# BACK TO THE FUTURE: HYDROGEN PRODUCTION, NOW AND THEN

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## ABSTRACT

The availability of a reliable and cost-effective supply of hydrogen will be essential in the development of the so-called Hydrogen Economy. Whereas most hydrogen is now produced from steam reforming of natural gas, renewable and sustainable resources will be the sources of choice. Getting from the current production paradigm to this idyllic future will require a transitional phase that exploits our abundant fossil resources in new ways, and challenges our sustainable technologies to reduce costs and improve efficiency and convenience. This paper discusses the current state of fossil-based and sustainable hydrogen production technologies and proposes innovative approaches to this Hydrogen Economy in a carbon-constrained world.

## INTRODUCTION

In the future, our energy systems will need to be renewable and sustainable, efficient and cost-effective, convenient and safe. Hydrogen has been proposed as the perfect fuel for this future energy system. Produced from water and sunlight in nearly inexhausible quantities, hydrogen could supply the energy needs of all sectors of the economy. But, the technologies needed for the Hydrogen Economy are not technically mature or are too costly to compete with other energy forms.

In its Hydrogen Program, the U. S. Department of Energy (DOE) conducts R&D for the development of safe, cost-effective hydrogen production technologies that support and foster the transition to the Hydrogen Economy. Although the long-term focus is on renewable technologies, the introduction of hydrogen into the transportation and utility sectors will require the availability of inexpensive hydrogen - most likely relying on fossil fuels such as natural gas, coal, and oil.

## A HOLY WAR FOR HYDROGEN ?

Hydrogen Economy purists frequently express dismay at the notion of using fossil fuels to produce hydrogen in the transition to a hydrogen-based energy system. The argument focuses on the "contamination" of the hydrogen utopia - where hydrogen produces no pollution in the production, storage, transportation, and use cycles. Producing "unholy" hydrogen from fossil fuels results in the production of anthropogenic $CO_2$, which cannot be (easily) recycled to produce more fuel. We should note that carbon emissions are not necessarily evil - $CO_2$ produced in a biomass-based hydrogen system is recycled in the biomass growth phase, and results in net zero (within a few percent) $CO_2$ emissions [1].

But we are faced with economic realities - hydrogen is pretty cheap when produced in large steam methane reformers, and may be even cheaper when produced by gasification of coal. Renewable-based technologies are not ready for commercialization, and face significant economic hurdles when they do get there. And it will not do us much good to develop these renewable production technologies if there are no viable end uses for our "holy" hydrogen. Pragmatists look to fossil fuels as stepping stones to the future, providing hydrogen at reasonable costs for the evolving end users. That doesn't mean we cannot improve upon today's technologies to provide the cleanest hydrogen possible. The DOE Hydrogen Program is dedicated to developing improved production technologies that can provide fossil-based hydrogen in the near-term at competitive prices, and renewable-based hydrogen in the mid- and long-term.

## NEAR-TERM FOSSIL-BASED HYDROGEN PRODUCTION TECHNOLOGIES

The production of hydrogen from fossil fuels, particularly natural gas, is an integral part of the DOE Hydrogen Program strategy to introduce hydrogen into the transportation and utility energy sectors. This strategy includes reducing the cost of conventional and innovative hydrogen production processes that rely on cheap fossil feedstocks to improve the economics of hydrogen use. The Program supports a number of projects that rely on improvements to existing processes, resulting in reduced costs and improved emissions.

Air Products and Chemicals is investigating a modification to the conventional steam methane reforming process that includes incorporation of a $CO_2$ adsorbent in the reforming reaction to remove $CO_2$ from the product stream [2]. This "upset" to the reaction equilibrium drives the reforming reaction ($CH_4 + 2H_2O = [CO + CO_2] + 4H_2$) to produce additional hydrogen at lower temperatures than conventional reformers. The cost of hydrogen is expected to be 25-30% lower with this process, primarily due to reduced capital equipment costs and reduced operating costs. In addition, the adsorption of the $CO_2$ in the reforming stage results in a high-purity $CO_2$ stream from the adsorbent regeneration step. This has interesting implications in a carbon-constrained world, discussed later.

The Program supports the development of a compact plasma reformer for hydrocarbon fuel reforming for industrial, distributed utility, and vehicular refueling applications. The Massachusetts Institute of Technology is examining the potential of the plasma reforming process to perform the reforming and water-gas shift in a single reactor [3]. Improvements to the process are expected to result in a reduction in specific energy consumption.

In a project cosponsored by the Hydrogen Program and the Office of Fossil Energy, Air Products and Chemicals is developing a ceramic membrane reactor for the simultaneous separation of oxygen from air and the partial oxidation of methane. If successful, this process could result in improved production of hydrogen and/or synthesis gas compared to standard reformers.

## MID-TERM RENEWABLE HYDROGEN PRODUCTION TECHNOLOGIES

Thermal processing of plant material (biomass) is similar to the processing of fossil fuels, with a number of the down-stream unit operations being essentially the same for both feedstocks. Hydrogen Program R&D focuses on the processing units that are feedstock-dependent, leveraging the vast database of experience available on the common unit operations. Using agricultural residues and wastes, or biomass specifically grown for energy uses, hydrogen can be produced using a variety of processes, including pyrolysis and gasification. These systems offer the opportunity to produce hydrogen from renewable resources in the mid-term (5-10 years).

Biomass pyrolysis produces a liquid product (bio-oil) that, like petroleum, contains a wide spectrum of components that can be separated into valuable chemicals and fuels. 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 a variety of products, including hydrogen. Catalytic steam reforming of the bio-oil or selected fractions is possible, using Ni-based catalysts that are similar to those used in steam methane reforming. By using high heat transfer rates and appropriate reactor configurations that facilitate contact with the catalyst, the formation of undesirable carbonaceous deposits (char) can be minimized. At the National Renewable Energy Laboratory (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 [4,5]. Evaluation of co-product strategies indicates that high value chemicals, such as phenolic resins, can be economically produced in conjunction with hydrogen [6].

One of the significant differences between solid fossil fuels (coal) and biomass is the moisture content (and affinity to moisture). Biomass is typically 50 weight percent (wt%) moisture (as received), requiring drying of the feed to about 15 wt% moisture for efficient and sustained operation in typical pyrolysis and gasification operations. However, in a supercritical water gasification process under development at the Hawaii Natural Energy Institute (HNEI) at the University of Hawaii, feed drying is not required, thus providing an opportunity to reduce equipment and operating costs. There are tradeoffs: particle size reduction requirements are more severe for this process (~1 mm) than for other biomass gasification and pyrolysis processes (~1 cm). A slurry containing approximately 15 wt% biomass is pumped at high pressure (>22 MPa, the critical pressure of water) into a reactor, where hydrothermolysis occurs. 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 [7]. HNEI, Combustion Systems Inc., and General Atomics are investigating appropriate slurry compositions, reactor configurations, and operating parameters for supercritical water gasification of wet biomass.

## LONG-TERM RENEWABLE 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 $CO_2$ 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 [8,9].

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 [10], 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 NREL. Various reactor designs are under development for photobiological hydrogen production processes (single-stage vs two-stage, single organism vs dual organism). At HNEI, a new, potentially low cost, outdoor tubular photobioreactor is under development to test a sustainable system for the production of hydrogen [11].

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 ($CO + H_2O = CO_2 + H_2$). 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 [12,13]. 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 $Pt\text{-}RuO_2/TiO_2$ 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 $TiO_2$, 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 $TiO_2$ should improve the absorption characteristics. Aerogels of $TiO_2$ 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, in conjunction with the University of Geneva, is investigating tandem/dual bed photosystems using sol/gel-deposited $WO_3$ films as the oxygen-evolving photocatalyst, rather than $TiO_2$. 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 for 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 at 11 suns [14]. 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 [15].

## THE ROLE OF HYDROGEN IN A CARBON-CONSTRAINED WORLD

After basking in a week of temperatures in the 70's in December in the Denver area while Russia is gripped in the worst early winter cold spell this century, one begins to wonder if perhaps all those "Chicken Little" environmentalists might be on to something. Concerns about global climate change are increasing around the world, and industries are beginning to address the economic impacts of environmentally-sound energy consumption.

Decarbonization of fossil fuels is proposed as a "quick fix" to increased energy consumption in a carbon-constrained world. Removal of carbon from fossil fuels prior to use in energy production is likely to be far less costly than attempting to remove $CO_2$ from dispersed sources. If fossil fuels are converted to hydrogen in a central facility, the collection of $CO_2$ (or elemental carbon, depending on the process) is relatively simple compared to collecting $CO_2$ from every fossil-fuel-consuming vehicle on the road.

Technical barriers exist. For steam methane reforming (the predominant hydrogen production technology in use today), collection of $CO_2$ from the hydrogen purification step will require process and operation changes that could impact overall energy efficiency and therefore cost. $CO_2$ disposal or sequestration, in a manner that keeps the greenhouse gas out of the atmosphere for a significant period of time (perhaps 100+ years), is the subject of numerous research projects throughout the world. Environmental effects of deep ocean disposal on marine life and water quality (pH in particular) have yet to be determined. Security of aquifer disposal is also uncertain. In addition, the use of hydrogen as a transportation fuel would require development of efficient delivery, dispensing, and on-board storage processes. Use of hydrogen in power production will required continued improvements in fuel cells and gas turbines.

## CONCLUSIONS

The production of hydrogen, from fossil fuels or from renewables, is only one part of the equation. Significant changes in our fuel infrastructure are required to address the use of this clean fuel. Codes and standards for the safe use of hydrogen are under development, and must be implemented to ensure the safety of the public. As with any new fuel or technology, education is essential. The DOE Hydrogen Program continues to support the development of technologies that will enable the transition to a clean and sustainable Hydrogen Economy, with emphasis on technical viability, environmental friendliness, and economic competitiveness.

## REFERENCES


[1] Mann, M.K., and P.L. Spath, 1997, "Life Cycle Assessment of a Biomass Gasification Combined-Cycle Power System," NREL/TP-430-23076.

[2] Hufton, J., S. Mayorga, T. Gaffney, S. Nataraj, M. Roa, and S. Sircar, 1998 "Sorption Enhanced Reaction Process (SERP) for the Production of Hydrogen," Proceedings of the 1998 U.S. DOE Hydrogen Program Review, NREL/CP-570-25315, 695-706.

[3] Bromberg, L., D. Cohn, A. Robinovich, and N. Alexeev, 1998, "Plasma Catalytic Reforming of Methane," Proceedings of the 1998 U.S. DOE Hydrogen Program Review, NREL/CP-570-25315, 627-638.

[4] Wang, D., S. Czernik, and E. Chornet, 1998, "Production of Hydrogen from Biomass by Catalytic Steam Reforming of Fast Pyrolysis Oil," *Energy & Fuels*, 12 (1), 19-24.

[5] 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.

[6] Wang, D., S. Czernik, D. Montane, M.K. Mann, and E. Chornet, 1997, "Hydrogen Production via Catalytic Steam Reforming of Fast Pyrolysis Oil Fractions," Proceedings of the Third Biomass Conference of the Americas, Montreal, 845-854.

[7] Matsunaga, Y., X. Xu, and M.J. Antal, 1997, "Gasification Characteristics of an Activated Carbon in Supercritical Water," *Carbon*, 35, 819-824.

[8] Ghirardi, M.L., R.K. Togasaki, and M. Seibert, 1997, "Oxygen Sensitivity of Algal Hydrogen Production," *Appl. Biochem. Biotechnol.,* 63-65, 141-151.

[9] 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.

[10] 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.

[11] 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.

[12] Maness, P.-C. and P.F. Weaver, 1997, "Variant $O_2$-Resistant Hydrogenase from Photosynthetic Bacteria Oxidizing CO," Proceedings of the Fifth International Conference on the Molecular Biology of Hydrogenase, Albertville, France.

[13] Weaver, P.F., P.-C. Maness, and S. Markov, 1998, "Anaerobic Dark Conversion of CO into $H_2$ by Photosynthetic Bacteria," International Conference on Biological Hydrogen Production, Plenum, NY, in press.

[14] Khaselev, O. and J.A. Turner, 1998, "A Monolithic Photovoltaic-Photoelectrochemical Device for Hydrogen Production via Water Splitting," *Science,* 280, 425.

[15] Rocheleau, R., 1998, "High Efficiency Photoelectrochemical $H_2$ Production using Multijunction Amorphous Silicon Photoelectrodes," *Energy & Fuels*, 12 (1), 3-10.