Production and storage of hydrogen: Present scenario and future perspective

Kaushik Nath¹ and Debabrata Das²*

¹Department of Chemical Engineering, G H Patel College of Engineering & Technology, Vallabh Vidyanagar 388 120
²Department of Biotechnology, Indian Institute of Technology, Kharagpur 721 302

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Hydrogen (H₂), an environmentally clean energy-carrier gas, is produced mainly from fossil fuel, biomass and water. H₂ (90%) is produced at high temperature by the reactions of natural gas or light oil fractions with steam, besides coal gasification and electrolysis of water. Among biological production of H₂, direct and indirect biophotolysis, fermentation, photosynthetic production and in vitro enzymatic conversion of biomass are important. H₂ is a substance with high energy content compared to its weight, however, energy content compared to volume is rather low. This poses challenges with respect to storage compared to storage of gasoline, a liquid. Current H₂ storage approaches involve compressed H₂ gas tanks, liquid H₂ tanks, metal hydrides, carbon-based materials/high surface area sorbents, and chemical H₂ storage. This paper reviews various production and storage strategies of H₂.

Keywords: Biomass, Hydrogen production and storage

Introduction

Petroleum based fuels (gasoline or diesel as well as natural gas and coal), on burning yield CO₂, the primary green house gas that causes global warming¹.². Combustion of fossil fuels at high temperature and pressure in internal combustion (IC) engine or in an electric power plant produces CO, oxides of nitrogen and sulfur (NOₓ & SOₓ), volatile organic chemicals and fine particulates that contribute to air pollution. When released into atmosphere, many of these compounds cause acid rain or smog. Damage of vast ecosystem, increased lung disease and cancer are the ultimate price mankind pay for consuming fossil fuels.

H₂ burning does not contribute to the greenhouse effect, ozone depletion and acid rains, but gives off water vapor and heat energy. It has the highest energy content per unit weight of any known gaseous fuel (143 GJ/t)³,⁴. Hydrogen economy is considered the most likely path toward sustainable development⁵. During 21st century, global energy scenario changes considerably, as the trend toward cleaner, more flexible and convenient energy carriers continue (Fig. 1). H₂, in particular, driven by the penetration of efficient end-use technologies, increases its share dramatically, accounting for approx. 49% of the global final consumption by the end of 21st century, and becomes the main global energy carrier⁶.

H₂ and fuel cell technology can be placed into three areas: i) H₂ production; (ii) H₂ storage and distribution; and (iii) applications. This paper reviews production technologies and several strategies for storage of H₂.

Hydrogen Production

H₂ is produced from coal, gasoline, methanol, natural gas and other fossil fuels (Table 1). Some fossil fuels

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*Author for correspondence
Tel: +91-3222-278053, 283758; Fax: +91-3222-255303
E-mail: ddas@hijli.iitkgp.ernet.in

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Fig. 1—Projection of global energy demand
(Source: NREL database)
that have high H₂ to O₂ ratio make better candidates for the reforming process.

**Hydrogen Production via Reforming**

Steam reforming is a reaction of natural gas (methane) or other light hydrocarbons (ethane or propane) with steam in the presence of a catalyst at 700-900°C. Methane is first catalytically reformed at elevated temperature and pressure to produce a syngas mixture of H₂ and CO. A catalytic shift reaction is then carried out to combine CO and H₂O to produce H₂ (Fig. 2).
The use of high-temperature primary energy systems such as Generation IV nuclear reactors or solar-thermal concentrating systems reduce the required input of carbon-containing feedstock\textsuperscript{7,8}. Capture of \( \text{CO}_2 \) for sequestration purposes in association with reforming process is an area relevant to \( \text{H}_2 \) production and power generation alike. Further R&D needs especially relate to \( \text{H}_2 \) purification and to gas separation\textsuperscript{9}. In this area in particular, there is ample scope for improvement through R&D, exploiting advances in membrane technology but equally in exploiting new reversible adsorption materials in pressure-swing or temperature-swing processes to separate \( \text{H}_2 \) and/or \( \text{CO}_2 \), or alternatively to exploit these materials for chemical compression\textsuperscript{9,10}.

**Coal Gasification**

Coal gasification involves three steps: i) Treatment of cola feedstock with high temperature steam (1330°C) to produce syngas; ii) A catalytic shift conversion; and iii) Purification of \( \text{H}_2 \). In the first step, coal is chemically broken down by high temperature (1330°C), high-pressure steam to produce raw synthesis gas\textsuperscript{11}, using oxygen blown gasifier to minimize NOx production and make the process more compatible for \( \text{CO}_2 \) sequestration. Moreover, carbon sequestration may offer a notable potential for novel options for the integration with mining, power generation and \( \text{H}_2 \) production\textsuperscript{11,12}. Introducing nitrogen into the reactor increases size and cost of downstream equipment and makes separation of \( \text{CO}_2 \) more difficult and costly\textsuperscript{12,13}.

Coal gasification is a proven technology, with large-scale processes currently in place for the production of \( \text{H}_2 \). However, new separation techniques may offer alternatives to PSA adsorption for \( \text{H}_2 \) removal, including separation using microporous membranes, palladium metallic membranes or dense ceramic membranes\textsuperscript{11}. Another alternative is conducting the reaction in an experimental ceramic membrane reactor, which may not require pure \( \text{O}_2 \) feed.

**Hydrogen Production via Electrolysis**

\( \text{H}_2 \) generation via electrolysis in decentralized systems offers the possibility to eliminate much of the distribution problems associated with central production. Large-scale electrolysis (capacity, 1500 kg/day) requires a huge scale-up in the size of electrolyzers\textsuperscript{14}. The largest integrated electrolyzer (capacity, 71,000 kg/day) is located at Assuan, Egypt. The efficiency (62-70%) of commercially available alkaline electrolyzers is based on the lower heating value (73%) and higher heating value (85%)\textsuperscript{14,15} of \( \text{H}_2 \). This includes all auxiliary energy requirements such as AC/DC rectification, pumps, control etc. Thus, this technology offers a rather high efficiency compared to the theoretical maximum (100%). Moreover, systems tailored for decentralized application with integrated electrolyzer subsystems promise to reduce cost and increase efficiency by eliminating the electric inverters. Research should be directed to optimizing the electric integration and packaging of such systems\textsuperscript{16}.

Pressurized electrolysis (3 MPa, even up to 14 MPa) has the advantage of reducing significantly the power requirements for subsequent \( \text{H}_2 \) compression or liquefaction. Increasing operating temperature of alkaline electrolyzers from 60-70°C to 120-140°C would increase thermal activation of the electrodes, and thus increase the efficiency. Proton Exchange Membrane (PEM) electrolyzers are a promising technology potentially benefiting from technological development synergies with PEM fuel cells. High-temperature electrolysis based on solid oxide technology, developed in Germany in 1980s, has proven to work well. Yet, serious difficulties arise from thermo-mechanical stresses within the functional ceramic materials\textsuperscript{17}.

**Hydrogen Production via Thermolysis**

Thermolytic water splitting is the multi-step thermo-chemical processes that use high-temperature heat to split water into \( \text{H}_2 \) and \( \text{O}_2 \). Such process could convert high temperature heat into \( \text{H}_2 \) (50% efficiency), thereby outperforming the efficiency of electricity/electrolysis pathway and offering an alternative to electrolysis for renewable \( \text{H}_2 \) generation\textsuperscript{18}. Thermolysis is mostly associated in the context of advanced nuclear reactors.
Direct thermolysis can be accomplished at very high temperatures (>2000°C). H\textsubscript{2} might be captured via membranes. Yet, it needs to be taken into consideration that other major developments applying functional materials at high temperatures, as magneto-hydrodynamic power generation, revealed notable obstacles with such materials\textsuperscript{19,20}. Circumventing this problem, H\textsubscript{2} can be split at lower temperatures and captured applying a sequence of chemical processes that allow in the end gathering the pure H\textsubscript{2}. Research strategies for thermolysis that devise pathways to get around side reactions should be pursued for the high potential of the technology\textsuperscript{21}.

**Photo-electrolysis**

Photocatalytic water splitting is the combination of photovoltaics (PV) cells with *in-situ* electrolysis of water. Thus, photovoltaic effect of semiconductor materials is not used to generate electricity as in PV, but to directly split water electrochemically\textsuperscript{5,6}. The effect has been proven on lab scale and further basic research is needed. As electricity is more easily collected than gases, which require additional cover and sealing of the device, the limit capital and maintenance cost for photo-electrolysis might remain higher than PV\textsuperscript{20}.

Anodic oxidation of water to oxygen is generally the performance-limiting step in a photoelectric cell (PEC) device. Progress toward performance improvement has primarily been achieved in the areas of light harvesting and corrosion resistance. Regarding photoanodes, work has been focusing on the development of thin films using nanocrystalline titania (TiO\textsubscript{2}), nanostructured polycrystalline tungsten trioxide (WO\textsubscript{3}), iron oxide (above all hematite Fe\textsubscript{2}O\textsubscript{3}), and, as a new stream of effort, a range of promising mixed-oxides (iron, titanium, cerium and molybdenum) and nitrides (indium and tin)\textsuperscript{22}.

**Plasma Reforming**

By pyrolysis of hydrocarbon feedstocks from natural gas, heavy fuel oil or biomass, H\textsubscript{2} and carbon blacks can be obtained. Such a pyrolysis process uses an electrically powered plasma torch implemented in a high temperature reactor. In this process, H\textsubscript{2} (purity 90%) is obtained when natural gas is used at specific electricity consumption of 1.1 kWh/Nm\textsuperscript{3} of H\textsubscript{2} \textsuperscript{23} (conversion rate of hydrocarbon feedstock, 100%). The first commercial plant (since mid 1999), located in Montreal, Québec, Canada, consists of two modules with a combined annual capacity of 20,000 ton of carbon black and of 50 million Nm\textsuperscript{3} of H\textsubscript{2}. The plant is operative since mid 1999. Since then, no further developments have taken place and the commercial status of the technology is unclear. Plasma reforming of hydrocarbons to H\textsubscript{2}-rich gases (without formation of carbon black) for small stationary and mobile applications are in the stage of basic and applied research\textsuperscript{24}.

**Biological Processes**

Biological H\textsubscript{2} production has become a focus of governmental support, particularly in Germany, the US and Japan, with least efforts in the other countries. A large number of microbial species, including significantly different taxonomic and physiological types can produce H\textsubscript{2}. Among various processes of biological production of H\textsubscript{2}, direct and indirect biophotolysis, fermentation, and photosynthetic production are important\textsuperscript{25}.

Direct biophotolysis employs dissociation of water molecules under sunlight in the presence of microalgae. It uses the same process found in plants and algal photosynthesis, but adapts them for the generation of H\textsubscript{2} gas, instead of carbon containing biomass\textsuperscript{26}. Cyanobacteria (blue-green algae, cyanophyceae or cyanophytes) can evolve H\textsubscript{2} by indirect biophotolysis of water. Production of H\textsubscript{2} by photosynthetic bacteria takes place under illumination and in presence of an inert anaerobic atmosphere (argon or helium), from the break down of organic substrates like, malate and lactate. These anions of organic acids are preferred substrates. Apart from different organic acids and carbohydrates, several wastewaters have also been attempted to be used as substrates for PNS bacteria to produce H\textsubscript{2}. Carbohydrates, mainly glucose, are preferred for fermentation, which predominantly give rise to acetic and butyric acids together with H\textsubscript{2}. Here, pyruvate the product of glucose catabolism is oxidized to acetyl-CoA, which can be converted to acetyl phosphate and results in generation of ATP and excretion of acetate. Pyruvate oxidation to acetyl-CoA requires ferredoxin (Fd) reduction. Reduced Fd is oxidized by hydrogenase, which generates Fd and releases electrons as molecular H\textsubscript{2}\textsuperscript{26,27}.

Research progress for identifying the major techno-economic bottlenecks (Table 2) of various bioprocesses for commercial production of H\textsubscript{2} appears promising. Enhancement in H\textsubscript{2} yield may be possible by using suitable microbial strain, process modification, efficient bioreactor design and also genetic and metabolic engineering technique, to redirect metabolic pathway. It is still too early to predict the ultimate techno-economic viability of any of the biohydrogen production routes currently in vogue.
H₂ (120 MJ/kg) has nearly three times the energy content per weight compared to gasoline (44 MJ/kg). This sounds promising for mobile applications, but for energy content per volume the situation gets reversed (8 MJ/l for liquid H₂ vs 32 MJ/l for gasoline). In addition, storage system of H₂ itself will have a larger weight than a comparable gasoline tank for most types of systems. Most important ones are storage (Table 3) as gas, as liquid, chemically bound in a solid (metal hydrides), and physisorbed or chemisorbed on a solid (carbon structures).

**Storage of Hydrogen**

Usually three different options are explored: i) Hydrogen may be compressed and stored in a pressure tank; (ii) Hydrogen may be cooled to a liquid state and kept cold in a properly insulated tank; and (iii) Hydrogen may be stored in a solid compound.

**Compressed Hydrogen Storage**

H₂ gas can be compressed using piston-type compressors or directly from high-pressure electrolysis. Piston-type compressors need sometimes to be modified because of large diffusivity of H₂ gas. Theoretical work needed for the isothermal compression H₂ can be calculated as
\[ \Delta G = RT \ln \frac{P}{P_o} \]

where \( P_o \) = initial pressure, \( P \) = final pressure, and \( T \) = absolute temperature.

Isothermal compression of \( \text{H}_2 \) (0.1-80 MPa) consumes 2.21 kWh/kg. The real process would not be isothermal, and would consume significantly more energy. For stationary use, restrictions on the weight and size of a gas cylinder are lower than for mobile applications. In stationary systems, where weight and size are not decisive factors, steel tanks are a good solution, but for vehicles, traditional pressure tanks are problematic regarding both weight and volume. There has been considerable breakthrough in the last few years in the development of a new type of composite tank (storage capacity, 10-12 wt % \( \text{H}_2 \)) which can store \( \text{H}_2 \) at 350 bar pressure and at the same time meet the current safety standards. Progress is also being made on tanks, which can store \( \text{H}_2 \) at 700 bar pressure. This will reduce the tank volume, which is necessary to achieve desirable driving distance. Lightweight composite tanks, which utilize space better than the usual cylindrical tanks, have also been designed. Three main types of tanks are steel, aluminum core encased with composite fiberglass and plastic core encased with composite fiberglass.

### Table 3 — Comparison of volumetric and gravimetric performances of various hydrogen storage media and tank technologies

<table>
<thead>
<tr>
<th>Type of hydrogen storage</th>
<th>Intrinsic maximum volumetric energy density* kWh/l</th>
<th>Intrinsic maximum hydrogen mass fraction§ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid ( \text{H}_2 ), 1 bar, 20 K</td>
<td>2.4</td>
<td>100</td>
</tr>
<tr>
<td>Compressed gaseous ( \text{H}_2 ) 700 bar, 300 K</td>
<td>1.3</td>
<td>100</td>
</tr>
<tr>
<td>Activated nanoporous carbon, 100 bar, 300 K &amp; 77 K</td>
<td>0.6</td>
<td>2.5</td>
</tr>
<tr>
<td>Interstitial metal hydrides (( \text{AB}_2 ), ( \text{AB}_5 ))</td>
<td>4.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Complex metal hydrides (alanates)</td>
<td>4.2</td>
<td>9.5</td>
</tr>
</tbody>
</table>

* The volumetric energy density is defined as the useful energy (kWh) divided by the maximum volume (liter) of the tank, with the equivalence: 1 kg \( \text{H}_2 \), 33.3 kWh

§ The “intrinsic” hydrogen mass fraction is the mass of hydrogen atoms divided by the total molecular mass

### Liquid Hydrogen Storage

Storing hydrogen in a liquid state (\( \text{LH}_2 \)) is particularly interesting for long distance transportation purposes and as fuel in spacecraft and airplanes. \( \text{LH}_2 \) can be stored at 21.2 K in cryogenic tanks. After cooling down \( \text{H}_2 \) using liquid nitrogen at 78 K, cold gas is liquefied through several liquefaction cycles. Liquefaction of \( \text{H}_2 \) from room temperature demands a theoretical work (3.23 kWh/kg) but a technical work (approx. 15.2 kWh/kg) is also needed in the process. Altogether almost one third of the combustion energy of \( \text{H}_2 \) is consumed in liquefaction process. Because of the low critical temperature of \( \text{H}_2 \) (33 K), liquid form must be stored in open systems. At room temperature, the pressure in a closed system could increase to 1000 MPa, which clearly challenges the strength of storage tanks. Another issue is boil-off losses, which is a function of the shape and size of the tank in addition to the thermal insulation.

\( \text{LH}_2 \) tanks (capacity, 0.07 kg/l) can store more \( \text{H}_2 \) in a given volume than compressed gas tanks (10,000 psi). Liquid tanks are being demonstrated in \( \text{H}_2 \)-powered vehicles and a hybrid tank concept combining both high-pressure gaseous and cryogenic storage is being studied. These hybrid (cryo-compressed tanks) insulated pressure vessels are lighter than hydrides and more compact than...
ambient-temperature, high-pressure vessels. Because the temperatures required are not as low as for liquid H₂, there is less of an energy penalty for liquefaction and less evaporative losses than for liquid H₂ tanks.

Storage in Solid Materials
For the last one or two decades, there has been intense research on H₂ absorbed inside or adsorbed on solid materials. Carbon nanotubes led to great interest in the possibilities of H₂ storage inside or on the surfaces of these tubes. A number of other carbon structures (nanosized cones, fibers and the buckminsterballs (C60)) are also studied. One mechanism for adsorption is physisorption on the surface, where H₂ molecules are bonded to a surface by van der Waals forces. The surface area determines maximum amount of H₂ physisorbed, and the shape and curvature determines physisorption energies. For carbon tubes, H₂ can also be absorbed inside cavities (inner diam. 0.7 nm up to several nanometers). Atomic H₂ can be chemisorbed on a carbon surface by forming a covalent C-H bond. Chemisorbed H₂ has a binding energy of more than 2-3 eV, compared to approx. 0.1 eV for physisorbed H₂. H₂ storage capacities (<1-20 wt %) for carbon structures are widely discussed.

Carbon Nanotube
Carbon nanostructures (nanofibers, nanotubes and fullerenes) have shown promising abilities to absorb H₂. Intense efforts are being made to develop methods for producing single-walled carbon nanotubes (CNT) economically on a large scale. CNTs are formed by rolled graphite sheets. Use of laser technology has made it possible to produce a high percentage of nanotubes with the exact diameter and level of purity needed. Production of nanotubes is growing rapidly. CNTs are described as usually closed on both sides by a hemisphere, i.e., half of a fullerene. Tubes formed by only one single graphite layer are called single wall nanotubes (SWNT). Tubes consisting of multiple concentric graphite layers are called multi-wall nanotubes (MWNT). Especially, absorption of H₂ in SWNT has attracted many research groups worldwide. The quantity of H₂ absorbed in nanostructured carbon materials varies between 0.4 and 67 mass%. Surface adsorption of a monolayer of H₂ leads to a maximum storage capacity of 3.3 mass%. Nanotubes have several interesting qualities, which to good effect can be used in H₂ technology in fuel cells, ultra condensers for efficient storage of retardation energy and H₂ storage.

Metal Hydrides
Certain metals and metal alloys have the ability to absorb H₂ under moderate pressure and temperature, creating hydrides. A metal hydride tank contains, in addition to a heat manipulation system, granular metal, which absorbs H₂ like a sponge absorbs water. The heat system draws heat away when H₂ is filled into the tank, and applies heat when H₂ is taken out of the tank. H₂ is released from the metal hydride when heat is applied. H₂-absorbing metals, alloys, intermetallic compounds and amorphous alloys are a vast research field with a great number of applications. These metals react with H₂, and go through a phase transition and form metal hydrides. Among their applications are moderators in nuclear reactors, negative electrodes in rechargeable batteries and H₂ storage materials in small vehicles. Formation of a metal hydride may involve gaseous H₂ or H₂ from an electrolyte used in battery technology. In the formation process of a metal hydride, H₂ molecules are adsorbed on the surface of a transition metal or an alloy, called the host material. Vander Waals forces will attract H₂ molecules to metal surface, leading to a physisorbed state. Further, chemical bonds between H₂ and metal can lead to stronger bonded chemisorbed state, and finally dissociated H atoms can diffuse into the metal lattice.

Hydrogen Applications
H₂ is a versatile energy carrier with the potential for extensive use in power generation and in many other applications. About half of all H₂ produced is used in the manufacture of ammonia, which is itself mostly used in making fertilizers; a further 37% is used in oil refineries for removal of impurities or for upgrading heavier oil fractions into lighter and more valuable products; 8% in methanol production and 4% in a wide variety of chemical, metallurgical and other uses. H₂ production (1%) is used in the world’s space programmes. The future widespread use of H₂ is likely to be in the transportation sector where it will help reduce pollution. As on today all these areas of H₂ utilization is equivalent to 3% of the energy consumption, but it is expected to grow significantly in the years to come.

The use of H₂ as a fuel for vehicles requires an inherent safety and both volumetric and gravimetric efficiency. Metal hydrides store H₂ in an essentially solid form and offer the potential for volumetric efficiency, high safety, low-pressure containment and ambient temperature operation. Unfortunately, most known hydrides are either heavy in comparison to H₂ as they carry or require high temperature for H₂ release. In the past few years, carbon
adsorbent materials have also gained attention as a possible, cost-effective storage medium for \( \text{H}_2 \). Whereas carbon was once considered only as a cryoabsorbent for \( \text{H}_2 \), there is growing evidence that it can be used at ambient temperature. However, much work has to be done for consistent and high-purity production of these materials for \( \text{H}_2 \) storage.

**Conclusions**

Green house gas emissions and energy security are major issues, besides local emissions and economic considerations, which become instrumental for emergence of \( \text{H}_2 \) as an alternative fuel of the future. A coherent energy strategy is required in which \( \text{H}_2 \) and fuel cells will play an important role. Electric power and \( \text{H}_2 \) together represent one of the most promising ways to achieving a coherent energy strategy, for \( \text{H}_2 \) complements electric power with enhanced storability. A strategic research approach needs to match societal requirements and the technical and economical potential, as well as the inherent limitations of technologies under consideration. On the other hand, \( \text{H}_2 \) storage is of paramount importance for future usage of \( \text{H}_2 \) because energy density is fairly low for existing storage technologies (10-20%) of that of gasoline or diesel. Thus, it limits the range of operation for transport, particularly of automobiles. As \( \text{H}_2 \) storage is that important, a lot of research has already been done qualifying gaseous and liquid \( \text{H}_2 \) as principal candidates for transport applications over other well-known technologies. Beyond further applied research on these issues, basic research on the other hand is also required for novel storage principles promising higher energy densities and emerging material classes like alanates.

**References**


