

THE ROAD TO THE HYDROGEN FUTURE: RESEARCH & DEVELOPMENT IN THE HYDROGEN PROGRAM

Catherine E. Gregoire Padró
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401

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INTRODUCTION

The U. S. Department of Energy (DOE) conducts R&D for the development of safe, cost-effective hydrogen energy technologies that support and foster the transition to a hydrogen economy. Of particular interest is the innovative research supported by the DOE's Hydrogen Program, focused primarily on exploration of long-term, high-risk concepts that have the potential to address large-scale energy needs.

Hydrogen can be produced directly from sunlight and water by biological organisms and using semiconductor-based systems similar to photovoltaics (PV), or indirectly, via thermal processing of biomass. These production technologies have the potential to produce essentially unlimited quantities of hydrogen in a sustainable manner.

Storage of hydrogen is an important area for research, particularly when considering transportation as a major user, and the need for efficient energy storage for intermittent renewable power systems. Although compressed gas and liquid hydrogen storage systems have been used in vehicle demonstrations worldwide, the issues of safety, capacity, and energy consumption have resulted in a broadening of the storage possibilities to include metal hydrides and carbon nanostructures. Stationary storage systems that are high efficiency with quick response times will be important for incorporating large amounts of intermittent PV and wind into the grid as base load power.

In addition to the extensive fuel cell development programs in other offices within DOE, the Hydrogen Program conducts fuel cell research focused on development of inexpensive, membrane electrode assemblies, and the development of reversible fuel cells for stationary applications. The Program also supports research in the development of hydrogen/methane blends and hydrogen-fueled internal combustion engines and generator sets.

A large hurdle to expanded use of hydrogen is public perception. Widespread hydrogen use represents an extraordinary educational challenge, as well as the absolute requirement that safety be intrinsic to all processes and systems. The development of reliable, low-cost hydrogen sensors is an important aspect of the Program, as is the development of codes and standards for the safe use of hydrogen.

DIRECT HYDROGEN PRODUCTION TECHNOLOGIES

The use of solar energy to split water into oxygen and hydrogen is an attractive means to directly convert solar energy to chemical energy. Biological, chemical, and electrochemical systems are being investigated within DOE as long-term (>10 years), high-risk, high-payoff technologies for the sustainable production of hydrogen.

Biological Systems

In nature, algae absorb light and utilize water and CO₂ to produce cell mass and oxygen. A complex model referred to as the "Z-scheme" has been identified to describe the charge separation and electron transfer steps associated with this process that ultimately drives photosynthesis. A number of enzymatic side pathways that can also accept electrons have been identified. Of interest is a class of enzymes known as hydrogenases that can combine protons and electrons obtained from the water oxidation process to release molecular hydrogen. These algal hydrogenases are quickly deactivated by oxygen. Researchers have identified mutant algal strains that evolve hydrogen at a rate that is 4 times that of the wild type, and are 3-4 times more oxygen tolerant [1,2].

Photosynthetic organisms also contain light harvesting, chlorophyll-protein complexes that effectively concentrate light and funnel energy for photosynthesis. These antenna complexes also dissipate excess incident sunlight as a protective mechanism. The amount of chlorophyll antennae in each cell is directly related to the amount of "shading"

experienced by subsequent layers of microorganisms in a mass culture. In a recent set of experiments, researchers have observed that green alga grown under high light intensities exhibit lower pigment content and a highly truncated chlorophyll antennae size. These cells showed photosynthetic productivity (on a per chlorophyll basis) that was 6-7 times greater than the normally pigmented cells [3], a phenomenon that could lead to significant improvements in the efficiency of hydrogen production on a surface-area basis.

These technical challenges are being addressed by a team of scientists from Oak Ridge National Laboratory (ORNL), the University of California Berkeley, and the National Renewable Energy Laboratory (NREL). Various reactor designs are under development for photobiological hydrogen production processes (single-stage vs two-stage, single organism vs dual organism). At the University of Hawaii's Natural Energy Institute (HNEI), a new, potentially low cost, outdoor tubular photobioreactor is under development to test a sustainable system for the production of hydrogen [4].

In addition to the photosynthetic production of hydrogen from water, the Program supports the development of systems to convert CO (found in synthesis gas) to hydrogen via the so-called water-gas shift reaction ($\text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2$). This reaction is essential to the widely-used commercial steam methane reforming process for the production of hydrogen. In the industrial process in use today, high-temperature (450°C) and low-temperature (230°C) shift reactors are required to increase the overall hydrogen production efficiency and to reduce the CO content to acceptable levels. In this project, microorganisms isolated from nature are used to reduce the level of CO to below detectable levels (0.1 ppm) at temperatures of around 25-50°C in a single reactor [5,6]. This process, under development at NREL, has significant potential to improve the economics of hydrogen production when combined with the thermal processing of biomass or other carbon-containing feeds.

Photochemical Systems

Among the technologies that have been investigated, photocatalytic water splitting systems using relatively inexpensive, durable, and nontoxic semiconductor photocatalysts show promise. Supported catalysts such as Pt-RuO₂/TiO₂ have sufficient band gaps for water splitting, although the current rate of hydrogen production from these systems is too low for commercial processes. Modifications to the system are required to address issues such as the narrow range of solar wavelengths absorbed by TiO₂, the efficiency of subsequent catalytic steps for formation of hydrogen and oxygen, and the need for high surface areas. Binding of catalyst complexes that absorb light in the visible range to the TiO₂ should improve the absorption characteristics. Aerogels of TiO₂ as a semiconductor support for the photocatalysts have potential for addressing reaction efficiency and surface area issues. The University of Oklahoma is investigating these systems.

The Florida Solar Energy Center (FSEC), in conjunction with the University of Geneva, is investigating tandem/dual bed photosystems using sol/gel-deposited WO₃ films as the oxygen-evolving photocatalyst, rather than TiO₂. In this configuration, the dispersion containing the wider band gap photocatalyst must have minimal light scattering losses so that the lower band gap photocatalyst behind it can also be illuminated.

Photoelectrochemical Systems

Multijunction cell technology developed by the PV industry is being used to develop photoelectrochemical (PEC) light harvesting systems that generate sufficient voltage to split water and are stable in a water/electrolyte environment. The cascade structure of these devices results in greater utilization of the solar spectrum, resulting in the highest theoretical efficiency for any photoconversion device. In order to develop cost effective systems, a number of technical challenges must be overcome. These include identification and characterization of semiconductors with appropriate band gaps; development of techniques for preparation and application of transparent catalytic coatings; evaluation of effects of pH, ionic strength, and solution composition on semiconductor energetics and stability, and on catalyst properties; and development of novel PV/PEC system designs. NREL's approach to solving these challenges is to use the most efficient semiconductor materials available, consistent with the energy requirements for a water splitting system that is stable in an aqueous environment. To date, a PV/PEC water splitting system with a solar-to-hydrogen efficiency of 12.4% (lower heating value, LHV) using concentrated light, has operated for over 20 hours [7]. HNEI is pursuing a low-cost amorphous silicon-based tandem cell design with appropriate stability and performance, and is developing protective coatings and effective catalysts. An outdoor test of the a-Si cells resulted in a solar-to-hydrogen efficiency of 7.8% LHV under natural sunlight [8].

INDIRECT HYDROGEN PRODUCTION TECHNOLOGIES

These systems offer the opportunity to produce hydrogen from renewable resources in the mid-term (5-10 years). Using agricultural residues and wastes, or biomass specifically grown for energy uses, hydrogen can be produced using a variety of processes.

Biomass pyrolysis produces a bio-oil that, like petroleum, contains a wide spectrum of components. Unlike petroleum, bio-oil contains a significant number of highly reactive oxygenated components derived mainly from constitutive carbohydrates and lignin. These components can be transformed into hydrogen via catalytic steam reforming using Ni-based catalysts. By using high heat transfer rates and appropriate reactor configurations that facilitate contact with the catalyst, the formation of carbonaceous deposits (char) can be minimized. The resulting products from the thermal cracking of the bio-oils are steam reformed at temperatures ranging from 750-850°C. At these conditions, any char formed will also be gasified. At NREL and the Jet Propulsion Laboratory, research and modeling are underway to develop processing technologies that take advantage of the wide spectrum of components in the bio-oil, and address reactivity and reactor design issues [9, 10]. Evaluation of co-product strategies indicates that high value chemicals, such as phenolic resins, can be economically produced in conjunction with hydrogen [11].

Biomass is typically 50 weight % (wt%) moisture (as received); biomass gasification and pyrolysis processes require drying of the feed to about 15 wt% moisture for efficient and sustained operation, in addition to requiring size reduction (particle size of ~1 cm). In supercritical gasification processes, feed drying is not required, although particle size reduction requirements are more severe. A slurry containing approximately 15 wt% biomass (required size reduction ~1 mm) is pumped at high pressure (>22 MPa, the critical pressure of water) into a reactor, where hydrothermolysis occurs, leading to extensive solubilization of the lignocellulosics at just above the supercritical conditions. If heat transfer rates to the slurry are sufficiently high, little char is formed, and the constituents of biomass are hydrolyzed and solubilized in the supercritical medium. Increasing the temperature to ~700°C in the presence of catalysts results in the reforming of the hydrolysis products. Catalysts have been identified that are suitable for the steam reforming operation [12]. HNEI, Combustion Systems Inc., and General Atomics are investigating appropriate slurry compositions, reactor configurations, and operating parameters for supercritical water gasification of wet biomass.

HYDROGEN STORAGE, TRANSPORT, AND DELIVERY

The storage, transport, and delivery of hydrogen are important elements in a hydrogen energy system. With keen interest in mobile applications of hydrogen systems, and as intermittent renewables penetration of the electric grid increases, storage becomes essential to a sustainable energy economy. Light weight and high energy density storage will enable the use of hydrogen as a transportation fuel. Efficient and cost effective stationary hydrogen storage will permit PV and wind to serve as base load power systems.

Compressed Gas Storage Tanks

Currently, compressed gas is the only commercially available method for ambient-temperature hydrogen storage on a vehicle. Compressed hydrogen stored at 24.8 MPa in a conventional fiberglass-wrapped aluminum cylinder results in a volumetric storage density of 12 kg of hydrogen per m³ of storage volume and a gravimetric density of 2 wt% (grams of hydrogen per gram of system weight). Carbon fiber-wrapped polymer cylinders achieve higher densities (15 kg/m³ and 5 wt%), but are significantly below target values required for hydrogen to make major inroads in the transportation sector (62 kg/m³ and 6.5 wt%). Advanced lightweight pressure vessels have been designed and fabricated by Lawrence Livermore National Laboratory [13]. These vessels use lightweight bladder liners that act as inflatable mandrels for composite overwrap and as permeation barriers for gas storage. These tank systems are expected to exceed 12 wt% hydrogen storage (at 33.8 MPa) when fully developed.

Carbon-based Storage Systems

Carbon-based hydrogen storage materials that can store significant amounts of hydrogen at room temperature are under investigation. Carbon nanostructures could provide the needed technological breakthrough that makes hydrogen powered vehicles practical. Two carbon nanostructures are of interest – single-walled nanotubes and graphite nanofibers. Single-walled carbon nanotubes, elongated pores with diameters of molecular dimensions

(12 Å), adsorb hydrogen by capillary action at non-cryogenic temperatures. Single-walled nanotubes have recently been produced and tested at NREL in high yields using a number of production techniques, and have demonstrated hydrogen uptake at 5-10 wt% at room temperature [14]. Graphite nanofibers are a set of materials that are generated from the metal catalyzed decomposition of hydrocarbon-containing mixtures. The structure of the nanofibers is controlled by the selection of catalytic species, reactant composition, and temperature. The solid consists of an ordered stack of nanocrystals that are evenly spaced at 0.34-0.37 nanometers (depending on preparation conditions). These are bonded together by van der Waals forces to form a "flexible wall" nanopore structure. Northeastern University estimates that excellent hydrogen storage capacities are possible in these structures.

Metal Hydride Storage and Delivery Systems

Conventional high capacity metal hydrides require high temperatures (300-350°C) to liberate hydrogen, but sufficient heat is not generally available in fuel cell transportation applications. Low temperature hydrides, however, suffer from low gravimetric energy densities and require too much space on board or add significant weight to the vehicle. Sandia National Laboratories (SNL) and Energy Conversion Devices (ECD) are developing low-temperature metal hydride systems that can store 3-5 wt% hydrogen. Alloying techniques have been developed by ECD that result in high-capacity, multi-component alloys with excellent kinetics, albeit at high temperatures. Additional research is required to identify alloys with appropriate kinetics at low temperatures.

A new approach for the production, transmission, and storage of hydrogen using a chemical hydride slurry as the hydrogen carrier and storage medium is under investigation by Thermo Power Corporation. The slurry protects the hydride from unanticipated contact with moisture and makes the hydride pumpable. At the point of storage and use, a chemical hydride/water reaction is used to produce high purity hydrogen. An essential feature of the process is recovery and reuse of spent hydride at a centralized processing plant. Research issues include the identification of safe, stable and pumpable slurries and the design of an appropriate high temperature reactor for regeneration of spent slurry.

END USE TECHNOLOGIES

Proton exchange membrane (PEM) fuel cells could provide low-cost, high-efficiency electric power, and be operated "in reverse" as electrolyzers to generate hydrogen. There has been a significant increase in industry activity for the development of PEM fuel cells for vehicular applications, with a number of active demonstration projects. Improvements in catalyst loading requirements, water management, and temperature control have helped move these power units from mere curiosities to legitimate market successes. In order to increase the market penetration in both the transportation and utility sectors, additional improvements are required. Los Alamos National Laboratory is developing non-machined stainless steel hardware and membrane electrode assemblies with low catalyst loadings to achieve cost reductions and efficiency improvements [16]. The most important barriers to implementation of low-cost PEM fuel cells are susceptibility of the metal or alloy to corrosion, water management using metal screens as flow fields, and effective stack sealing. Operating the PEM fuel cell "in reverse" as an electrolyzer is possible, but optimum operating conditions for the power production mode and for the hydrogen production mode are significantly different. Design issues for the reversible fuel cell system include thermal management, humidification, and catalyst type and loading.

In an effort to promote near-term use of hydrogen as a transportation fuel, the Program is investigating the development of cost effective, highly efficient, and ultra-low emission internal combustion engines (ICE) operating on pure hydrogen and hydrogen-blended fuels. Research at SNL is focused on the development of a hydrogen fueled ICE/generator set with an overall efficiency of >40% while maintaining near zero NO_x emissions [15].

SAFETY

Hydrogen leak detection is an essential element of safe systems. The development of low-cost fiber optic and thick film sensors by NREL and ORNL, respectively, will provide affordable and reliable options for hydrogen safety systems. NREL is using optical fibers with a thin film coating on the end that changes optic properties upon reversible reaction with hydrogen. Changes in the reflected light signal is an indication of the presence of hydrogen. Sensitivity and selectivity are important research issues. ORNL is focused on the development of monolithic, resistive thick film sensors that are inherently robust,

selective to hydrogen, and easy to manufacture. Research issues include developing appropriate techniques for active (versus traditional passive) thick film applications.

Recognizing the importance of safe use of hydrogen, the DOE, in conjunction with Natural Resources Canada, has compiled a comprehensive document of prevailing practices and applicable codes, standards, guidelines, and regulations for the safe use of hydrogen. The *Sourcebook for Hydrogen Applications* is intended to be a "living document" that can be updated to reflect the current state of knowledge about, and experience with, safely using hydrogen in emerging applications. DOE also supports the development of codes and standards under the auspices of the International Standards Organization.

CONCLUSIONS

The DOE Hydrogen Program conducts R&D in the areas of production, storage, and utilization, for the purpose of making hydrogen a cost-effective energy carrier for utility, buildings, and transportation applications. Research is focused on the introduction of renewable-based options to produce hydrogen; development of hydrogen-based electricity storage and generation systems that enhance the use of distributed renewable-based utility systems; development of low-cost technologies that produce hydrogen directly from sunlight and water; and support of the introduction of safe and dependable hydrogen systems including the development of codes and standards for hydrogen technologies.

REFERENCES

- [1] Ghirardi, M.L., R.K. Togasaki, and M. Seibert, 1997, "Oxygen Sensitivity of Algal Hydrogen Production," *Appl. Biochem. Biotechnol.*, 63-65, 141-151.
- [2] Seibert, M., T. Flynn, D. Benson, E. Tracy, and M. Ghirardi, 1998, "Development of Selection/Screening Procedures for Rapid Identification of Hydrogen-Producing Algal Mutants with Increased Oxygen Tolerance," International Conference on Biological Hydrogen Production, Plenum, NY, in press.
- [3] Melis, A., J. Neidhardt, I. Baroli, and J.R. Benemann, 1998, "Maximizing Photosynthetic Productivity and Light Utilization in Microalgal by Minimizing the Light-Harvesting Chlorophyll Antenna Size of the Photosystems," International Conference on Biological Hydrogen Production, Plenum, NY, in press.
- [4] Szyper, J.P., B.A. Yoza, J.R. Benemann, M.R. Tredici, and O.R. Zaborsky, 1998, "Internal Gas Exchange Photobioreactor: Development and Testing in Hawaii," International Conference on Biological Hydrogen Production, Plenum, NY, in press.
- [5] Maness, P.-C. and P.F. Weaver, 1997, "Variant O₂-Resistant Hydrogenase from Photosynthetic Bacteria Oxidizing CO," Proceedings of the Fifth International Conference on the Molecular Biology of Hydrogenase, Albertville, France.
- [6] Weaver, P.F., P.-C. Maness, and S. Markov, 1998, "Anaerobic Dark Conversion of CO into H₂ by Photosynthetic Bacteria," International Conference on Biological Hydrogen Production, Plenum, NY, in press.
- [7] Khaselev, O. and J.A. Turner, 1998, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," *Science*, 280, 425.
- [8] Rocheleau, R., 1998, "High Efficiency Photoelectrochemical H₂ Production using Multijunction Amorphous Silicon Photoelectrodes," *Energy & Fuels*, 12 (1), 3-10.
- [9] Wang, D., S. Czernik, and E. Chomet, 1998, "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil," *Energy & Fuels*, 12 (1), 19-24.
- [10] Miller, R.S. and J. Bellan, 1997, "A Generalized Biomass Pyrolysis Model Based on Superimposed Cellulose, Hemicellulose and Lignin Kinetics," *Comb. Sci. and Techn.*, 126, 97-137.
- [11] Wang, D., S. Czernik, D. Montane, M.K. Mann, and E. Chomet, 1997, "Hydrogen Production via Catalytic Steam Reforming of Fast Pyrolysis Oil Fractions," Proceedings of the Third Biomass Conference of the Americas, Montreal, 845-854.
- [12] Matsunaga, Y., X. Xu, and M.J. Antal, 1997, "Gasification Characteristics of an Activated Carbon in Supercritical Water," *Carbon*, 35, 819-824.
- [13] Miltitsky, F., and B. Myers, and A.H. Weisberg, 1998, "Regenerative Fuel Cell Systems," *Energy & Fuels*, 12 (1), 56-71.
- [14] Dillon, A.C., K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, and M.J. Heben, 1997, "Storage of Hydrogen in Single-Walled Carbon Nanotubes," *Nature*, 386, 377-279.
- [15] Van Blarigan, P., 1998, "Advanced Hydrogen Fueled Internal Combustion Engines," *Energy & Fuels*, 12 (1), 72-77.
- [16] Cleghorn, S., X. Ren, T. Springer, M. Wilson, C. Zawodzinski, T. Zawodzinski, and S. Gottesfeld, 1997, "PEM Fuel Cells for Transportation and Stationary Power Generation Applications," *Int. J. Hydrogen Energy*, 23, 1137-1144.