyte membrane or proton exchange membrane fuel cells (PEMFCs)** use a thin polymer membrane (such as perfluorosulfonated acid polymer) as the electrolyte. The membranes as thin as 12–20 μm have been developed, which are excellent proton conductors. The catalyst is typically platinum with loadings about 0.3 mg/cm², or if the hydrogen feed contains minute amounts of CO, Pt–Ru alloys are used. The operating temperature is usually below 100°C, more typically between 60°C and 80°C.

- **Phosphoric acid fuel cells (PAFCs)** use concentrated phosphoric acid (~100%) as the electrolyte. The matrix used to retain the acid is usually SiC, and the electrocatalyst in both the anode and cathode is platinum black. The operating temperature is typically between 150°C and 220°C [64,65].

- **Molten carbonate fuel cells (MCFCs)** have the electrolyte composed of a combination of alkali (Li, Na, K) carbonates, which is retained in a ceramic matrix of LiAlO₂. Operating temperatures are between 600°C and 700°C where the carbonates form a highly conductive molten salt, with carbonate ions providing ionic conduction. At such high operating temperatures, noble metal catalysts are typically not required [64,65].

- **Solid oxide fuel cells (SOFCs)** use a solid, nonporous metal oxide, usually Y₂O₃-stabilized ZrO₂, as the electrolyte. The cell operates at 900°C–1000°C where ionic conduction by oxygen ions takes place [64,65].

### 1.5.5 Energy Conversions Involving Metal Hydrides

Hydrogen’s property to form metal hydrides may be used not only for hydrogen storage but also for various energy conversions. When a hydride is formed by the chemical combination of hydrogen with a metal, an element, or an alloy, heat is generated, that is, the process is exothermic. Conversely, in order to release hydrogen from a metal hydride, heat must be supplied. The rate of these reactions increases with an increase in the surface area. Therefore, in general, the hydriding substances are used in powdered form to
speed up the reactions. Elements or metals with unfilled shells or subshells are suitable hydriding substances. Metal and hydrogen atoms form chemical compounds by sharing their electrons in the unfilled subshells of the metal atom and the K shells of the hydrogen atoms.

Ideally, for a given temperature, the charging or absorption process and the discharging or desorption process take place at the same constant pressure. However, actually, there is a hysteresis effect, and the pressure is not absolutely constant—for a given temperature, charging pressures are higher than the discharging pressures. The heat generated during the charging process and the heat needed for discharging are functions of the hydriding substance, the hydrogen pressure, and the temperature at which the heat is supplied or extracted. Using different metals and by forming different alloys, different hydriding characteristics can be obtained. In other words, it is possible to make or find hydriding substances that are more suitable for a given application, such as waste heat storage, electricity generation, pumping, hydrogen purification, and isotope separation.

Hydriding substances can be used for electricity storage in two ways. In one of the methods, electricity (direct current) is used to electrolyze the water, and the hydrogen produced is stored in a hydriding substance. When electricity is needed, the hydrogen is released from the hydriding substance by adding heat and used in a fuel cell to produce direct-current electricity. Heat from a fuel cell can be used to release hydrogen from the metal hydride. In the second method, one electrode is covered with a hydriding substance (e.g., titanium–nickel alloy). During the electrolysis of water, the hydriding substance covering the electrode immediately absorbs the hydrogen produced on the surface of the electrode. Then, when electricity is needed, the electrolyzer operates in a reverse mode as a fuel cell producing electricity using the hydrogen released from the metal hydride.

### 1.6 Hydrogen Safety

Since 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 [66]. Since natural gas has over three times the energy density per unit volume, the 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 (1308 m/s), hydrogen would initially escape much faster than natural gas (sonic velocity of natural gas is 449 m/s).

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 should not contribute to hydrogen safety risks.
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. A 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, namely, 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 parameter that determines if a leak would ignite is the lower flammability limit, and hydrogen's lower flammability limit is four times higher than that of gasoline, 1.9 times higher than that of propane, and slightly lower than that of natural gas. It also has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The range has little practical value. In many actual leak situations, the key parameter that determines if a leak would ignite is the lower flammability limit, and hydrogen's lower flammability limit is four times higher than that of gasoline, 1.9 times higher than that of propane, and slightly lower than that of natural gas. It also has a very low ignition energy (0.02 mJ), about one order of magnitude lower than other fuels. The lower flammability 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. Since the lower flammability limit is 4%, an explosion is possible only under the most unusual scenarios; for example, 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.

A 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 some 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, while 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.

In conclusion, hydrogen appears to pose safety risks of the same order of magnitude as gasoline or natural gas. The perception that hydrogen is an unsafe fuel needs to be addressed if a hydrogen economy is to replace the existing fossil fuel–based economy.

1.7 Conclusions

In this chapter, an overview of the hydrogen economy was presented. Many of the aforementioned topics are discussed in much greater detail in the remainder of the handbook.
References


