New Horizons For Hydrogen

Producing Hydrogen from Renewable Resources

Recent events have reminded us of the critical need to transition from crude oil, coal, and natural gas toward sustainable and domestic sources of energy. One reason is we need to strengthen our economy. In 2008 we saw the price of oil reach a record $93 per barrel. With higher oil prices, growing demand for gasoline, and increasing oil imports, an average of $235 billion per year, has left the United States economy to pay for foreign oil since 2005, or $1.2 trillion between 2005 and 2009. From a consumer perspective, this trend is seen with an average gasoline price of $2.50 per gallon since 2005, compared to an average of $1.60 between 1990 and 2004 (after adjusting for inflation). In addition to economic impacts, continued reliance on fossil fuels increases greenhouse gas emissions that may cause climate change, health impacts from air pollution, and the risk of disasters such as the Deepwater Horizon oil spill. Energy efficiency in the form of more efficient vehicles and buildings can help to reduce some of these impacts. However, over the long term we must shift from fossil resources to sustainable and renewable energy sources.

Renewable Hydrogen

Hydrogen (H_2) is the most abundant element in the universe. And although it does not exist naturally by itself on Earth, it can be produced from a wide variety of resources — coal, oil, natural gas, biomass, and water (H_2O). This versatility enables us to produce hydrogen where and when we need it.

About 95% of the H_2 we use today comes from reforming natural gas. The remainder, high-purity H_2 from H_2O electrolysis, is primarily produced using electricity generated by burning fossil fuels. But to realize the full benefits of H_2 — sustainability, increased energy security, diverse energy supply, reduced air pollution and greenhouse gas emissions — it must be produced cleanly, efficiently, and affordably from domestically available renewable resources.

The ultimate goal is a sustainable cycle of H_2 production and use. In the first stage of this cycle, H_2 is produced from renewable resources, such as via photo electrolysis of H_2O, in which energy from the sun is used to convert H_2O into H_2 and oxygen (O_2). The H_2 is then used to power a fuel cell, in which H_2 and O_2 from air recombine to produce electricity, heat, and H_2O. This cycle produces no pollution and no greenhouse gases. Advanced technologies that produce renewable H_2 as part of this cycle will play a leading role in the widespread commercialization of H_2.

The National Renewable Energy Laboratory (NREL) is developing technologies for producing H_2 from renewable and sustainable resources, including biomass conversion; electrolysis using electricity from renewable resources, in particular from wind energy; and direct water splitting using microorganisms or semiconductors. Some technologies are ready for real-world demonstrations. Others are emerging and will require long-term R&D investment. All focus on the goal of producing clean, sustainable H_2.

Hydrogen from Biomass

NREL has been developing methods for converting biomass to fuels, chemicals, heat, and power. Building on the successes of these efforts, biomass is now one of the best near-term options for producing renewable H_2.

Biomass resources are abundant and widely distributed throughout the United States. And because biomass consumes atmospheric carbon dioxide (CO_2) during growth, it can have a small net CO_2 impact compared with fossil fuels, temporarily sequestering carbon during the cycle and reducing our nation's greenhouse gas emissions.

Biomass feedstocks such as agricultural and forest residues, consumer wastes, and crops specifically grown for energy production are composed of three interconnected polymeric materials — cellulose, hemicellulose, and lignin. Of the technologies used to break down this biomass structure and produce H_2, perhaps the ones closest to being competitive with conventional means are the thermochemical processes of gasification and pyrolysis.

Gasification research. This is a two-step process in which biomass is thermochemically converted into a combustible gas:

1. The volatile components of the fuel are released (in the presence of O_2, air, or steam) at temperatures below 600°C by a set of complex reactions. This yields a mixture of CO_2, carbon monoxide (CO), tar, H_2, and H_2O, with by-products of char and ash.

2. The char is gasified at 800°–850°C through reactions with O_2, steam, and H_2. This yields a mixture of gases that primarily consists of CO, CO_2, and H_2. Some of the unburned char is combusted to provide the heat needed for the gasification.

The overall reaction is:

$$Biomass + O_2 \rightarrow CO + H_2 + CO_2$$
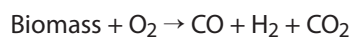
The gas product of this process requires conditioning to remove tars and inorganic impurities. CO_2 is converted to additional H_2 via the water-gas-shift reaction:

$$CO + H_2O \rightarrow CO_2 + H_2$$
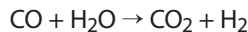
Pyrolysis research. This is a process that thermally degrades biomass to a mixture of gases, char, and an O_2-rich liquid called bio-oil. Pyrolysis takes place at 450°–550°C in the absence of O_2. The overall reaction is:

$$Biomass + Energy \rightarrow Gases + Char + Bio\text{-}Oil$$

The relative proportions of the three products depend on the pyrolysis method, the characteristics of the biomass, and the reaction conditions — heating rate, temperature, and residence time. For example, pyrolysis has been used to produce charcoal for centuries. This requires relatively slow reaction rates at low temperatures (400°C) to maximize solid yield. Fast pyrolysis is used to maximize either the gas or the liquid products, depending on the temperature.

The bio-oil and gases are converted to H_2 using catalytic steam reforming, followed by the water-gas-shift reaction. The catalytic steam reforming reaction takes place at 750°–850°C over a nickel-based catalyst:

$$Bio\text{-}Oil/Gases + H_2O \rightarrow CO + H_2$$
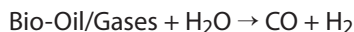
The CO is converted into additional H_2 via the water-gas-shift reaction, resulting in the overall reaction:

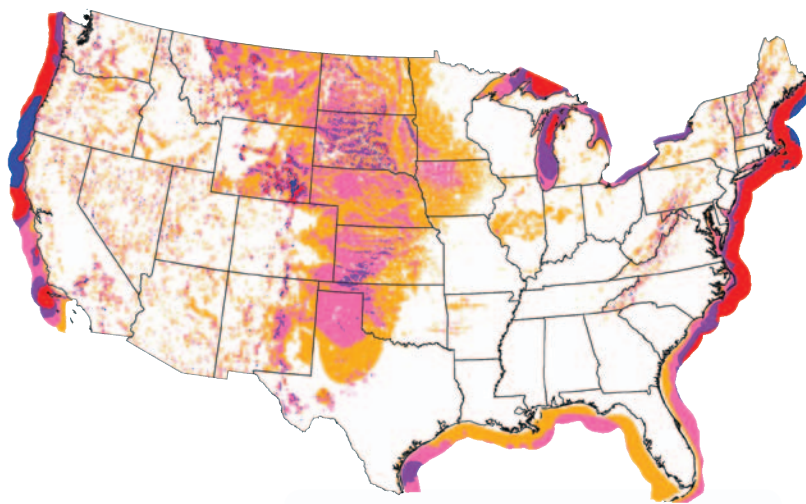$$Bio\text{-}Oil/Gases + H_2O \rightarrow CO_2 + H_2$$
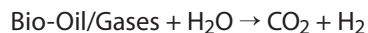
As the final step in gasification and pyrolysis, the H_2 and CO_2 are separated to yield H_2 that is 99.99% pure, meeting the requirements for use in a fuel cell.

Coproducts. Although well understood, the processes of biomass gasification and pyrolysis face challenges. To be competitive, higher process efficiencies and better heat and mass integration are needed. The processes must be flexible enough to handle a range of low-cost feedstocks and their variations in chemical and physical characteristics. Large-scale technology demonstrations of the entire biomass-to-H_2 process are needed to optimize the process and prove its viability. We must also be able to derive other valuable products from biomass.

This is where pyrolysis has an advantage over gasification. Because bio-oil is composed of two distinct fractions, it can be separated based on H_2O solubility. The water-soluble fraction can be converted to H_2 via catalytic steam reforming, and the H_2O-insoluble fraction can be used to make high-value adhesives or fuel components.

New catalysts. Scientists are designing cost-effective, feedstock-flexible reforming catalysts that can be applied in fluidized bed reactors that are used for pyrolysis liquid steam reforming. Commercially available catalysts developed for fixed beds cannot withstand the harsh conditions required to produce H_2 from pyrolysis liquids, resulting in catalyst losses (attrition) of 10%–20% by weight per day. NREL has developed new attrition-resistant, nickel-based catalysts that are suitable for fluidized bed application. Testing on pyrolysis oils from pine and mixed hardwoods verified that the new catalysts can produce H_2 with efficiencies as good as or better than those of the best commercial catalysts. These catalysts are being modified for use with other feedstocks.

All these investigations — coproducts, feedstock evaluation, and catalyst development — contribute to the development of an optimized, reliable, cost-effective process for producing H_2 from biomass.

Wind Electrolysis

Many renewable technologies — photovoltaics (PV), wind, biomass, hydroelectric, and geothermal — can generate the clean and sustainable electricity needed to run an electrolyzer. An electrolyzer has one objective: to split H_2O into H_2 and O_2. But for electrolytic H_2 production to be cost effective and environmentally benign, we need a low-cost source of renewable electricity. During the past 25 years, advances in wind turbine technology have dramatically reduced the cost of wind power. Today, the cost of wind electricity is typically $0.03–$0.07/kWh for utility-scale projects. This puts wind electrolysis in a good position to be the first economical renewable H_2 production system.
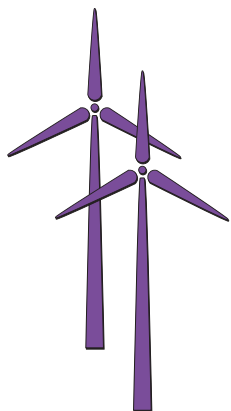
In wind electrolysis, the kinetic energy of the wind turns the blades of a turbine, and the rotor spins a shaft, which connects to a generator to make electricity. An electrolyzer uses this electricity to separate H_2O into H_2 and O_2:

$$2H_2O + electricity \rightarrow 2H_2 + O_2$$

Polymer electrolyte membrane (PEM) electrolyzers, which are being investigated for this application, consist of a membrane sandwiched between two catalyst-coated electrode plates. At the positively charged electrode (anode), H_2O is split into proton ions (H^+), O_2 and electrons (e-) are given up to complete the circuit. The O_2 is collected or released, and the protons move through the PEM under the influence of the applied electric field. On the other side of the membrane two protons combine with electrons entering the cathode, the negatively charged electrode, to form H_2.

Alkaline electrolyzers typically use potassium hydroxide (KOH) as the ion-conducting electrolyte. The K^+ and OH^- mobile ions, in an H_2O solution, complete the electrical circuit to produce the same overall reaction shown above. The alkaline electrolyte is not consumed in the electrolysis process. In large-scale alkaline electrolysis systems it takes about 55 kWh of electrical energy to produce 1kg of H_2 (~62% efficient). A kg of H_2 has roughly the same energy content as a gallon of gasoline (34kWh).

Producing both electricity and H_2 from wind turbines offers the promise of optimizing electrolysis and power system efficiencies to lower costs of the H_2 product. For example, producing and storing H_2 with wind power can improve the ability to dispatch electricity when needed, which is a limitation associated with the natural variability of wind energy. When the wind turbine is producing electricity, H_2 can be produced via electrolysis and stored for later use. The stored H_2 can then be used in a fuel cell to produce electricity during
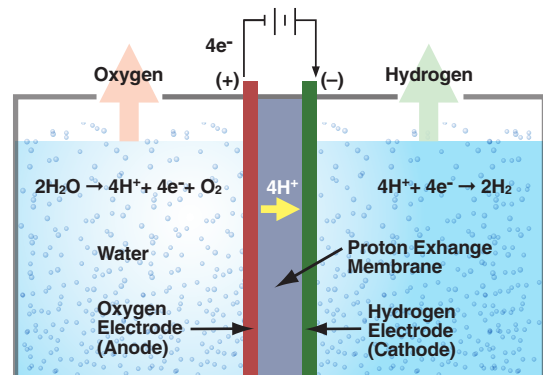
In a PEM electrolyzer cell, H_2O is split into protons (H^+), electrons (e-), and O_2 at the anode. The protons move through the membrane to the cathode, where they combine with electrons to form H_2.

times of low power production or during peak demand. The stored H_2 can also be used in many other applications. For example, it can be used in internal combustion engines for vehicle transportation, to make ammonia (NH_3) for fertilizer, to cool large electrical power generators, in fuel cells for backup power instead of batteries, and in the hydrogenation of vegetable oil.

Coupling wind turbines with low-cost electrolyzers can also reduce the cost of a system by minimizing redundancy. For example, variable-speed wind turbines rely on power electronics to convert the "wild alternating current (AC)" (variable frequency, variable voltage) produced at the generator to direct current (DC), which before being connected to the grid must be converted back to AC at grid frequency (60 Hz). Electrolyzers designed for grid-connected operation also incorporate power electronics to convert AC from the grid to DC power required by the electrolyzer cell stack. These power converters represent a significant percentage of the total cost of the wind turbine and electrolyzer.

To make wind electrolysis cost effective, researchers will have to lower the cost of wind electricity, design more efficient electrolyzers, and optimize the wind/electrolyzer integrated system. They will then still need to resolve the logistics of integrating wind electrolyzer systems with utility systems at local, regional, and national levels.

One step toward meeting these challenges is the demonstration of integrated renewable electrolysis systems at NREL's Distributed Energy Resources Test Facility at the National Wind Technology Center. For this demonstration, NREL has designed power-converters to eliminate redundancy in the wind-electrolysis system and allow the power output of wind turbines to match the power requirements of electrolyzers. Success here will help pave the way for commercializing the concept.

Direct Hydrogen Production

Photoelectrochemical (PEC) devices or photosynthetic microorganisms use energy from sunlight to dissociate H_2O into H_2 and O_2. They are the ultimate clean and sustainable H_2 production methods. Although not ready for prime time, these technologies show great promise and are the focus of long-term R&D efforts at NREL.

Photoelectrochemical research. A PEC H_2 system integrates PV material with an electrolyzer to produce H_2 directly from H_2O, using only sunlight. This system offers many benefits over two-step processes in which the PV cells and electrolyzer are separate components of the system. Combining the two components in a single PEC device can eliminate most of the electrolyzer costs and reduce semiconductor processing because surface contacts, interconnects, and wiring are no longer necessary. It can also increase the efficiency of the process by 30%, further reducing the cost of delivered H_2.

The basic PEC H_2 production system consists of a semiconductor electrode and a platinum metal electrode immersed in an

The H_2 cycle: When generated from renewable sources, such as via photo electrolysis, H_2 production and use are part of a clean, cyclic process.
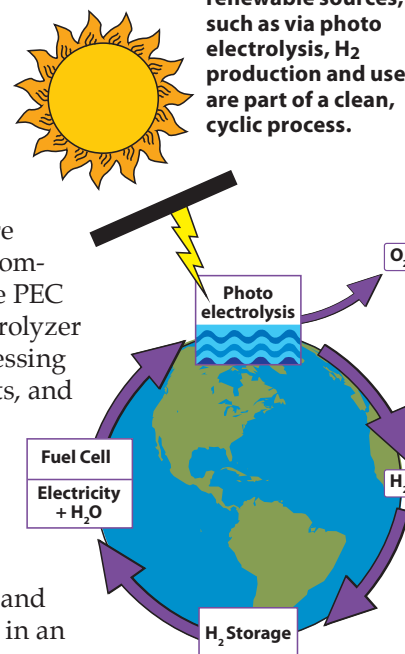
The Right Energetics

For a PEC H_2 structure, system energetics are a function of the intrinsic electronic properties of the semiconductor material and the electrochemistry at the interface of the semiconductor and the electrolyte.

According to the band theory of solids, which describes the electrical conductivity of solid materials, the available energy levels for electrons in a material form a valence band and a conduction band. The energy difference between the two bands is called the band gap energy. When a semiconductor absorbs light (photon) energy, electrons from the valence band are excited into the conduction band to generate a current. Only photons with energy equal to or greater than the band gap of the material can free an electron from the valence band to the conduction band. To absorb a large portion of the solar spectrum, the band gap must be less than 2.2 eV. For PEC applications, the electrical output must also be large enough to drive the water-splitting reaction (greater than 1.23 eV). The ideal material for a PEC H_2 system has a band gap of 1.6–2.2 eV.

In a PV system, a solid-state junction is the active layer where charge transfer occurs. In a PEC system, the interface between the semiconductor and the electrolyte is the active layer. The characteristics of the band edges (the top edge of the valence band and the bottom edge of the conduction band) at this interface determine whether water splitting takes place. For a given semiconductor material, the energetic positions of the bands at the semiconductor surface are fixed. For water splitting to occur, the band edges must overlap the energy levels of the H_2- and O_2-evolving reactions (the H_2O oxidation-reduction potential). Specifically, the conduction band edge must be higher in energy than the H_2-evolving half reaction (–0.41 eV), and the valence band edge must be lower in energy than the O_2-evolving half reaction (0.82 eV).

In addition, charge must transfer from the semiconductor surface to the H_2O quickly. If electrons build up on the surface of the semiconductor, they shift the band edges in a negative direction and possibly out of the range required for water splitting. To accommodate this possibility, band-edge characteristics can be shifted to the required energetic positions through chemical modification of the semiconductor electrode surface.

aqueous electrolyte. But instead of using electricity from an external source like wind power, the semiconductor absorbs light energy and generates the electrical current that drives the electrolysis reaction, splitting H_2O into H_2 at the semiconductor surface and O_2 at the metal electrode surface.

Although simple in concept, the challenge is to find a material that can drive this one-step process. The light-harvesting system must have the correct energetics to drive the electrolysis, and the system must be stable in an aqueous environment for this to be viable (see "The Right Energetics," on page 4).

So far, no single semiconductor has been identified that satisfies all of the criteria for use in a H_2-evolving PEC system. The most stable semiconductors in aqueous solution are oxides, but their band gaps are too large for efficient light absorption, or their semiconductor characteristics are poor. Semiconductors with better solid-state characteristics are typically thermodynamically unstable with respect to oxidation.

Finding a material that can drive the process is the key to the success of PEC H_2 production. Materials now under evaluation — gallium nitrides, amorphous silicon, and copper indium gallium diselenide films (CIGS) — build on materials developed for PV. A variety of surface treatments — protective coatings and band-edge engineering — are also being evaluated to address energetic issues, corrosion problems, and catalysts for the water-splitting reactions.

Gallium nitrides, although expensive, are good candidates for PEC H_2 systems because they show high efficiencies, are chemically stable, and their band gaps can be adjusted by altering their composition to produce alloys of gallium nitride. Gallium phosphide nitride and indium gallium nitride are being evaluated to determine if they can be tailored to meet the requirements for solar water-splitting.

NREL scientist John Turner demonstrates the ability of a PEC cell to produce H_2 from H_tO using energy from a light source.

Amorphous silicon (a-Si) multijunction systems developed for PV offer a lower-cost alternative to gallium nitride materials. Triple-junction a-Si devices have voltages sufficient for water splitting, and the cells can be tailored to produce voltages matched to the energetic requirements of water splitting, maximizing overall efficiency. But a-Si is unstable in aqueous solutions and must be protected by a corrosion-resistant coating in a PEC H_2 system. To maintain the function of the semiconductor, the coating material must be stable, transparent, and conductive. For this, researchers are evaluating silicon nitride compositions.

Semiconductor materials based on polycrystalline thin films, such as CIGS, are also promising alternatives. They are made with inexpensive techniques and can reach efficiencies greater than 15%, both of which help reduce costs. Incorporating sulfur into CIGS increases the band gap into the range required for PEC water splitting. A viable CIGS water-splitting device would greatly decrease PEC H_2 production costs.

Once we identify a semiconductor material with the ideal band gap and chemical stability, it still will not split H_2O unless the semiconductor band edges overlap the H_2O redox potential. This energetic mismatch can be overcome by using a tandem semiconductor system or by modifying the semiconductor band edges. NREL researchers have demonstrated a solar-to-H_2 conversion efficiency of 12.4% using a unique structure based on a gallium indium phosphide/gallium arsenide ($GaInP_2$/GaAs) tandem system. In this configuration, the GaAs cell generates the additional voltage needed to overcome the energetic mismatch between the $GaInP_2$ semiconductor and the H_2O redox reactions. Researchers are investigating the effects of adsorption of organometallic compounds on the band-edge properties of $GaInP_2$. In theory, these materials should shift the band edges into the water-splitting range, and speed up the charge transfer rate at the surface. Understanding and controlling the interfacial properties of semiconductor electrodes is key to successfully producing H_2 from PEC systems.

The development and characterization of new semiconducting materials and systems are critical for the future viability of PEC-driven H_2 generation. Continuation of the collaborative relationship between PV and PEC H_2 R&D will accelerate progress in identifying and synthesizing more efficient, lower-cost, and electrochemically stable solid-state materials and systems.

Photobiological research. The green alga, *Chlamydomonas reinhardtii*, is one of several microorganisms that use sunlight to produce H_2 directly from H_2O. Like all green plants, it also produces

O_2 during photosynthesis. Unfortunately, O_2 inhibits the function of algal hydrogenase, the enzyme in *Chlamydomonas* that catalyzes the release of H_2 gas. So under normal sunlight and atmospheric conditions, the alga cannot sustain H_2 production for more than a few minutes.

Before photobiological H_2 production can become a viable commercial-scale option, scientists need to find ways to control the O_2 sensitivity of the hydrogenase. Researchers are attacking this problem by generating new forms of the H_2-producing catalysts, hydrogenases that can sustain H_2 production in the presence of O_2 and by developing processes that temporally separate the O_2- and H_2-accumulating reactions in the algae.

One of our previous strategies to address the green algal, O_2-sensitivity issue directly was to engineer a [FeFe]-hydrogenase with higher tolerance to O_2 through a "knowledge-based" molecular approach. The approach relied on first generating and implementing a theoretical basis to understand how O_2 accesses the hydrogenase catalytic site. Due to the lack of an X-ray structure for the algal hydrogenase, this approach focused on the known structure of *Clostridium pasteurianum* [FeFe]-hydrogenase Cp1. Results obtained over the last four years from molecular dynamics simulations and solvent accessibility mapping of CpI suggested there are two pathways by which O_2 can reach the hydrogenase's catalytic site. From these theoretical studies emerged a hypothesis that the kinetics of O_2 diffusion, and therefore enzyme inactivation should be amenable to modification through the molecular engineering of the two gas pathways. Targets for mutagenesis were selected and evaluated computationally for an effect in limiting O_2 access to the catalytic site. An important conclusion from this evaluation phase was that H_2 diffusion in hydrogenase (but not O_2 diffusion) was not significantly altered by any of the pathway mutations. Based on the guidance provided by the theoretical results, we generated clostridial carbonic anhydrase 1 (Ca1) hydrogenase mutants that were tested experimentally for kinetics of O_2 inactivation.

Although NREL has not yet confirmed the gas diffusion hypothesis, current results demonstrate that increased O_2 tolerance can be observed when some hydrogenases (either mutant or wild-type) are isolated in the absence of reductant. These results are novel and suggest, for the first time, that clostridial [FeFe]-hydrogenases can be isolated under (chemically) non-reducing conditions in a variety of redox states, where one state is O_2 insensitive. This had been previously described for [FeFe]-hydrogenases from a species of *Desulfovibrio*, but believed to be restricted only to those [FeFe]-hydrogenases. These results raise the

question of how hydrogenases that are known to display higher O_2 tolerance *in vitro*, such as Cp1 and Ca1, will behave *in vivo* under photosynthetic, anaerobic, or partially aerobic conditions. To answer these questions, we recently refocused our efforts on developing and constructing an expression cassette for the clostridial [FeFe]-hydrogenase Ca1 in C. *reinhardtii* in order to examine its effects on H_2 production in a photosynthetic, aerobic organism. Preliminary studies suggest the Ca1 gene is expressed in this model alga. Further investigation of the expression level, translocation, maturation, and catalytic activity of the clostridial hydrogenase in C. *reinhardtii* are being performed.

In a second approach, researchers are identifying and characterizing the process conditions that allow the algae to accumulate either O_2 or H_2, but not both simultaneously. They designed a metabolic switch to cycle algal cells between a photosynthetic growth phase, which produces O_2, and an H_2 production phase. The switch is based on withholding sulfur, essential for maintaining normal photosynthesis; without it, the algae decrease their photosynthetic activities to low levels (such that any O_2 evolved is immediately consumed by the respiratory activity of the culture) and become anaerobic in the light. As a consequence, they switch to a metabolic pathway that utilizes the reductants generated by H_2O oxidation to produce H_2 gas instead. This pathway, which involves a hydrogenase enzyme, releases large amounts of H_2, even in the presence of limited photosynthetic O_2 evolution.

The process is reversible, and the cycle can be repeated many times. To optimize H_2 production by sulfur-deprived cultures, researchers studied the effect of cell density in the photobioreactors, the level of sulfate deprivation, the light intensity, the pH of the medium, and the presence of organic substrates in the medium. Current research is focusing on improving immobilization techniques to allow for higher areal light conversion efficiencies and protection from atmospheric O_2. The development of an immobilized process has allowed NREL to use sulfur-deprived green algae as a platform to test other barriers identified by the Fuel Cell Technologies Program as impeding the development of commercial systems. NREL has demonstrated that antenna truncation (performed by the University of California–Berkeley) enhances H_2 production at high light intensities, and that the dissipation of the proton gradient by a leaky ATP synthase (generated by Johns Hopkins University) enhances the rates of H_2 production by about 50%. This platform is now being used to further study issues aimed at the development of a more cost-effective process for large-scale utilization.
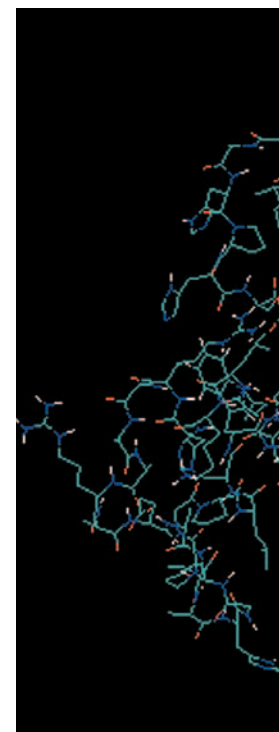
Structural model of the hydrogenase enzyme from the green alga *Chlamydomonas reinhardtii*. The colored lines depict individual atoms that constitute the enzyme: dark blue for nitrogen, red for O_2, white for H_2, yellow for sulfur, and light blue for carbon. The catalytic center for the hydrogenase — the portion of the enzyme that synthesizes H_2 gas — is depicted in ball form, showing atoms of iron (green) and sulfur, along with carbon, nitrogen, and O_2.
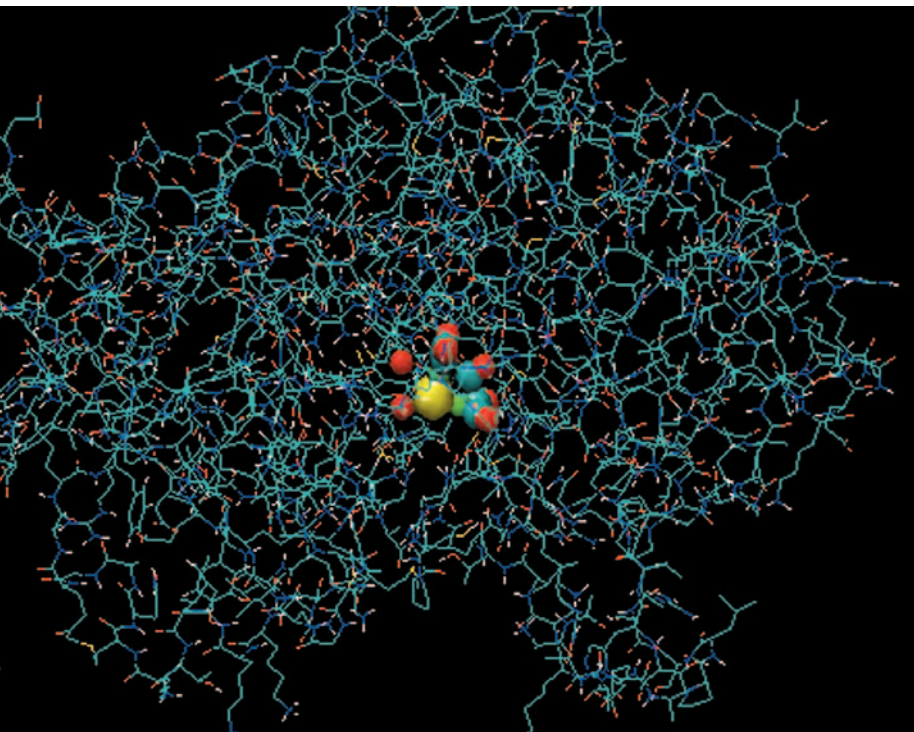
Researchers are making steady progress in understanding and directing the metabolic activity of *Chlamydomonas reinhardtii,* but photobiological H_2 production is still an emerging technology with much to learn. Further investigation and optimization of both approaches will determine the most cost-effective, efficient route to H_2 production.

Fermentation

Many anaerobic bacteria carry out the dark fermentation reaction during which the metabolism of an organic substrate such as sugar results in the production of H_2, CO_2, and other reduced end products. Catalyzed by the hydrogenase enzyme, H_2 production (proton reduction) enables the continuous breakdown of organic substrate to maximize cell growth. H_2 production therefore affords an evolutionary advantage for the fermentative microbes. H_2 production via fermentation has gained considerable interest in recent years because of its high rate of production, the wide variety of feedstock it can utilize, and the simple reactor design and operation (darkness). Nevertheless, the relatively high cost of glucose feedstock and the relatively low yield of H_2 per hexose consumed need to be addressed before its potential can be realized.

One viable strategy to lower the feedstock cost is to tap into the innate ability of certain microbes that can degrade lignocellulose to sugar, followed by its conversion to H_2, all in one organism in a consolidated approach. This strategy does not require the exogenous cellulases in a more costly two-step process. One such organism NREL scientists investigate is *Clostridium thermocellum,*

a thermophilic microbe reported to have very high rate of cellulose hydrolysis. This organism also contains up to four hydrogenase enzymes to accomplish H_2 production, reinforcing the importance of H_2 production during cellulose degradation. Potential sources of the lignocellulosic materials include agricultural residues, dedicated energy crops, and wood residues, which have immense potential for lowering the feedstock cost. The research is focused on optimizing the various parameters controlling fermentation in scale-up bioreactors, operating in a semicontinuous mode for periodic feedings of a solid substrate. The outcome will yield optimal parameters of solid and hydraulic retention time to increase the rate and longevity of the H_2 production reaction.

NREL researchers use two approaches to improve the yield of H_2.

- Develop genetic tools and techniques to modify the metabolic pathway in C. *thermocellum*. The successful outcomes will increase the H_2 yield and reduce the accumulation of other reduced end products (formic, acetic, and lactic acids). The NREL team has achieved initial success in transforming C. *thermocellum,* a critical first step toward genetic engineering to improve the yield of H_2. Nevertheless, significant advances are still necessary to engineer this organism at ease to achieve our goal.

- Work with researchers from Pennsylvania State University to integrate dark fermentation with their novel microbial electrolysis cell process to improve overall H_2 yield. Thus far the integrated system has resulted in very high yield of H_2. Current work focuses on reducing the system cost and complexity to deem the integration a viable process. These multiple approaches can likely circumvent the technical barriers to improve the technoeconomic feasibility of H_2 production via dark fermentation.

Conclusion

The success of renewable H_2 is directly tied to advances in renewable technologies under development at NREL — thermochemical conversion processes, power system integration, electrochemical materials development, metabolic engineering of algae, and more. These advanced technologies are varied and complex, and each comes with its own set of challenges that must be addressed before they are ready for commercialization. It will take the creativity, hard work, and collaboration of scientists, engineers, and analysts from many disciplines throughout the Laboratory to meet these challenges and continue to move toward a sustainable H_2 future.

For More Information

Belokopytov, B.S.; Laurinavichius, K.S.; Laurinavichene, T.V.; Ghirardi, M.L.; Seibert M.; Tsygankov, A.A. 2009. "Towards the Integration of Dark- and Photo-Fermentative Waste Treatment. 2. Optimization of Starch-Dependent Fermentative Hydrogen Production." *International Journal of Hydrogen Energy* 34:3324–3332.

Eckert, C.; Dubini, A.; Yu, J.; King, P.; Ghirardi, M.; Seibert, M.; Maness, P.C. 2010. "Hydrogenase Genes and Enzymes Involved in Solar Hydrogen Production." *In State of the Art and Progress in Production of Biohydrogen*, David Levin and Nuri Azbar (eds). Bentham Science Publishers, in press.

Ghirardi, M.L.; Mohanty, P. 2010. "Oxygenic Hydrogen Photoproduction – Current Status of the Technology." *Current Science* 98:499–507.

Marda, J.; DiBenedetto, J.; McKibben, S.; Evans, R.; Czernik, S.; French, R.; Dean, A. 2009. "Non-Catalytic Partial Oxidation of Bio-Oil To Synthesis Gas for Distributed Hydrogen Production." *International Journal for Hydrogen Energy* 34:8519–8534.

Rennard, D.; French, R.; Czernik, S.; Josephson, T.; Schmidt, L. 2010. "Production of Synthesis Gas by Partial Oxidation and Steam Reforming of Biomass Pyrolysis Oils." *International Journal of Hydrogen Energy* 35:4048-4059.

Shet, S.; Ahn, K.S.; Deutsch, T.; Wang, H.; Ravindra, N.; Yan, Y.; Turner, J.; Al-Jassim, M. 2010. "Synthesis and Characterization of Band Gap-Reduced ZnO:N and ZnO:(Al,N) Films for Photoelectrochemical Water Splitting." http://dx.doi.org/10.1557/jmr.2010.0017 *Journal of Materials Research*

NREL's hydrogen and fuel cell research Web site: www.nrel.gov/hydrogen/