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**THE  
HYDROGEN TECHNOLOGY  
ASSESSMENT**

*Opportunities for Industry and Research*

Phase I

A Report of the

**National Hydrogen Association**

Washington, DC

for the

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## Foreword

This is a report of work conducted by the staff of the National Hydrogen Association (NHA) under the direction of its Technology Review Committee. The work was sponsored by the National Aeronautics and Space Administration to develop information on current and emerging hydrogen-related technologies.

This is a Phase I report of an ongoing effort. The NHA has attempted to present the available information in factual form, and has made a conscientious effort to not overstate the status of current hydrogen development. Expectations about the future are conservatively stated, unless there is no path the authors can see that will allow certain developments to have a viable future.

The impact of external environmental concerns is not generally considered since many of the costs that may eventually impact competitive technologies are not internalized today. Hydrogen is considered in this study simply as an energy carrier that may be able, in some instances, to perform better than the jobs now being done by other energy resources. Environmental considerations will usually make the case for hydrogen technologies stronger. The environmental benefits of hydrogen will be realized as the real environmental cost of other fossil fuels are discovered, documented, and reflected in the costs of these fuels.

Over the course of several years this study will shed light on the core hydrogen question: *What paths exist that will allow hydrogen to be a viable fuel for various energy market sectors?* Hydrogen can be produced fairly inexpensively today by steam reforming natural gas. Unless it can be produced as inexpensively as today's fuels, there will be no commitment to make the huge infrastructure changes required to accommodate hydrogen as an important future form of energy. In the course of looking at paths to follow, a number of cherished visions of the future do not have known economic solutions today. It is quite likely that no single technology will become the panacea for hydrogen production, for storage, or for end-use. Various hydrogen technologies will become established in niche markets and grow until either the resource on which they are based is exhausted or they are out competed for market share by another technology.

Finally, the identification of economically and technically attractive hydrogen production and storage technologies only shifts the discussion to the development of efficient and cost-effective end-use applications (e.g. fuel cells). A solution to this problem then moves the discussion to questions concerning concurrent hydrogen technology commercialization and infrastructure change. Over the course of this study, the technical and economic attractiveness of production, storage, and use of hydrogen will be addressed. This will define the context in which policy discussions about commercialization and infrastructure change can begin.

All financial figures are in 1989 dollars unless otherwise noted. Older information was updated with the "all commodities" producer price indexes.

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Chairman, Mr. Lee Gaumer	Air Products & Chemicals
Dr. John Appleby	Texas A&M University
Mr. Robert Beddome	Union Carbide/Linde Division
Mr. Christopher Blazek	Institute of Gas Technology
Mr. Addison Bain	NASA
Mr. William Hoagland	SERI
Mr. Keith Krause	Liquid Air Corporation
Mr. Ben Mehta	Electric Power Research Institute
Dr. James Schwarz	Syracuse University
Mr. Denys Wickens	Airco Industrial Gases

## Abbreviations and Acronyms

AC	alternating current
ALS	Advanced Launch Systems
APPA	American Public Power Association
atm	atmospheres
Btu	British thermal units
CERI	Clean Energy Research Institute
CESHR	Center for Electrochemical Systems and Hydrogen Research
DC	direct current
DOE	Department of Energy
EPRI	Electric Power Research Institute
FSEC	Florida Solar Energy Center
g	grams
GRI	Gas Research Institute
HHV	Higher Heating Values
HNEI	Hawaii Natural Energy Institute
IC	internal combustion
ICE	internal combustion engine
IGT	Institute of Gas Technology
JPO	Joint Program Office
kg	kilogram
kW	kilowatt



kWh	kilowatt hour
LH <sub>2</sub>	liquid hydrogen
LHV	lower heating value
MBtu	million British thermal units
MW	megawatt
NASA	National Aeronautics and Space Administration
NASP	National Aero-Space Plane
NHA	National Hydrogen Association
PEM	Proton Exchange Membrane
psi	pounds per square inch
PV	photovoltaic
R&D	research and development
scf	standard cubic feet
SERI	Solar Energy Research Institute

## **Report Format**

The report content is structured in the following manner:

### **Hydrogen-Related Technologies**

An overview of the status of various hydrogen production and storage and transport technologies is performed.

### **Hydrogen Application Technologies**

The application of internal combustion, gas turbines, and all fuel cell technologies are examined.

### **Major Hydrogen Research Programs in the United States**

The federally funded hydrogen research programs at six universities laboratories and SERI is discussed.

### **Hydrogen Application Strategies**

An estimate of the energy cost of hydrogen in two end-use applications vs. conventional alternatives is performed.

### **Conclusions and Recommendations for Future Work**

The conclusions are written from the view that once hydrogen is established in market niches, the system using hydrogen will slowly be modified to optimize its use, and new technologies developed specifically for hydrogen will be introduced.

## 1: Introduction

The purpose of this Phase I report is to begin to form the information base of the economics and energy uses of hydrogen-related technologies on which the members of the National Hydrogen Association (NHA) can build a hydrogen vision of the future. The secondary goal of this report is the development of NHA positions on national research, development and demonstration opportunities. The third goal, with the aid of the established hydrogen vision and NHA positions, is to evaluate ongoing federal research goals and activities. The evaluations will be performed in a manner that compares the costs associated with using systems that achieve those goals against the cost of performing those tasks today with fossil fuels. From this ongoing activity should emerge an NHA information base, one or more hydrogen visions of the future, and cost and performance targets for hydrogen applications to compete in the market place.

Building this information base is an educational process of developing a government/industry consensus on the accuracy of the information in the database, the technically and economically viable hydrogen futures, and economic and performance goals that hydrogen technologies should achieve to be an economically competitive in hydrogen based systems.

This information will be used by NHA and its members in formulating technical and policy positions, and initiatives to further hydrogen development. It may be used by NASA and DOE to evaluate the direction and progress of their research efforts and to develop an industrial relationship to promote hydrogen. Because the study is ongoing and the report will be updated annually, the report will be compiled in a loose-leaf binder for ease in adding new pages and updating existing pages as the need arises.

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## 2: Hydrogen-Related Technologies

### Hydrogen Production

The systems suitable for hydrogen production range from the decades-old steam reforming, to technologies that may only be realistic, if ever, well after the turn of the century. The systems covered in this chapter may be grouped into chemical processes that chemically and biologically break down fossil fuels and biomass into simpler molecules including hydrogen; and electrolytic and thermochemical processes that take advantage of renewable resource-produced electricity. High temperature thermal energy, and water splitting processes, such as photosynthesis, photochemical, and photobiological processes, are presented because they serve importantly as a reference for future comparisons and as useful examples for what the future may hold.

Photovoltaic and wind energy conversion devices are not direct hydrogen production systems. They produce electrical energy which, in turn, is used to electrolytically produce hydrogen. Nevertheless, because wind and other renewable resources are important links between solar energy and hydrogen production, and because their costs are important for determining the cost of renewable hydrogen, wind and other renewable resources could be part of a hydrogen production system.

Analysts studying the future potential of hydrogen production by particular methods such as renewable resource energy conversion technologies may find this catalogue useful. The references will also guide the reader to additional information. The continuation of this study in future years will both broaden the scope of the systems covered and update the technology information.



## Hydrogen Production

### Steam Reforming

The steam reforming process converts light carbon fuels (natural gas, for instance) into hydrogen and carbon dioxide.

*Technology*--In a typical steam reformer system, natural gas feedstock is compressed, preheated to 400°C, then passed through a desulfurization vessel. The desulfurized feed is mixed with steam, the steam/natural gas mixture is preheated to about 500°C and fed into the reforming

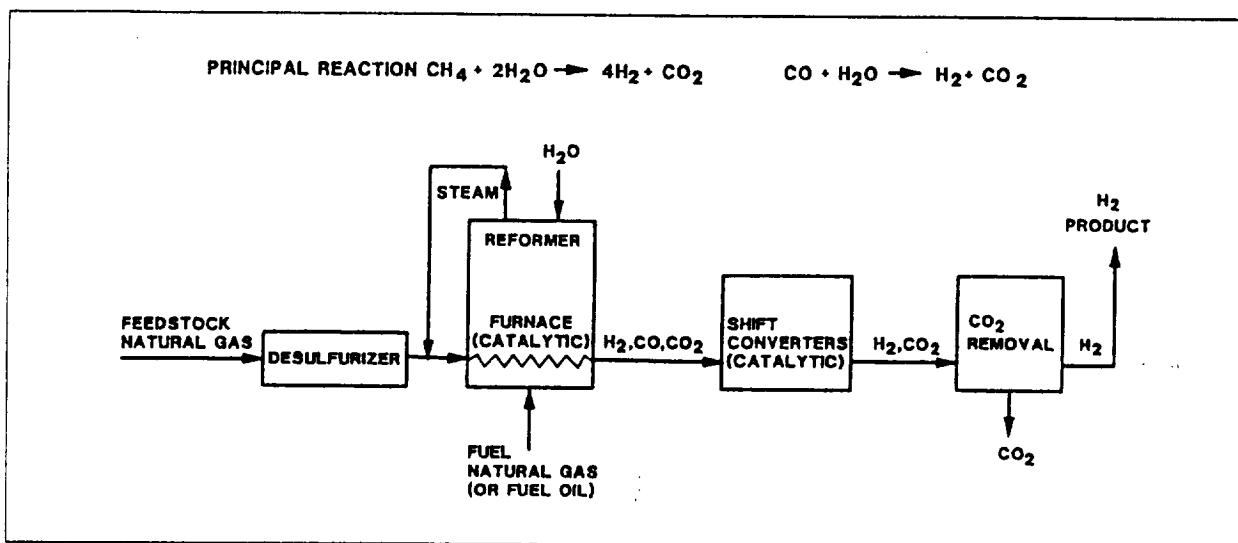


Figure 1: Process diagram for producing hydrogen by steam reforming of natural gas.

furnace in the presence of a catalyst. The reforming and water-gas shift reactions proceed to near equilibrium as the feed mixture passes over the catalyst in externally heated tubes. The reformer product leaving the furnace at about 800°C is cooled to about 350°C and passed through an adiabatic water shift converter which reduces the CO content of the stream and produces additional hydrogen. After cooling, the at-pressure reformer product is processed through a pressure swing adsorption unit (PSA) which rejects all contaminants except helium, releasing 70-90% of the hydrogen contained in its input feed as 99.9999% pure hydrogen gas. Waste from the PSA provides most, and sometimes all, of the fuel required by the reforming furnace.

If 97% pure hydrogen under 200 psig conditions is required, the PSA unit is replaced with a low temperature shift convertor which operates like the high temperature shift convertor, only at 200°C using nickel catalysts rather than chromium and iron catalysts.

*Commercial Availability* -- Steam reforming has been commercially available for decades. The prominent purification technology today is Pressure Swing Adsorption.

Hydrogen Production

Steam Reforming

**Energy Efficiency** -- The energy efficiency of the reforming processes described above are presented in Table 1.

Process	Energy Efficiency (LHV)
Conventional	75%
PSA	65%

**Cost** -- Today's consumer cost of hydrogen steam-reformed from \$2/MBtu natural gas is \$5.60 for hydrogen

Plant Size (Million SCF/day)	Hydrogen Cost (\$/MBtu)
100	5.60
10	9.80
1	15.90

production of 100 million scf/day and higher at

Table 1: Energy value of hydrogen produced divided by energy value (lower heating value) of fuel consumed in process, for conventional and PSA reforming.

lower production volumes as Figure 2 shows. The price of the hydrogen produced is also dependent upon the cost and availability of the natural gas or other fuel feedstock.

Table 2: Consumer cost of hydrogen as a function of plant size.

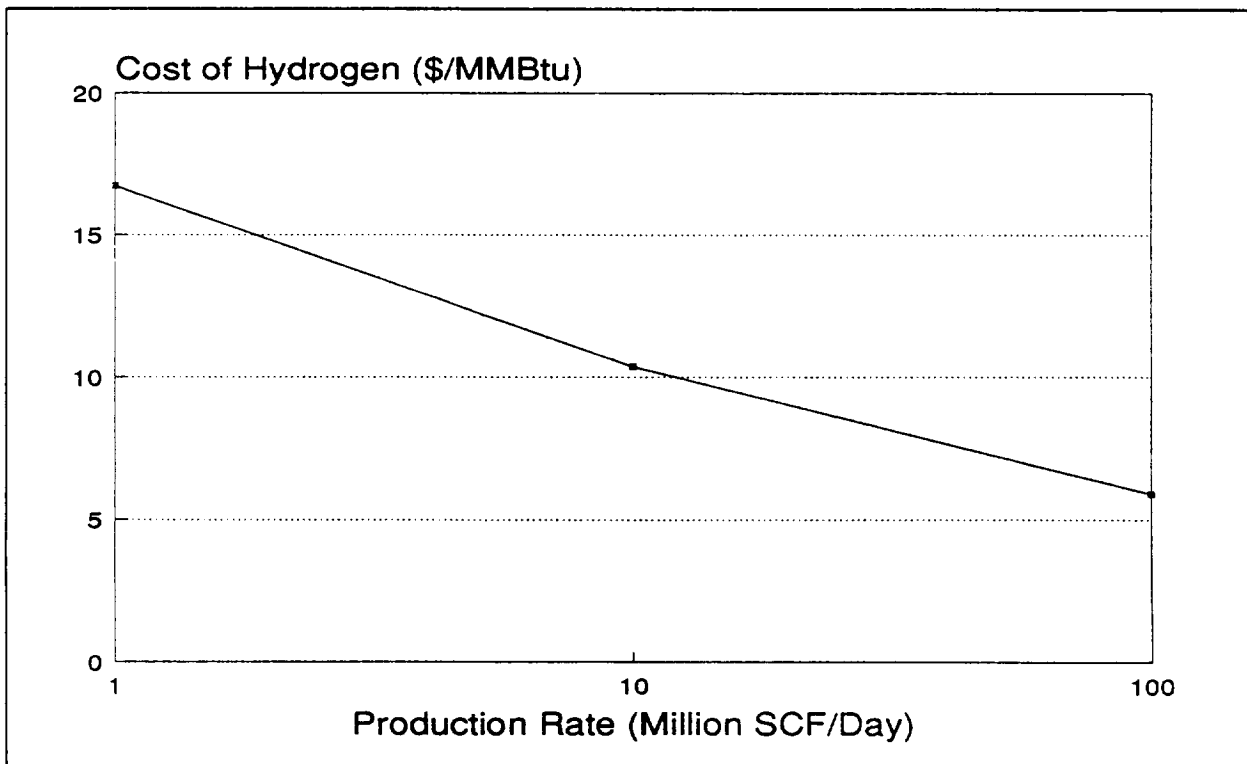


Figure 2: Cost of steam reformed hydrogen as a function of the size of the plant (natural gas at \$2/MBtu).



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1. Appleby, A.J. and Foulkes, F.R., Fuel Cell Handbook, Van Norstrand Reinhold, New York, 1989.
2. Beddome, R.A., *Liquid Hydrogen Manufacturing and Distribution Technology*, paper in Technology Transition Corporation's report to EPRI (GS-7248), National Hydrogen Association's 1st Annual U.S. Hydrogen Meeting, Washington, DC, March, 1990.
3. Moore, R.B., and Nahmias, D, *Gaseous Hydrogen Markets and Technologies* paper, Ibid.

Hydrogen Production

## Hydrogen Production

### Partial Oxidation

Partial oxidation is a process for converting hydrocarbons heavier than naphtha to hydrogen. Therefore, it is useful for heavier petroleum products for which steam reforming is not applicable.

**Technology** -- The process involves incomplete combustion of a hydrocarbon fuel in the presence of oxygen or air. In this process the steam reformer is replaced with a reactor vessel which could be supplied with air or oxygen from an air separation plant. The partial oxidation reactor product contains a very hot mixture of hydrogen, CO, CO<sub>2</sub>, steam, and a small amount of methane gas with entrained molten ash or slag. The product stream is typically quenched with water as it exits the reactor to solidify the slag for downstream removal with cyclones, gas filtration or in a slurry. The H<sub>2</sub>S is selectively removed with an acid gas system, and after passing through a water shift reactor the gas is purified in a PSA similar to a steam reformed product.

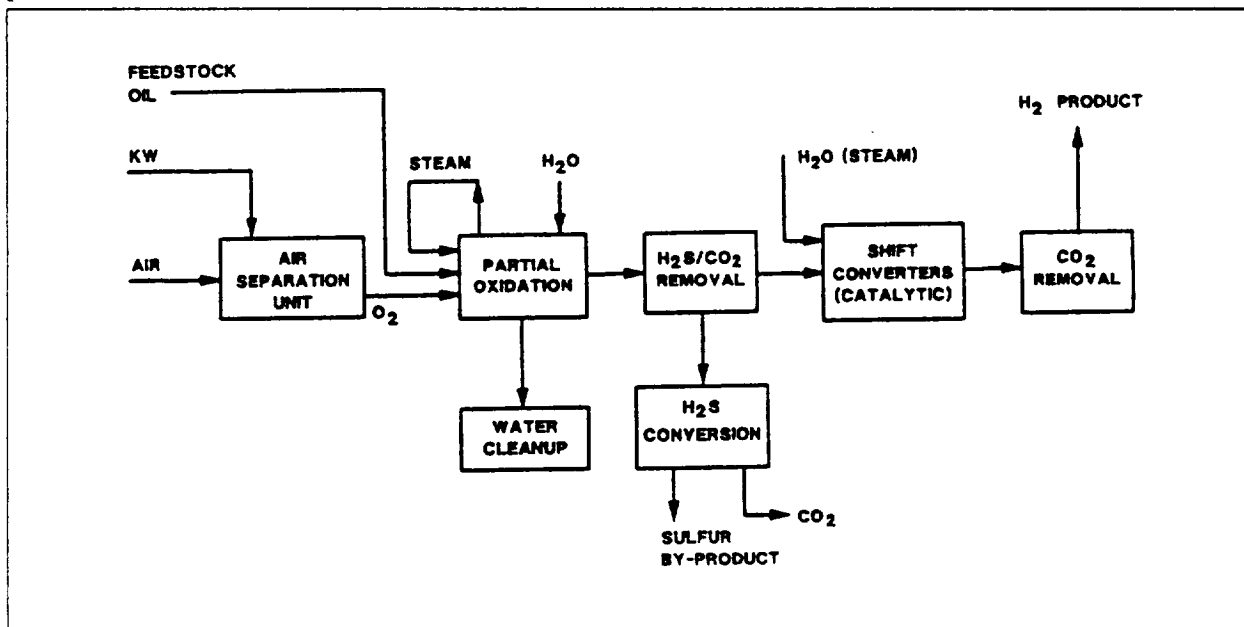


Figure 3: Process diagram of hydrogen production by partial oxidation of sulfur heavy oil.

If oxygen is used in the process, the capital cost of the facility is typically 50% higher than the cost of a steam reformer facility. If air is used, at between 875-975°C, in the partial oxidation step, the Btu content of the resulting fuel is low because of the high nitrogen content from the air.

**Commercial Availability** -- This technology is commercially available today.

**Energy Efficiency** -- The efficiency of partial oxidation is generally lower than for steam reforming -- often about 50% although the theoretical efficiency is about 78% for residual oil.

**Cost** -- Partial oxidation is used in cases where a cheaper and/or more reliable form of feedstock is available. In large quantities of 200 MM scf/day, hydrogen can be produced for under \$10/MMBtu with \$4/MMBtu bunker C oil (See figure 4).

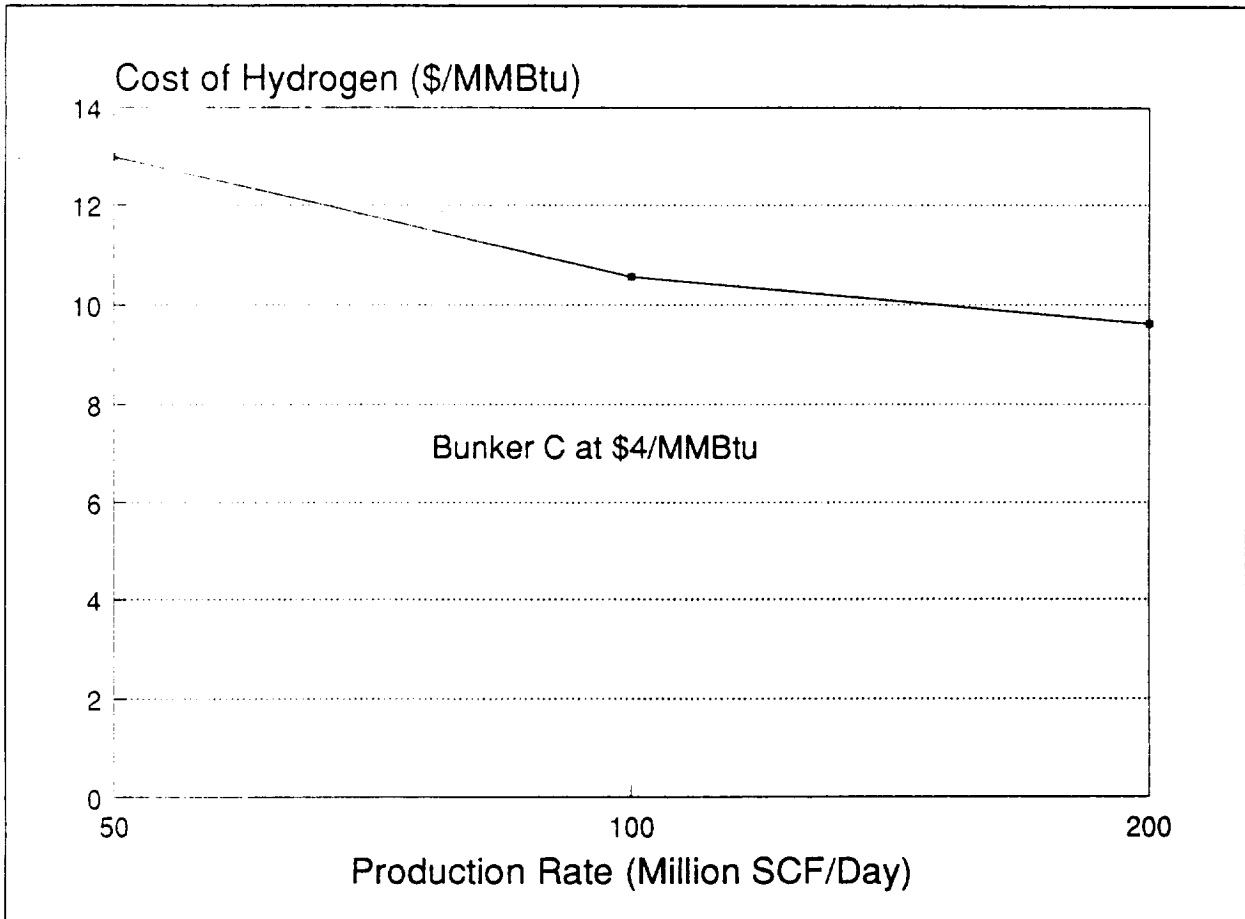


Figure 4: Cost of hydrogen produced from the partial oxidation of oil as a function of the size of the plant (Bunker C at \$4/MMBtu).

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3. Beddome, R.A., *Liquid Hydrogen Manufacturing and Distribution Technology* paper in Technology Transition Corporation's report to EPRI (GS-7248), National Hydrogen Association's 1st Annual U.S. Hydrogen Meeting, 1990.
4. Moore, R.B., and Nahmias, D, *Gaseous Hydrogen Markets and Technologies* paper, Ibid.
5. Private communication with R. B. Moore on cost of hydrogen production as a function of facility size for partial oxidation processes (Texaco, Shell). Information was developed using non-proprietary data from Air Products energy economics database.

Hydrogen Production

## Hydrogen Production

### Coal Gasification

Coal Gasification is a process similar to partial oxidation except for the additional cost and complexity of handling a solid fuel.

**Technology** -- Coal particles are introduced into a gasifier where they are partially oxidized by oxygen from an air separation plant in the presence of  $H_2O$ . The water waste stream from the gasifier is cleaned by removing the chemicals from the stream. Chemical feedstocks may be derived from the resulting coal tars by reacting them with oxygen, steam, and water.

The gas stream out of the gasifier (principally carbon monoxide and hydrogen) is quenched in a water bath and scrubbed. The cleaned gas enters a catalytic shift converter similar to that used in partial oxidation, followed by a PSA unit if high purity or high pressure hydrogen is desired.

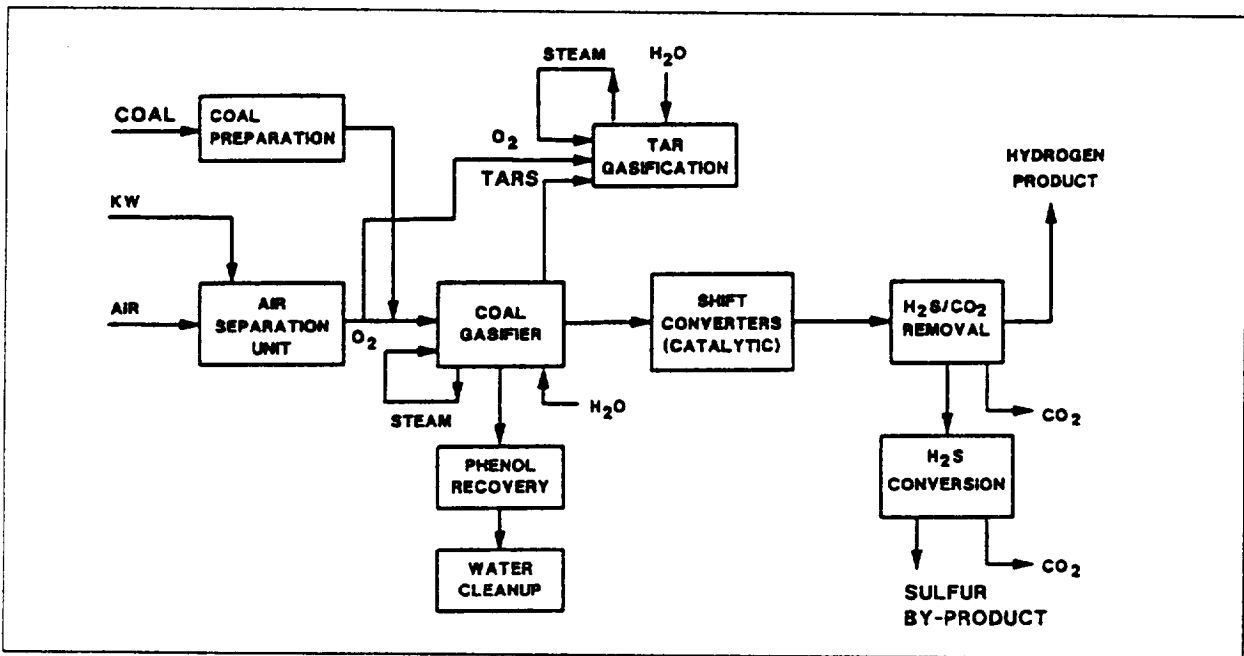


Figure 5: Process diagram for production of hydrogen by coal gasification.

Then, hydrogen sulfide and carbon dioxide are removed as in the partial oxidation case. The hydrogen sulfide and carbonyl sulfide is converted to elemental sulfur, hydrogen, and carbon dioxide.

**Commercial Availability** -- There are a number of gasification processes using fixed bed (Lurgi), entrained flow systems (Texaco, Shell), high temperature fluidized-bed technologies, or

molten salt reactors. The temperatures, pressures, and concentrations of the gases is a function of the gasification technology used.

**Energy Efficiency** -- The theoretical efficiency for gasification processes is 55%.

**Cost** -- Generally, the lower cost (per Btu) of coal does not compensate for the higher capital cost of coal gasification systems, compared to steam reforming. Processing costs on the order of \$11 to \$13/MMBtu are typical (See figure 6).

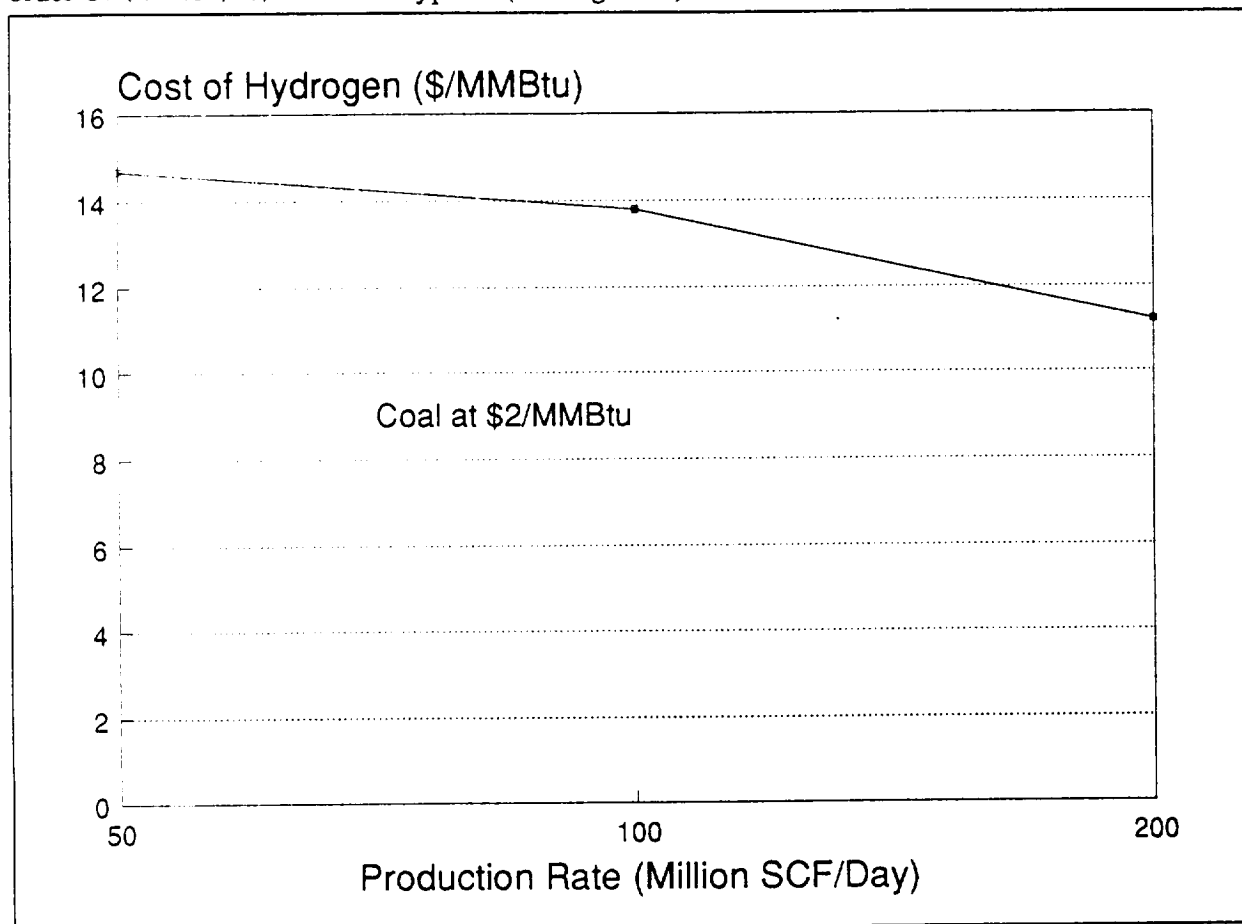


Figure 6: Cost of hydrogen produced from the gasification of coal as a function of the size of the plant (Illinois No. 6 with industry economics).

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4. Beddome, R.A., *Liquid Hydrogen Manufacturing and Distribution Technology* paper in Technology Transition Corporation's report to EPRI (GS-7248), National Hydrogen Association's 1st Annual U.S. Hydrogen Meeting, Washington, DC, March, 1990.
5. Moore, R.B., and Nahmias, D, *Gaseous Hydrogen Markets and Technologies* paper, Ibid.
6. Private communication with R. B. Moore on cost of hydrogen production as a function of facility size for coal gasification processes (Texaco). Information was developed using non- proprietary data from Air Products energy economics database.

Hydrogen Production

## Hydrogen Production

### Electrolysis

The electrolytic process uses electrical energy to split water ( $H_2O$ ) into its basic elements - hydrogen and oxygen. Electrolysis can be used with electric energy produced from renewables such as solar photovoltaic cells, wind or hydropower to produce hydrogen (see wind and photovoltaic sections later in this chapter.).

**Technology** -- In the basic electrolytic processes, the reactants are ions in an electrolyte. When electrodes are immersed in the aqueous solution (electrolyte) and a DC voltage is applied, the ions in the electrolyte migrate to one or the other electrodes. The positive ions (cations) move toward the negatively charged electrode, and the negatively charged ions (anions) move toward the positively charged electrode. At the electrodes, the ions are neutralized, and either form a gas that is liberated or form a deposit on the electrode plate.

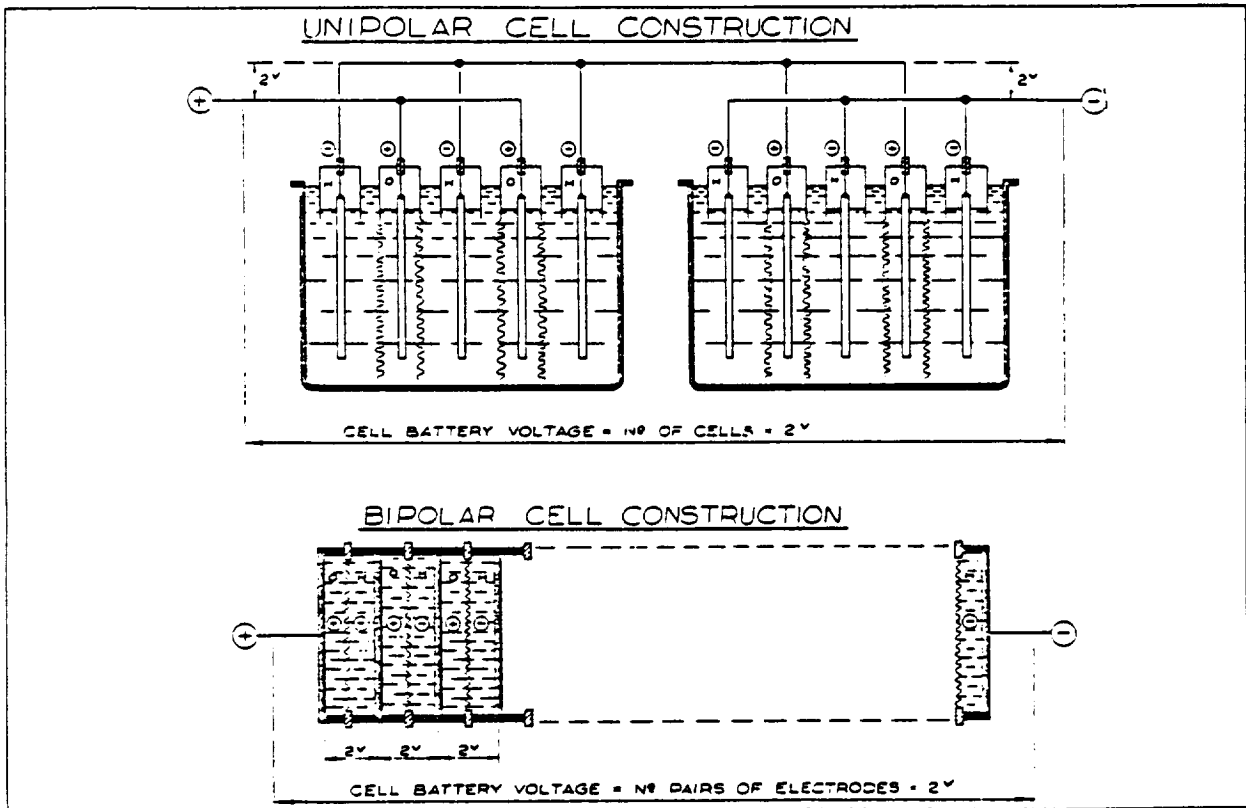


Figure 7: Diagram of unipolar and bipolar electrolytic cells.

Membranes can be added to the electrolytic solution. By charging these membranes and adding an electric potential, the process of diffusion of ions through the electrolyte can be enhanced.

In Solid Polymer water electrolysis, an ion exchange membrane is used as the electrolyte and diaphragm to prevent gas recombination. The ionic current is developed by protons migrating through the membrane. This process does not require additional electrolytes to increase conductivity.

A typical hydrogen facility has demineralized water and electricity fed into the electrolytic unit which produces hydrogen and oxygen. The hydrogen and oxygen can be compressed in stages to high pressure and stored. The hydrogen and oxygen produced could also be sent to a liquefaction unit and stored cryogenically. The cost of the liquefaction facility could equal that of the electrolysis plant.

Steam electrolysis is a process based on the fact that not all of the energy required for electrolysis needs to be electricity, only the Gibbs free energy. The remainder of the required energy can be supplied as heat. Between 0°C and 200°C, the total energy required for decomposition of water rises less than 2%, but the electric energy required to liberate one standard cubic foot of hydrogen decreases from .08 kWh to .067 kWh. Thus, where heat is available or with solar energy, the electrical efficiency of the electrolytic cell increases significantly. Corrosion of components including membranes has prevented the further development of this technology.

**Commercial Availability** -- Electrolysis units are available in large and small sizes. This technology is commonly used for producing small quantities of hydrogen for industrial or research applications.

Membrane electrolytic cells are under development for their higher efficiency characteristics. The same basic technology can be used in fuel cells in a reversible process flow.

Steam electrolysis is being promoted by at least one developer but is not commercially available.

**Energy Efficiency** -- The electrochemical efficiency of electrolytic cells varies from 66% to 82%. The electrical efficiency of the ac to dc conversion is 95%.

Alkaline unipolar or bipolar electrolytic cell efficiency for the membrane cell is about 75%. The efficiency of solid polymer systems is about 85%.

**Cost** -- The cost of electrolysis plants varies with size from \$3/10<sup>3</sup>/scf/day for a 1 MW facility, to \$1/10<sup>3</sup> scf/day for a 10MW facility. Maintenance and labor costs vary greatly due to the percentage of plant costs as a function of size. Although estimates are difficult, figure 8 shows the cost of various sizes of electrolysis plants using utility economics and not including hydrogen storage, compression, or the cost of electricity.

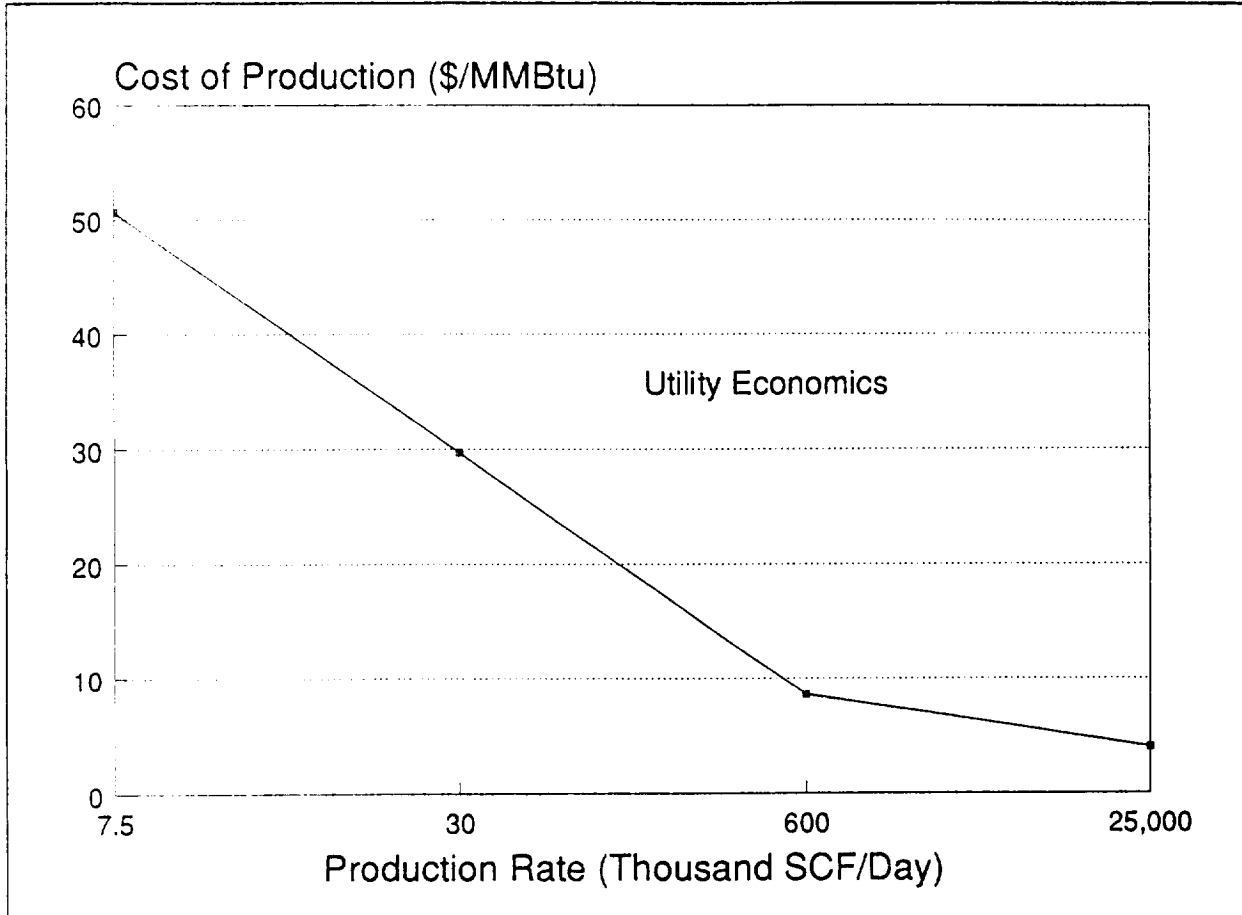


Figure 8: Cost of electrolytically produced hydrogen as a function of size of the electrolysis plant (Excludes cost of electricity).

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## Hydrogen Production

### Photovoltaic

Photovoltaic cells convert sunlight directly into electricity by the interaction of photons and electrons within a semiconductor material. To produce hydrogen, the electrical energy must be converted to hydrogen through electrolysis.

**Technology** -- A material such as silicon is doped with the same number of atoms of an element with one more or one less electron than silicon. In this way a p-type and n-type silicon are formed. A thin layer of each material is joined to form a junction. The n-type material is placed above the p-type semiconductor, and a circuit connects the n-silicon and the p-silicon. Photons strike the electrons in the n-type material, providing the bound electrons with enough energy to go into the conduction band. The internal voltage provided by the junction causes the current to follow in the circuit. In the electron deficient p-type material, electrons are combined with holes. Various currents and voltages can be supplied through series and parallel arrays. The electricity produced by these cells is dc.

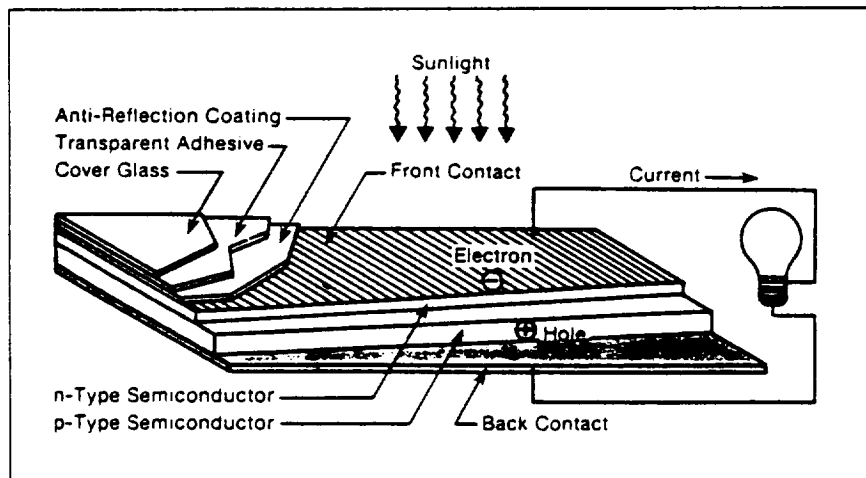


Figure 9: Typical cell made of crystalline silicon.

A solar photovoltaic system consists of the collector module, the balance of the system (structural support of solar modules; in the case of the concentrator systems, the tracking system; wiring; etc.), and the dc to ac inverter system.

**Energy Efficiency** -- The efficiency of solar cells varies greatly. Efficiency depends on the nature of the materials used, whether it is part of a concentrator system, and whether the cell is a multi-junction system. Cell efficiencies can range from 6% for some inexpensive single cell materials to over 34% for two-junction high concentration solar cells.

Photovoltaic cell development seems to be following two different courses. One is the production of flat plate, 10% to 15% efficient, inexpensive, single junction cells -- thin films like amorphous silicon and copper indium diselenide. The other is the development of relatively expensive, very efficient, multi-junction concentrator crystalline silicon cells.

**Costs** -- Current costs of flat plate modules are \$600/m<sup>2</sup> or \$5 to \$6/W<sub>peak</sub> with an efficiency of 12%. Targets for the technology are on the order of \$1/W<sub>peak</sub> with a 15% module efficiency by the end of the decade.

The cost of the entire system today is over \$6,000/kW in the Southwestern U.S. These costs should drop by 50% over the next 5 years based on increased production capacity coming on line, improvement in cell efficiencies, and reductions in balance of plant costs. (For additional information, see application strategies, Section 5, page 5-6).

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## Hydrogen Production

### Wind

Wind is an indirect source of solar energy caused by differences in atmospheric temperature.

**Technology** -- In 1986 SERI published a wind atlas of the United States which classified the country's wind potential using a grid that is 1/4 degree in latitude by 1/3 of a degree in longitude. The wind atlas classified each square of the grid into one of seven categories for equivalent wind speed and wind power at sea level on an average annual basis. Sites from level three (wind speed > 6.4 meters/sec) and above could be considered satisfactory wind sites; and those of level 5 (wind speed > 7.5 meters/sec) and above could be considered prime wind sites.

The most common type of wind machine is a horizontal axis machine in which the axis of rotation of the turbine blade is parallel to the direction of the wind stream. Vertical axis wind machines, such as the Darrieus wind turbine and the Savonius design, are in use, but are much less common than the horizontal axis machines. Horizontal wind machines can be lift-type or drag type machines. Lift-type machines use air foil type blades to achieve the fast rotating speeds required for operating electric generators. Drag-type machines convert wind pressure to rotational energy via friction between the blade and the air. These wind machines provide high torque for mechanical shaft power (water pumping). The typical wind turbine has a cut-in and cut-out for minimum and maximum wind speeds. During operation, the speed of the turbine is generally constant through feedback from the generator or through changes in the gear ratios for various speeds. Orientation of the blades into the wind is accomplished in smaller machines by a tail vane and in larger machines by a motor drive.

A wind turbine system consists of a wind turbine that generates shaft horsepower, an ac or dc generator that converts shaft horsepower to electricity, and a control system that orients the turbine, controls blade speed, and cuts the energy conversion system in and out depending on wind speed. If the power generated is ac, it flows to a switch yard in a wind energy farm. The switch yard contains the utility interface equipment. If the power generated is dc, it has to be inverted to ac power before being transmitted to the switch yard.

**Commercial Availability** -- There are over 1,500 MW of operating wind power in the United States today. Most of it is in California and Hawaii.

The average power output from wind turbines is 1.03 MW/km<sup>2</sup> for a level 3 site, and 1.62 MW/km<sup>2</sup> for a level 5 site. Many of these sites are likely to be environmentally protected, or in urban areas, and are therefore not suitable for economic development. If these sites are excluded, along with 50% of the forest land, 30% of the farm land, and 10% of the range land, then the remaining class 5 and above sites could provide 27% of the nation's electricity and 10% of its energy. If class three and four sites could be tapped economically, then 350% of current U.S. electric production and 125% of total U.S. energy could be supplied by wind.

A 300 KW variable speed wind turbine system as shown in figure 11 will be operational in April, 1991

**Energy Efficiency** -- Electric energy efficiency is 25% to 35% of the wind energy in the arc of the blade.

**Cost** -- The best wind generation units in California operating at prime sites have an availability of over 90% and an annual capacity factor of 35%.

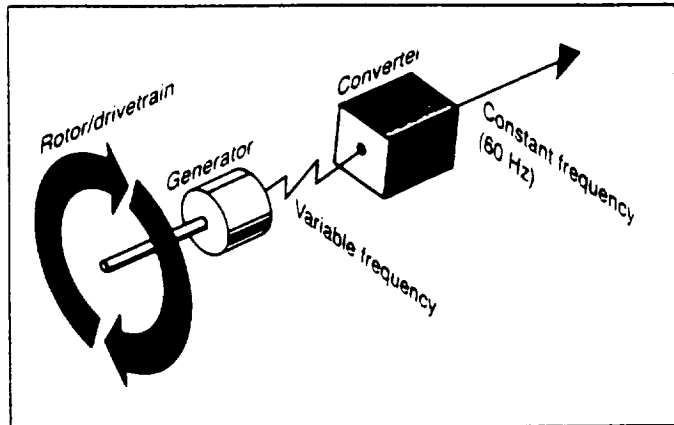


Figure 10: Variable-speed wind generator concept.

The installed cost of these systems is between \$1,000 and \$1,100/kW for wind turbine systems in the 50 kW to 150 kW size range. They are assumed to have a 20-year life with major maintenance every 5 years. Maintenance costs for these units is approximately 1.4¢/kWh. These units generate power for under 7¢/kWh.

Research is underway to decrease the cost of energy from these units to under 5¢/kWh by 1995 increasing the size of the unit to 300 kW and making the turbine variable speed. Speed variance increases the efficiency of the wind turbine blades by allowing the turbine to take advantage of higher wind speeds before cutting out. The converter maintains a constant frequency output, despite the generator's variable output frequency.

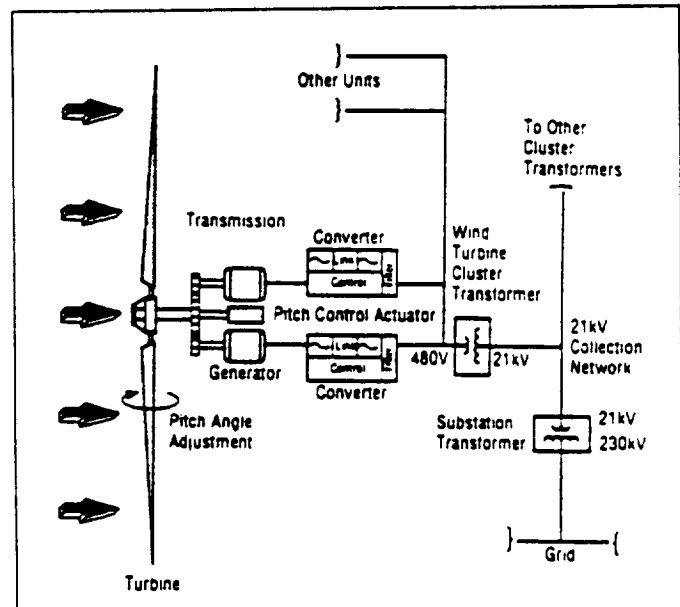


Figure 11: Block diagram of variable speed wind turbine with balance-of-plant facility.

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Hydrogen Production

## Hydrogen Production

### Thermochemical

Thermochemical production of hydrogen involves the thermal splitting of water at high temperature through a series of chemical reactions, which ultimately release hydrogen.

**Technology** -- No simple two-step chemical process for water splitting has been identified. A number of four-step processes have been proposed, some with claimed efficiencies as high as 85%. The Institute of Gas Technology performed an evaluation of 125 thermochemical cycles, and found few, if any, attractive.

**Commercial-Availability** -- Most of the work on these technologies has been to look at the efficiencies of these cycles and demonstrate their performance on a laboratory scale. As has been pointed out by researchers, there are formidable problems facing scale-up of any thermochemical water splitting scheme. These problems include:

- Lack of availability of high temperature nuclear sources;
- Technical problems associated with obtaining and maintaining high yields in highly integrated unit operations;
- The movement of a large mass of materials required in the chemical reactions to produce relatively small amounts of hydrogen;
- Corrosion of materials in these processes; and
- Loss of materials in these processes.

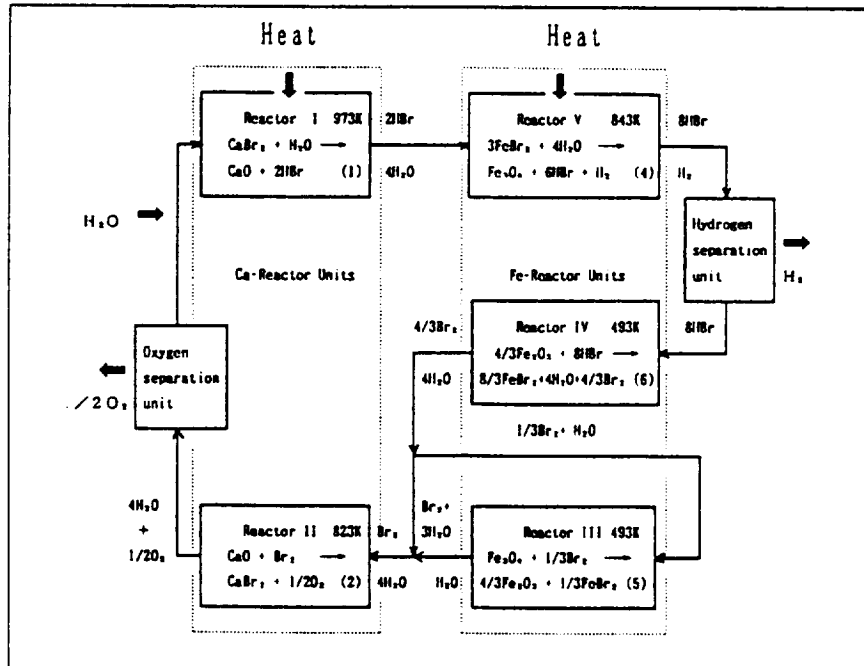


Figure 12: Thermochemical process

These factors make the development of thermochemical water splitting unlikely to be a major player in hydrogen production in the near future.

*Energy Efficiency* -- Researchers have claimed efficiencies as high as 85%.

*Cost* -- No information is available.

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## Hydrogen Production

### Biological

The biological production of hydrogen involves processes such as fermentation and photosynthesis.

**Technology** -- Biological hydrogen production processes may be divided into photosynthetic processes and fermentation processes.

The fermentation processes involve hydrogen-producing bacteria which use enzymes to break down sugars and starches forming a hydrogen-rich gas using waste material as a substrate. The bacteriological dark-phase production of hydrogen can only involve reactions with negative free energy. These bacteria cannot break down organic acids because they cannot overcome the positive energy necessary to drive the action.

Some common types of bacteria have been used in studies including *E. coli* and *Citrobacter* which produced hydrogen as long as the pH of the substrate was above 5. The anaerobic fermentation of the bacteria *Citrobacter freundii*

has been used to produce hydrogen and carbon dioxide (60:40) from stillage (cane-molasses) for a period of one week. Other studies at SERI using photoactive bacteria produced hydrogen in sunlight at an efficiency of 2% while consuming virtually all the organics in the substrate. Phototropic bacteria like *R. rubrum* and *R. capsulatus* in whey have shown themselves to be effective hydrogen producers in the presence of air.

Another biological process, photosynthetic hydrogen production, involves a two-photon process that provides the energy necessary for the enzymes in the cell to split water. Algae and Cyanobacteria can produce hydrogen under certain circumstances with low efficiency (under 1%).

**Commercial Availability** -- This technology is in the developmental phase.

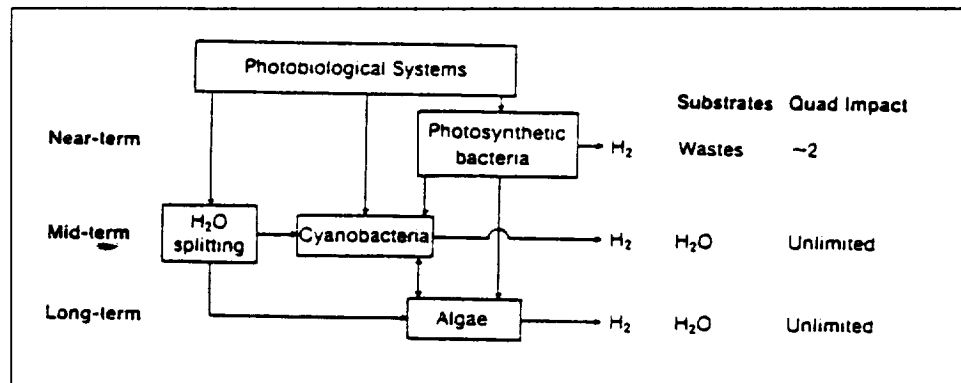


Figure 13: Photobiological hydrogen production options.

Fermentation processes could have application today as a means of producing hydrogen from organic waste products. There is still much fundamental work to be done to understand the basic cell reactions for these organisms.

Photosynthetic hydrogen production is also still in the research phase and although there is long term potential for this technology, oxygen tolerance and increased efficiency must be developed. It is becoming clear that the presence of CO<sub>2</sub> initiates the Calvin Cycle in which carbon out-competes hydrogen as a reductant, effectively ending the photoevolution of hydrogen.

The photoactive material in the photobiological production of hydrogen might have long term applications in photosynthetic technology. In the near term, these and other plants may have value as gasified biomass for hydrogen production. If the delivered cost of the biomass is similar to the delivered cost of coal, then biomass may provide a partial answer to finding a source of renewable hydrogen to replace steam reforming.

*Energy Efficiency* -- Process efficiencies of 1 to 2% have been demonstrated in the laboratory.

*Cost* -- No information is available.

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Hydrogen Production

## Hydrogen Production

### Photolysis

Photolysis production of hydrogen involves the direct splitting of water by solar energy.

**Technology** -- The direct splitting of water to produce hydrogen and oxygen may be a low cost means of producing hydrogen. The energy required to split the hydrogen and oxygen bond in water is 1.229 eV. Thus, a single photon would require at least 2.458 eV to cause an oxidation reduction to occur to split the water molecule. A two-photon process would require at least 1.229 eV to accomplish the same purpose, and a four photon processes would require only .615 eV. The ideal limit for the efficiency of a one photon system is 5.3%, and for a two photon system, 30.7%. The difference is principally the portion of the solar spectrum these systems can use. The ideal limit is not achievable. Losses (due to the unavailability of certain photoactive atoms to absorb the photon's energy) that range from .3 to .4 eV per photon must be included when considering the photon energy necessary to drive the water splitting reaction at any meaningful rate. For a two photon system, this means losses of about .8 eV or 17% with a threshold wave length of 610 nm.

The photocatalyst for these systems can be electrochemical, chemical, or biological. The most advanced of these systems are the photoelectrochemical system where hydrogen is reduced on one surface of a semiconductor plate, and oxygen oxidized at the other surface of the semiconductor plate in the presence of a catalyst. If biological materials were used, they would be placed on a substrate so that they could be easily removed and replaced when their hydrogen production rate falls.

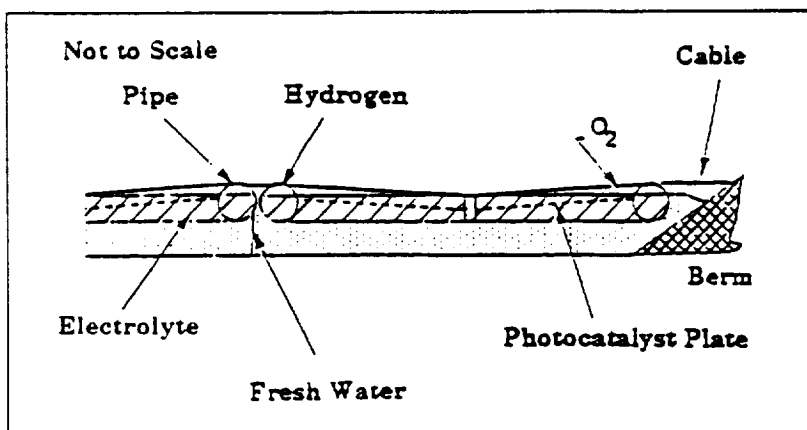


Figure 14: Side view of a flat plate solar collector for a photolysis system.

Since hydrogen production in biological materials is a two-photon process, hydrogen and oxygen are produced at different sites and must remain separate. Photochemical hydrogen production attempts have used photosensitive molecules like organic dyes in systems that mimic semiconductors. These may be multiphoton systems. Recombination may be a serious problem for these systems.

The balance of the system would include modules in which photoactive material would be placed. The modules would contain electrolyte, water, pipes for hydrogen and oxygen, and the photocatalyst plate. The modules would be covered by a glazing, and placed on a pond. The

modules themselves would be made of polyvinylchloride and polybutylene. The glazing would likely be cast fiberglass reinforced polyester. The modules would be taped together and held under tension by cables.

**Commercial Availability** -- This is an applied research activity in which no satisfactory photocatalyst system has been identified at this time.

**Energy Efficiency** -- Assuming a 13% efficient catalyst, the overall efficiency of producing hydrogen is 9.4%. The losses are due to reflective losses off the glazing and water, and the accumulation of dirt.

**Cost** -- No clear path to achieving technical performance and life targets required for feasibility has been established. If some day those targets are achieved, then conceptual designs have been done on the balance of the plant which indicate that this may become an attractive option for hydrogen production. It is estimated that a system of this type manufactured and installed for a 10 MM scf/day plant would produce hydrogen at 100 psig for \$9.83/MBtu. This assumes catalyst and module life of 15 years. Corrosion is a major concern in developing photosensitive systems. This approach may offer the possibility of delivering hydrogen at less than \$12.50/MBtu.

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## Hydrogen Production

### Pyrolysis of Biomass

Biomass may offer one of the least expensive near-term renewable paths to hydrogen production.

**Technology** -- In 1987, just under 3 quads of U.S. energy was developed from biomass, representing 3.7% of U.S. primary energy production. The largest contributor was wood and wood wastes constituting almost 2.75 quads of energy, two thirds of which was from the forest products industry (pulp and paper). It is estimated that in the year 2000, 14.6 quads of primary energy could be recovered from biomass. 70% of this energy would be available from wood and wood wastes, with solid waste contributing another 2 quads.

The theoretical maximum energy potential from biomass is estimated at 54.9 quads. Less than half of biomass is wood and wood wastes, almost 30% is agricultural residues, 15% of which is aquatic biomass. If conversion to biomass is assumed to be 50% efficient, then biomass could play a substantial role in the production of hydrogen by having the realistic potential of providing 7.3 quads of hydrogen in 2000.

Hydrogen production from biomass would involve collecting, transporting, and preparing the biomass for pyrolysis/gasification. The process involves preparing a biomass/water slurry which is heated to high temperature (on the order of 1000°F) under pressure in a reactor. This decomposes and partially oxidizes the biomass producing a gas stream rich in

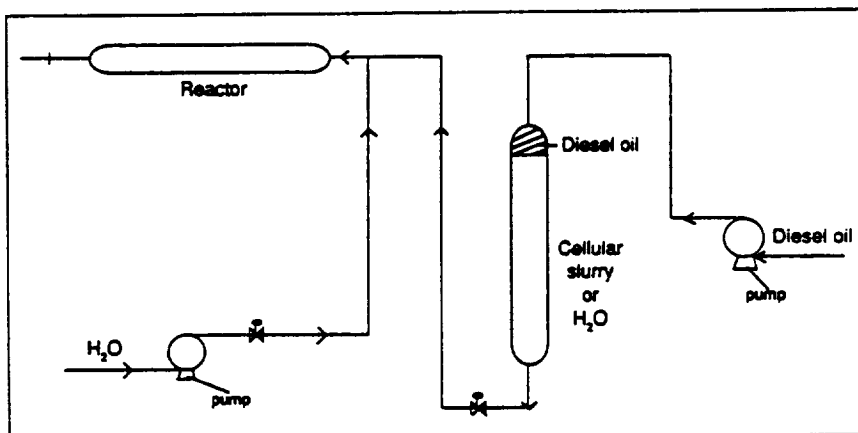


Figure 15: Test set-up for pyrolysis of biomass in supercritical water slurry.

CO<sub>2</sub>, CO, nitrogen, methane and hydrogen. Ash would be removed as a slag from the bottom of the reaction vessel. The gas stream would then go to a high temperature shift reactor and a pressure swing adsorption unit to produce high purity hydrogen. Except for pretreatment of the biomass, and the design of the reaction vessel, the system is similar to a coal gasification plant. The front end of the processing facility would have to be larger than that of a comparably sized coal gasification facility because of the lower heat content per pound of biomass as compared to coal. This might result in a higher capital cost for the biomass facility than a comparable coal facility, depending on the extent of the coal beneficiation and gas clean up.

**Commercial Availability** -- This project is in the research phase.

**Energy Efficiency** -- Ongoing research at the University of Hawaii under DOE contract on the gasification of aquatic biomass in supercritical water, has yielded hydrogen-to-CO<sub>2</sub> ratios of 2.2:1. (*Gracilaria sp.*) was gasified at 550 °C at 34.5 MPa with a residence time of 28 seconds in the reactor vessel. The overall reaction for the process was  $C_6H_{10}O_5 + 7H_2O \rightarrow 6CO_2 + 12H_2$ . Hydrogen and carbon dioxide were available at 5,000 psi.

Studies are continuing on hydrogen production from sewage sludge and kelp.

**Cost** -- The cost of this technology is hard to quantify, but using the cost of coal gasification as a guide, hydrogen from biomass might have a capital and operating cost twice that of a steam reforming plant per MBtu of hydrogen produced (\$10 to \$15/MBtu for \$2/MBtu biomass delivered). This excludes the cost of growing, harvesting, and transporting the biomass. To achieve a \$2/MBtu price for biomass, it is estimated that crop yields would have to increase from 5 tons/acre/year, to 10 tons/acre/year, and transportation must be less than 50 miles. Currently, feedstock costs run \$2.50/MBtu for the most favorable region in the U.S.

If hydrogen is used for transportation, then biomass appears to offer the best near term option for an affordable renewable energy source.

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## Hydrogen Storage and Transport

The storage of hydrogen is well-understood for today's applications of hydrogen in aerospace and industrial manufacturing. This section discusses these technologies in order to provide a useful reference point.

Hydrogen storage is an important consideration for new applications. The National Aero-Space Plane (NASP), a sub-orbital supersonic aircraft requires liquid or slush hydrogen - the only fuels with a high enough energy density for these unique aircraft. Terrestrial vehicles require systems that provide adequate volumetric storage to offer comparable range as compared with today's gasoline tanks. Utility applications may require caverns or other systems for bulk hydrogen storage.

To a large extent, storage technologies hold the key to new applications of hydrogen as a fuel.

Hydrogen Storage and Transport



## Hydrogen Storage and Transport

### Hydrogen Compression, Storage and Transport

The compression of hydrogen for storage and transport is the oldest method of handling hydrogen, whether for bulk application or merchant markets. This summary discusses compression and compressed gas technology in terms relevant to a widespread distribution and application of hydrogen.

*Technology* -- There are over 750 km of hydrogen pipelines in operation world-wide. Extrapolating current hydrogen pipeline practice to a bulk fuel, the processes of compressing, storing, and transporting hydrogen would parallel that of natural gas.

Hydrogen would typically be compressed with a reciprocating piston compressor with volumetric efficiency comparable to that of compressing natural gas. The size of the compressor is inversely proportional to the energy content of the gas being compressed. Thus, to deliver the same quantity of energy for hydrogen rather than natural gas at 750 psi, it would require approximately 4 times the compressor capacity and 6 times the horsepower. Natural gas rotary compressors are not effective in compressing hydrogen because the low molecular weight of the gas requires multiple compression stages for a modest increase in pressure. However, large, high-speed centrifugal compressors are likely to be developed for hydrogen pipeline applications because of their lower capital and maintenance costs.

Once the gas is compressed, it can be shipped in natural gas pipelines to bulk storage facilities. Up to about 700 psi, conventional carbon steel pipelines used for natural gas can be used for hydrogen; above 700 psi, embrittlement in the welds becomes an increasing concern. Above 700 psi, seamless, stainless steel pipe, specially welded, and fusion bonded epoxy coated have been used for hydrogen transport.

For natural gas, compressor stations are used whenever the pressure of the gas leaving one station is 1.5 times the pressure of the gas entering another. For a pipeline with a pressure drop of 3 psi/mi, having an average pressure of 750 psi, a compressor station would be needed approximately every 100 miles. Deciding where to locate compressor stations is an economic judgement.

A hydrogen pipeline system would operate in the same manner as a natural gas pipeline system. The reciprocal compressors compress hydrogen rather than natural gas, but it would take more of them. Based on this information, it is estimated that hydrogen gas pipelines would have a cost per mile per MBtu of 2 to 3 times that for natural gas pipelines.

Bulk storage of hydrogen in gaseous form also follows the example of natural gas. Bulk storage of hydrogen rich town gas has been performed in aquifers in France. Bulk storage of helium in a depleted natural gas field has been successfully practiced for years by the U.S. Government near Amarillo, Texas; and salt caverns in the U.K. and United States are used for

bulk storage of hydrogen for refining applications. A number of storage options are available. The high rate of diffusion of hydrogen will require care in construction and more extensive leak detection a necessity.

**Commercial Availability** -- There appear to be no technical obstacles to bulk hydrogen pipeline transport. The only issues are economics and the need for such a system.

**Cost** -- A 1972 estimate of the costs of bulk storage by Derek Gregory presents the relative costs of various types of hydrogen storage. Table 3 provides these costs in 1989 dollars.

Storage Method	\$/MBtu
Depleted Oil or Gas Field @ 1,000 psi	7.03
Dissolved Salt Cavern @ 1,000 psi	20.00
Mined Cavern @ 1000 psi	39.50
High Pressure Bottled Storage @ 2,400 psi	1,670
Above Ground Pressure Vessel @ 1,000 psi	2,010

Table 3: Relative cost of compressed hydrogen storage options.

Identifying compressor costs and requirements, and updating the costs and requirements of various bulk storage options are a high priority when putting the economics into perspective.

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## Hydrogen Storage and Transport

### Liquefaction and Liquid Storage and Transport

Liquefaction is the process of converting gaseous hydrogen to a liquid form, for storage and transport. Hydrogen liquefaction is a costly and energy intensive process that allows for the storage and transport of large quantities of hydrogen at higher densities than pressurized hydrogen.

**Technology --** The process for producing liquid hydrogen is shown in figure 16 and begins with the cooling of gaseous hydrogen (25% parahydrogen and 75% orthohydrogen) to 90°K with a stream of cold nitrogen gas. The hydrogen is then cooled to 80°K and converted to 45% parahydrogen (parahydrogen has the atoms spinning in the opposite direction) by boiling a liquid nitrogen stream at atmospheric pressure. This process assists in lowering the temperature of the hydrogen and removing the heat generated in the ortho to parahydrogen conversion. This process assists in lowering the temperature of the hydrogen and removing the heat generated in the ortho to parahydrogen conversion.

All refrigeration below 80°K is supplied by radial inflow, high speed hydrogen expanders. This is typically a two-step process. In the first step, a series of three expanders are used to expand the hydrogen, cooling it to 50°K, 68% parahydrogen. In the second step, a series of four expanders are used to cool the hydrogen. The final step is a Joule-Thomson throttling into the low-level catalytic converter in which the hydrogen is cooled with low pressure boiling to 21°K until at least 95% of the hydrogen is para.

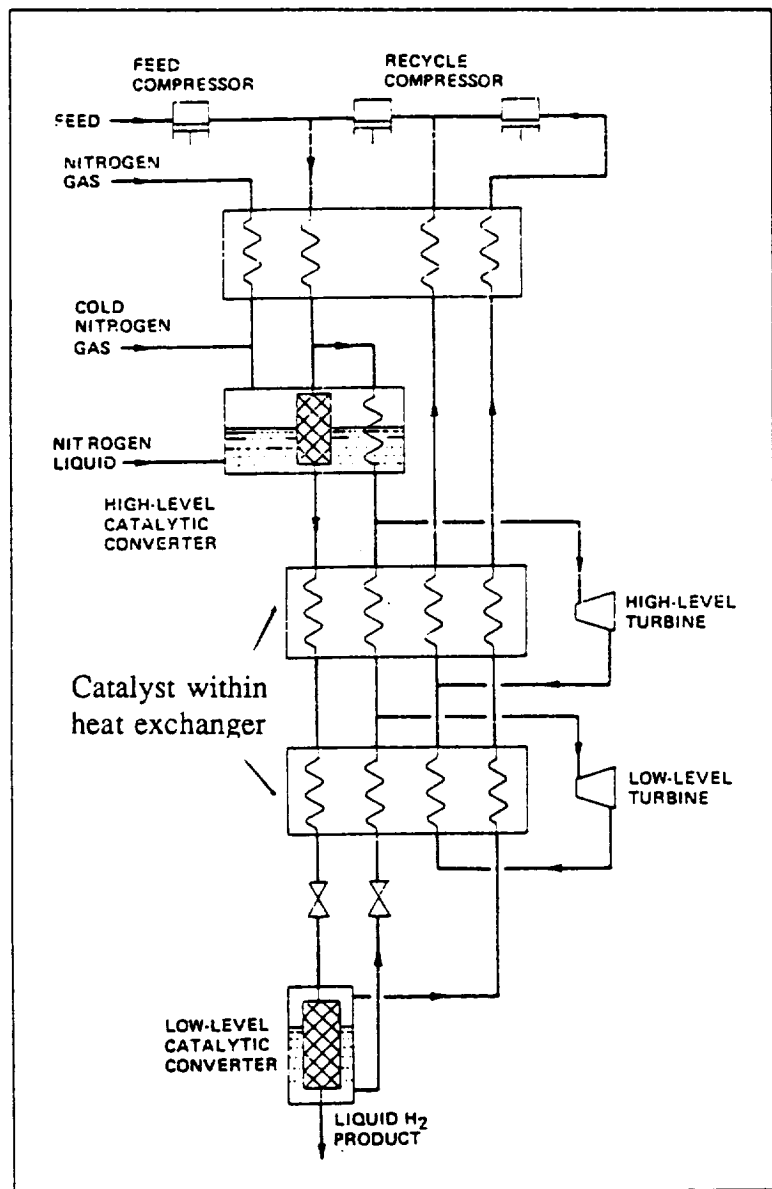


Figure 16: Flow diagram for hydrogen liquefaction and conversion.

From the liquefier, the hydrogen liquid is fed through vacuum insulated piping to a double-walled vacuum insulated storage tank.

From these tanks, the product can be delivered to railroad tank cars, tractor trailers, or barges. To transfer the liquid hydrogen from the tanks, it is either pumped or flowed using pressure differential and gravity.

**Commercial Availability** -- Liquid hydrogen is commercially available, principally because NASA began requiring large volumes of it for the space program. As a result, merchant hydrogen is increasingly delivered in liquid form for many industrial applications.

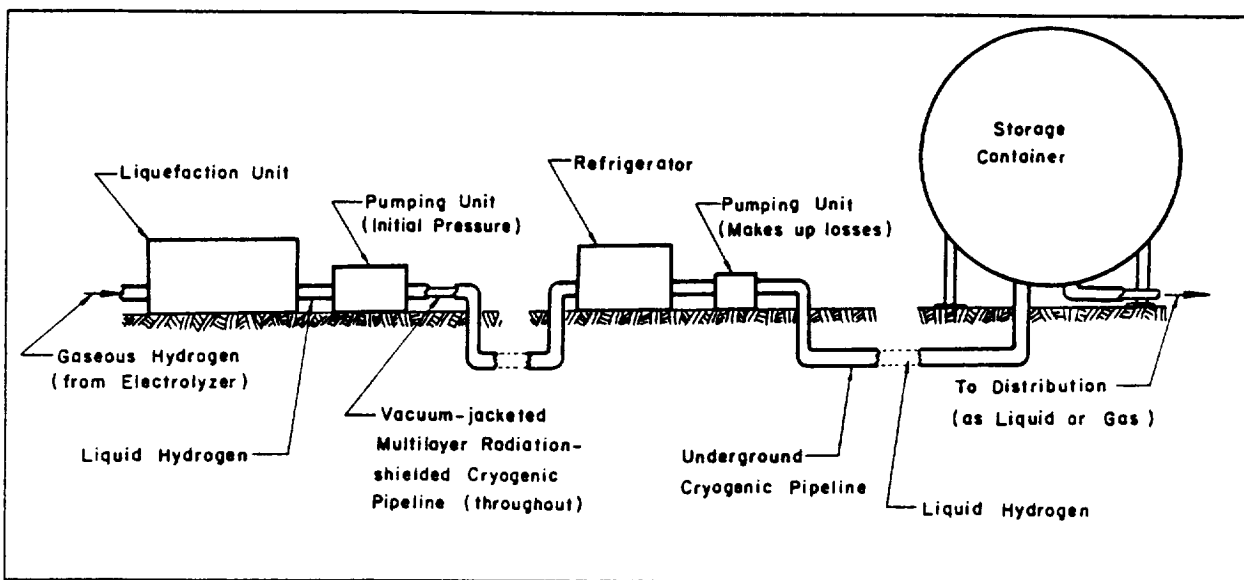


Figure 17: Cryogenic liquid hydrogen transmission and storage system.

**Energy Efficiency** -- The losses from the spherical tanks are on the order of 1/4%/day, while that from a 13,200 gallon tractor trailer is about .4% per day. As the liquid warms, gaseous hydrogen is "boiled" from the storage tanks and vented. In many instances, this vented hydrogen is burned.

**Cost** -- The cost of liquefaction is considered confidential by the manufacturers of merchant hydrogen, but it is delivered as a liquid to NASA at the Kennedy Space Center and the Marshall Flight Center at a price between \$1.25/lb and \$1.50/lb.

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Hydrogen Storage and Transport

## Hydrogen Storage and Transport

### Adsorption on Activated Charcoal Storage

Adsorption of hydrogen on activated charcoal is one of the emerging technologies for storage of hydrogen in vehicles.

**Technology** -- It is well-known that a gas adsorbing on a porous material such as activated charcoal can approach the energy storage density of the liquid form of that gas in properly sized pores. It has been demonstrated that hydrogen at refrigeration temperatures of 150°K and 55 atmospheres can be efficiently adsorbed on superactivated charcoal. If all voids are filled with hydrogen, the material has a storage capacity of .23g/in<sup>3</sup> (.014g/cm<sup>3</sup>), yielding a theoretical storage capacity of 10%. Superactivated carbon has a density of 8.6 lb/ft<sup>3</sup> (.14g/cm<sup>3</sup>). The carbon is prepared in the storage vessel at room temperature, and compacted to 70% of its fill volume.

The storage vessel for this system is a 6061-T6 aluminum liner with a carbon fiber/epoxy filament winding. The dimensions of the cylinder tested were 8" OD by 25" L. The internal volume of the system was 1010 in<sup>3</sup> (.0166m<sup>3</sup>). The pressure vessel weighed 6.7 lb (3.0 kg), but a vessel as light as 5.2 lb (2.4 kg) could have been used. The total weight of the activated charcoal, hydrogen, and pressure vessel is about 12.3 lb (5.6 kg). The vessel can carry 230 g of hydrogen with a heating value of about 26,000 Btu. The hydrogen is pressurized to 80 atm during the adsorption phase and the pressure is reduced to 55 atm during storage.

**Commercial Availability** -- Experimental work at Syracuse University, funded through SERI, has demonstrated 5% hydrogen storage by weight (about 50 g of hydrogen per kg of superactivated charcoal at 55 atm and 150°K).

The use of this storage technology for transportation applications requires a storage tank that will hold enough fuel to produce 50 kWh of energy from a fuel cell. A 50% efficient fuel cell would require a little less than 7 lb (3 kg) of hydrogen adsorbed on 140 lb (60 kg) of activated charcoal.

The requirements for a viable transportation option are:

- >60% efficient fuel cell;
- electric drive vehicle;
- insulated composite storage tank that can keep the activated charcoal at about 150°K for at least one week;
- computer controlled refueling and regulation of flow to the fuel cell; and

- refueling stations where hydrogen is refrigerated and may also be produced.

This hydrogen transportation application is in the research and development phase.

**Energy Efficiency** -- See Application Strategies, Section 5, p.5-6.

**Cost** -- For a large (9600 MBtu) stationary storage application where storage usage was 50%, there were 360 cycles/year for 7 hours/day, and the electricity price was 0.63/kWh, it was shown that refrigerated hydrogen adsorption would cost \$6.96/MBtu per cycle.

For a 300 mi range vehicle, storage of 885,000 Btu is required for an IC engine. This requires 77 kg of hydrogen. The cost of adsorption storage for this application is \$7.46/MBtu per cycle. Per fill up, the storage for an IC auto would be \$6.60.

Component	\$/MBtu per cycle
Storage Unit	1.76
Refrigerator & Compressor	3.18
Energy Cost	2.52
<b>Total</b>	<b>7.46</b>

**References --**

1. Young, Karl S., *Advanced Composites Storage Containment for Hydrogen and Methane*, Hydrogen Energy Progress VIII: Proceedings of the 8th World Hydrogen Energy Conference, Vol 2., Honolulu, Pergamon Press, New York, July 1990 pp. 967-972.
2. Amankwah, K.A.G., Noh, J.S., and Schwarz, J.A., *Hydrogen Storage on Superactivated Carbon at Refrigeration Temperatures*. National Hydrogen Association's First Annual U.S. Hydrogen Meeting, Washington, D.C., March, 1990, pp. 15-1 to 15-12.
3. Written communication from Dr. J. A. Schwarz updating current progress on adsorption on activated charcoal storage.

**Table 4:** Component Costs of activated charcoal storage for an internal combustion engine



## Hydrogen Storage and Transport

### Metal Hydride Storage

Metal hydride storage of hydrogen has been a subject of research for many years. Hydrides can store hydrogen at energy densities higher than simple compression, making them useful for applications, such as in vehicles, for which the volume of the storage capacity must be minimized.

**Technology** -- Certain metal compounds have an affinity to absorb and desorb hydrogen. The absorbed hydrogen produces heat of absorption when the hydrogen atoms position themselves interstitially in the lattice structure of the metal compound, forming a metal hydride. The application of heat energy at the proper temperature and pressure are required for dehydrogenating the metal.

Metal hydride storage offers the potential of safe, efficient and economic storage if a sufficient quantity of hydrogen can be stored in an inexpensive enough metal. An attractive metal compound would have the following characteristics:

- High hydrogen adsorption
- Temperature-dependent dissociation pressure
- Moderate disassociation temperatures
- Rapid kinetics for absorption and dissociation of hydrogen
- Good cycling characteristics
- Able to tolerate gas impurities
- Low material and fabrication cost

**Energy Efficiency**-- A number of metal hydrides that could be appropriate for space applications might not be appropriate for terrestrial applications like vehicles. Compounds such as  $\text{LiH}$ ,  $\text{CaH}_2$ , and  $\text{UH}_3$  have desorption temperatures too high for vehicle applications where heat from the engine exhaust might be used to dehydrate the metal. Even materials such as  $\text{LaNi}_5\text{H}_6$  and  $\text{FeTiH}_2$ , which desorb hydrogen at room temperature require 20% of their stored energy for dissociation. Unfortunately, these compounds are capable of adsorbing relatively small quantities of hydrogen. Magnesium hydride looks attractive for vehicle applications if its relatively slow kinetics for adsorption and desorption can be increased and if its  $287^\circ\text{C}$  desorption temperature can be lowered. In this application the magnesium is chemically doped with nickel to increase hydrogen adsorption and speed reactions times. Zirconium manganese, zirconium manganese

niobium, and zirconium manganese iron are being evaluated as possible metal hydride compounds with dissociation temperatures about 150°C.

Research to find a suitable metal hydride system that will absorb 6% by weight hydrogen continues. Magnesium hydride doped with nickel seems to offer the best potential.

**Commercial Availability** -- This technology is in the research phase.

**Cost** -- A recent cost analysis of large scale hydrogen storage options developed the cost for a FeTiH<sub>2</sub> system. The total system cost was \$13.07/MBtu. Depending on the application, a portion of the energy cost, the heating cost, might be derived from waste heat. FeTi was only assumed to store 1.4% hydrogen by weight. If a magnesium hydride system is successfully developed it would be expected to a storage capacity of at least 6% by weight. This should significantly lower the capital cost of the storage system with a heat exchanger, but it might raise the energy cost for the system.

Component	\$/MBtu
Compressor	.57
Metal Vessel with Heat Exchanger	7.66
Energy Cost for Compression and Heating	5.10
Total	13.07

Table 5: Cost analysis of FeTiH<sub>2</sub> hydride storage system.

**References** --

1. T-Raissi, Ali et al., *Hydrogen Storage Research at Florida Solar Energy Center, Hydrogen Energy Progress VIII: Proceedings of the 8th World Hydrogen Energy Conference*, Vol. 2, Honolulu, July, 1990, Pergamon Press, New York pp. 945-952.
2. Amankwah, K.A.G. et al., *Hydrogen Storage on Superactivated Carbon at Refrigeration Temperatures*, Proceedings of the National Hydrogen Association's 1st Annual U.S. Hydrogen Meeting, Washington, DC, March, 1990; published by EPRI GS-6563, pp.15-1 - 15-12.
3. Suda, S., *Metal Hydrides*, International Journal of Hydrogen Energy, Vol 12, No. 5, Pergamon Press, London, 1990, pp. 323-331.

## Hydrogen Application Technologies

The various technologies necessary for the application of hydrogen must also be considered. Applications bear on the overall efficiency and cost of any hydrogen system and, therefore, on the competitiveness of hydrogen as a substitute or complement to conventional fuels.

As with other parts of this report, some of the technologies are current and commercial, while others are still under development.

Hydrogen Application

## Hydrogen Application

### Internal Combustion Engine for Passenger Vehicles

A hydrogen fueled vehicle powered with an IC engine would differ very little from a conventional gasoline powered vehicle. It would have an internal combustion engine designed to burn hydrogen, use the same transmission as today's vehicle, and carry hydrogen storage on board, instead of a gasoline storage tank.

**Technology** -- A hydrogen engine would be 15% to 50% more efficient than a gasoline engine primarily because of more efficient air/fuel mixing. It would have an order of magnitude of reduction in hydrocarbon, carbon dioxide and carbon monoxide emissions over a gasoline engine with pollution control. The only pollutant that the hydrogen engine would produce is NO<sub>x</sub>, a product of most high temperature combustion processes. However, this pollutant would be produced at lower levels than gasoline vehicles with pollution control equipment. There is a trade off between engine power, efficiency, and production of NO<sub>x</sub>. At lean air to fuel ratios, the hydrogen engine is more efficient and NO<sub>x</sub> production is reduced; power is also reduced because there is less fuel in the air/fuel mixture (lower volumetric heating).

The low ignition energy and fast flame propagation of hydrogen has led to problems of backfire and pre-ignition with hydrogen fueled IC engines. These have largely been overcome by injecting hydrogen under pressure into the combustion chamber at about 5 degrees before the piston is at top dead center and after the intake air valve has been closed. This is possible without a pump, if hydrogen is stored as a liquid or as a very high pressure gas. However, if hydrogen is stored in a hydride or adsorbed on activated charcoal, then a pump must be used to raise the pressure of the hydrogen, or another approach must be taken to prevent pre-ignition (premixing with water injection).

On-board storage of hydrogen can be accomplished in one of four ways: liquid hydrogen, pressurized gas, metal hydride, or adsorption on activated charcoal at refrigeration temperatures. Although hydrogen adsorption at refrigeration temperatures appears attractive, extensive development and demonstration is required to evaluate the technical performance and relative economics for auto applications. Similarly, very high pressure (5,000 psi to 10,000 psi) on-board gaseous hydrogen storage has basic issues to resolve, including overall system design and safety.

**Energy Efficiency** -- A comparison of the two remaining technologies -- liquid hydrogen storage and metal hydride storage -- shows that liquid hydrogen storage provides better range, efficiency, and performance than metal hydride storage, but it has higher fuel cost, infrastructure costs, and additional safety issues regarding hydrogen boil off at its extremely low temperature. Resolution of the safety issues concerning liquid hydrogen might make it the preferred storage technology over metal hydride storage at \$1/gallon gasoline equivalent. Liquid hydrogen is routinely transported in bulk nationwide safely. Safe system design and operation are important and the design skills are in place to implement them.

The performance of a liquid hydrogen fueled vehicle should be comparable to that of a gasoline vehicle with a similar size engine. For a liquid hydrogen powered vehicle with approximately a 260 mile range, the weight, including storage vessel and excluding the gasoline vehicle's pollution control equipment, is estimated to be comparable to a filled gasoline tank of similar energy content. The weight of a metal hydride storage system of a vehicle with a 130 mile range would be from 200 pounds to 600 pounds (100 to 300 kg) more than that of a gasoline vehicle with twice that range, depending on the storage system used. The increased vehicle weight would have a negative impact on vehicle performance. Fill times for both of the storage technologies would be 5 to 10 minutes.

**Cost --** The incremental cost of producing vehicles with either of these technologies over the cost of producing a gasoline vehicle is unknown. It is estimated that the engine would cost \$50 to \$200 more than a gasoline engine, for either hydrogen storage technology. The liquid hydrogen storage system including Dewars (80 l to 100 l), a hydrogen fuel pump, and a boil off control system is estimated to cost between \$700 and \$1,700 more than the gasoline tank. The cost of a metal

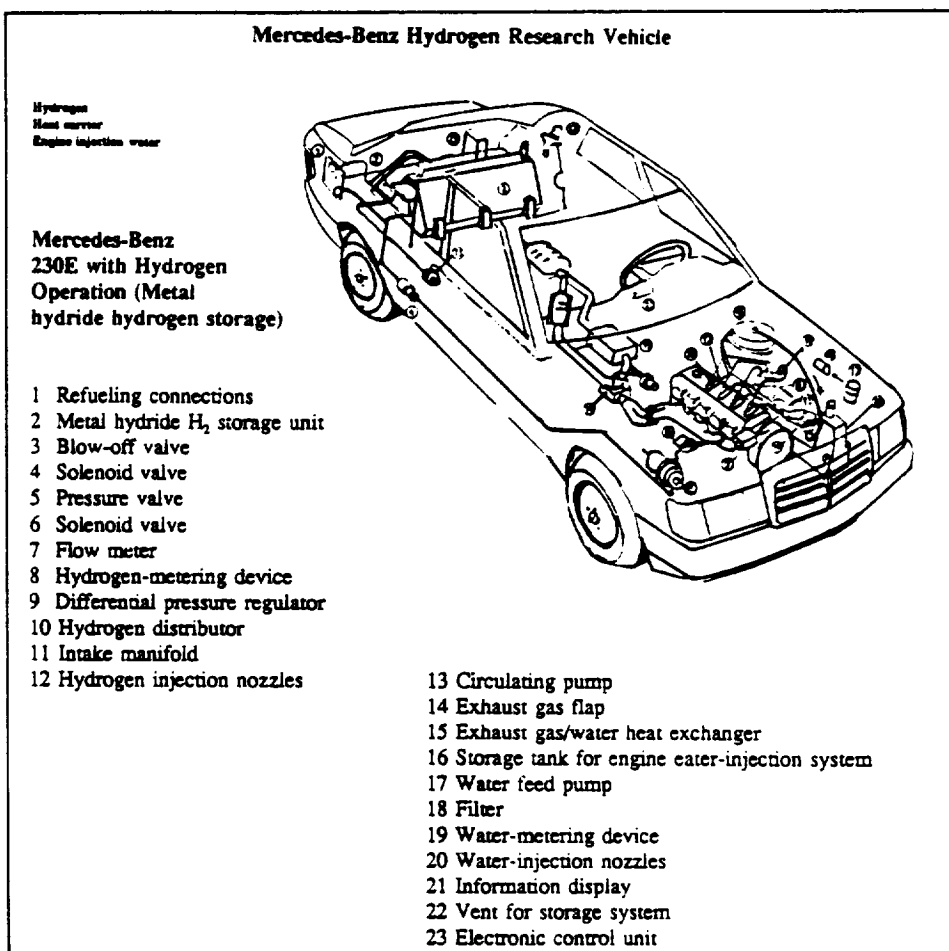


Figure 18: Mercedes-Benz Hydrogen Research Vehicle.

hydride storage system is highly dependent on the storage medium and percent of hydrogen it can store. Chassis reinforcement would require an additional several hundred dollars. A mass produced FeTi hydride storage system with 1.4% hydrogen storage by weight (providing a passenger vehicle with a 130 mile range) could cost \$1,500 to \$2,400. A magnesium hydride storage system, if it can be practically developed, would be much less expensive.

**Commercial Availability** -- Research and development needs to be done on improved storage, fuel, and engine systems for both liquid hydrogen and metal hydride storage systems.

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1. DeLuchi, M.A., *Hydrogen Vehicles: An Evaluation of Fuel Storage, Performance, Safety, Environmental Impacts, and Cost*, International Journal of Hydrogen Energy, Vol. 14, No. 2, Pergamon Press, Oxford, 1989, pp. 81-130.
2. Sher, E. and Y. Hacoheh, *Measurements and Predictions of the Fuel Consumption and Emission of a Spark Ignition Engine Fueled with Hydrogen-Enriched Gasoline*, Proceeding of the Institute of Mechanical Engineers, Part A: Power Engineering, Vol. 203, Institute of Mechanical Engineers, 1989, pp. 155-162.
3. Watson, H. C. et al., *Reduction of Cyclic Variability and Lean Limit Operation of Alternate Fuels by Pilot Hydrogen in Unmodified SI Engines*, Hydrogen Energy Progress VII: Proceedings of the VIII World Energy Conference, Vol. 3, Honolulu, Pergamon Press, New York, July, 1990, pp. 1263-1274.
4. Deutsch, Claudia H., *As Oil Prices Rise, the Hydrogen Car is Looking Better*, New York Times, August 26, 1990, p.8.

Hydrogen Application



## Hydrogen Application

### Hydrogen Fired Gas Turbine

Combustion of hydrogen and oxygen in a gas turbine was demonstrated over 30 years ago. In 1956, Pratt & Whitney converted a standard J-57 aircraft engine to operate on liquid hydrogen. An axial tube injection system was used to provide hydrogen to the combustor. After this successful demonstration, Pratt & Whitney developed a combustion turbine (the 304 engine) to operate on hydrogen for high altitude aircraft in 1958. Conversion of combustion turbines to hydrogen from jet fuel was reported as an easy accomplishment.

**Technology** -- Hydrogen embrittlement criteria for turbine blades operating on hydrogen are similar to those of today's fuels. The use of hydrogen avoids the problems of sediments and corrosion on turbine blades which prolongs life and reduces maintenance. Gas inlet temperatures can be pushed beyond normal gas turbine temperatures of 800°C. If inlet turbine temperatures could be raised to 950°C, efficiency would improve from 30% to 40% for combustion turbines. The only pollutant from the use of hydrogen in the combustion turbine is nitrogen oxide.

**Energy Efficiency** -- For aircraft use, hydrogen would be stored as a liquid. The specific energy to weight ratio of hydrogen is higher than that of hydrocarbon fuels. Hydrogen will weigh .38 times as much as an equivalent quantity of gasoline. In large sizes, liquid hydrogen and its storage tanks should be lighter than jet fuel and its storage tanks. However, the low density of hydrogen presents problems for its use as an aircraft fuel. Liquid hydrogen is 4.42 lbs/ft<sup>3</sup> (70 kg/m<sup>3</sup>) and gasoline is 44.9 lb/ft<sup>3</sup> (718 kg/m<sup>3</sup>). For the same energy content hydrogen occupies 3.9 times the volume of gasoline. This means that liquid hydrogen aircraft would have larger fuel storage tankage than current aircraft, but would have greater lift capability.

Liquid hydrogen is easily compressed for injection into the gas turbine. The liquid hydrogen flowing into the combustion turbine could be used to cool the compressor inlet air prior to injection, and permit a decrease in compressor shaft power used to compress the air.

**Commercial Availability** -- The National Advisory Committee for Aeronautics (NASA's predecessor) sponsored several successful flights of a B-57 Aircraft with one engine operating on hydrogen. In the early 1990s, Germany is planning to modify an airbus to fly on hydrogen. For a hypersonic aircraft, hydrogen might be an attractive fuel because of its combustion characteristics and the use of the liquid fuel to cool the aircraft and combustion turbines. In the mid-1960's, NASA promoted the use of hydrogen for the supersonic transport. In the course of that activity NASA had Air Products & Chemicals assess the problems of making hydrogen available in large quantities at major airports around the world. The Air Force/NASA Joint Program Office is planning to use either liquid hydrogen or slush hydrogen in the National Aero-Space Plane (NASP).

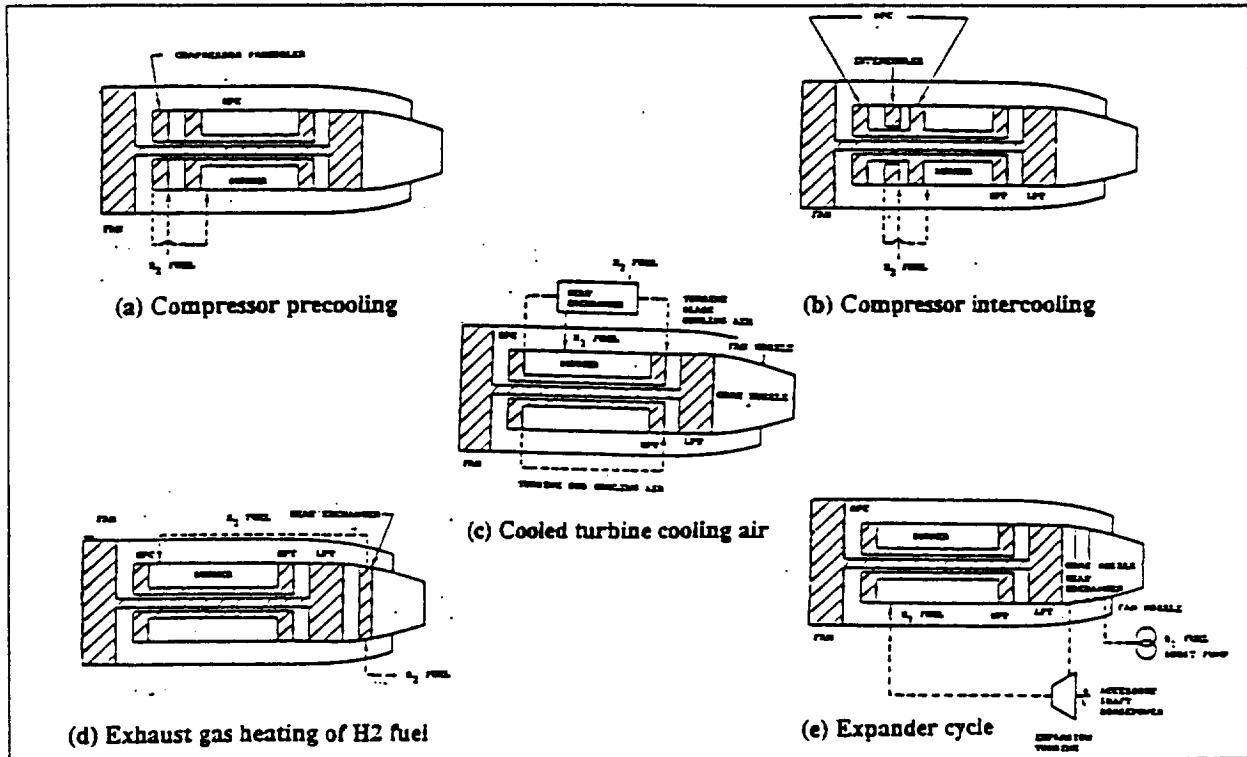


Figure 19: Schematic Engine Cycles Investigated by AiResearch in LH<sub>2</sub> Fuel Studies.

**References --**

1. Gregory, D.P.. A Hydrogen-Energy System, Prepared for the American Gas Association, by the Institute of Gas Technology, Chicago, August, 1972, pp. VII - 28-36.
2. Winter, Carl-Jochen and Joachim Nitsch, (translated by Peter and Sarah Hoffman, Hyattsville, MD), Hydrogen as an Energy Carrier: Technology-Systems-Economy, Springer-Verlag, Berlin , 1988.
3. Wurster, R., "The Euro-Quebec Hydro-Hydrogen Pilot Project," Hydrogen Energy Progress VIII: Proceedings of the 8th World Hydrogen Energy Conference, vol. 1. Pergamon Press, New York, July, 1990, pp. 59-70.
4. Bryant, William R., et al., Hydrogen Fuel for Subsonic Transport Aircraft, Prepared for NASA by ARC under Contract No. NASW-4430, Washington, DC, October 1990, pp. 61-67.

5. Sloop, John L., *Liquid Hydrogen as a Propulsion Fuel*, Washington, DC, NASA, 1978, pp. 98-160.

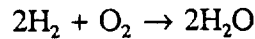
Hydrogen Application

## Hydrogen Application

### Fuel Cells (All Technologies)

A fuel cell is an electrochemical device that converts chemical energy to electricity. A fuel cell operates as a redox battery with external reactants. The ideal reduction chemical for a fuel cell is hydrogen. Oxygen is the oxidation agent.

The basic fuel cell chemical reaction is:



Hydrogen and oxygen combine to produce water, heat and dc electricity. The thermal energy produced in the reaction may be useful for supplying thermal needs of the other power plant equipment or thermal needs external to the power plant. This energy may be well suited for cogeneration, depending on the fuel cell technology. The temperature of the available thermal energy is higher for high temperature fuel cells and the amount of thermal energy is greater for the less efficient fuel cell technologies. Most applications of fuel cells favor higher electrical efficiency technologies even though less thermal energy is available.

The fuel cell consists of a stack of individual cells, each of which is a "sandwich" of an anode and cathode with an electrolyte in between. The electrolyte is the medium through which electrically charged ions propagate from the cathode to the anode. Fuel cells are named for the type of electrolyte used in this propagation (e.g., phosphoric acid, molten carbonate, alkaline, solid polymer or solid oxide). Fuel cell reactions take place at the cathode and anode in the presence of a catalyst (e.g., nickel or platinum). The anode and cathode are electrically connected externally to the load to complete the electric circuit.

For all fuel cells, the following electrochemical activities take place:

- Hydrogen and a negatively charged ion containing oxygen react in the presence of a catalyst on the anode surface, producing water, electrons and, in some fuel cells, an electrically neutral compound which is a constituent of the electrolyte (e.g., CO in molten carbonate fuel cells).
- A negative charge builds up on the anode, causing the electrons to flow to the cathode.
- At the cathode, oxygen and electrons combine to form a negatively charged ion containing oxygen and, in some fuel cells, a secondary compound (e.g., CO<sub>2</sub> in molten carbonate fuel cells), which migrate to the anode.

For every electron given up at the anode, an electron is received at the cathode.

The individual cells are connected in series to form a cell stack of higher voltage which becomes the basic building block of a fuel cell system. The cells or stacks are connected in parallel to collect a larger current. All the power produced is dc.

In addition to the fuel cell stacks, an operating fuel cell power plant typically needs the following systems:

- Fuel processor (see *Hydrogen Production: Steam Reforming*) which produces hydrogen from fossil fuels and removes contaminants that might poison the catalyst, such as sulfur;
- Invertor which converts the dc power to ac for most applications;
- Thermal management system which carries excess heat away from the stacks and maintains the proper operating temperature; and
- Sensors and control system to determine system needs and safely operate the fuel cell power plant.

Interesting applications of fuel cells sometimes avoid the need for the fuel processor or invertor. Applications in which hydrogen is available from another source do not require the fuel processing system. Applications for which dc power is useable do not require the invertor.

There are a number of different fuel cell (electrolyte) systems. Presented in this phase of the Technology Assessment are:

- Solid Polymer,
- Molten Carbonate, and
- Alkaline.

## Hydrogen Application

### Alkaline Fuel Cell

Alkaline fuel cell technology is the oldest fuel cell technology and the simplest in concept. It was the first to be used in the U.S. space program which itself was the first "commercial" application of fuel cells. Neglected by research programs (except in Europe) for several decades, there is a resurgence now due to growing interest in the transportation application of fuel cells, for which low temperature, high efficiency, high energy density and fewer material problems are important.

**Technology** -- The alkaline electrolyte fuel cell usually employs KOH as the electrolyte. Alkaline fuel cells are better suited for applications where pure hydrogen is available, as opposed to fossil fuel-reformed hydrogen, since the electrolyte reacts with CO<sub>2</sub> present in fossil fuels.

Common operating temperature and pressure are provided in Table 6. Alkaline fuel cells are capable of a cold start, an essential capability of fuel cells for vehicle application.

Temperature	Pressure
65-90°C	2-4 atm

Table 6: Operating temperature and pressure of alkaline fuel cells.

Platinum loading is a cost issue for vehicle applications, although it may be possible to eliminate it entirely, provided suitable substitute catalysts exist.

Energy density is one of the key features of alkaline fuel cells. The ultimate goal for short-term space power needs is approximately 6 kW/kg, although current test stacks are able to achieve 250 W to 1.8 kW/kg. With more cost-effective components and materials it may be possible to design a hydrogen alkaline fuel cell system that can compete in weight and volume with an internal combustion engine for vehicle applications. In Europe, a Dutch company has reached power densities of 100 W/kg with technology suitable for vehicle applications, with a goal of 150 W/kg.

**Commercial Availability** -- The alkaline fuel cell is a technically mature technology, although not yet economically competitive in terrestrial applications.

U.S. space missions since 1970 have utilized alkaline fuel cells with module power capacities up to 15 kW. Much greater capacities are projected for the future.

A Dutch company has built a limited manufacturing plant for approximately 5 MW/yr.

**Energy Efficiency** -- The alkaline fuel cell offers a high efficiency of 52% LHV combined with a simple system, in applications for which hydrogen is available.

Hydrogen Application

Alkaline Fuel Cell

**Cost** -- Although many alkaline fuel cell systems have been built, they have not been cost-reduced for competitive commercial applications. This is the objective of the newly emerging alkaline fuel cell programs in Europe and other regions. The current commercial goal is \$200 to 300/kW for an alkaline fuel cell vehicle power unit, still too high to compete with internal combustion engines.

Heat Rate	Efficiency
6,000 Btu/kWh	57%

Table 7: Efficiency of alkaline fuel cells.

**References** --

1. Appleby, A. J. and Foulkes, F. R., Fuel Cell Handbook, Van Nostrand Reinhold, London, 1989.



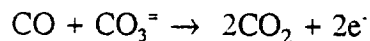
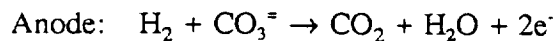
## Hydrogen Application

### Molten Carbonate Fuel Cell

The molten carbonate fuel cell is a high temperature energy conversion technology suitable for utility power plants. It is a highly efficient technology particularly suited to the use of fossil fuels. The technology has been demonstrated in kW sizes and is being scaled up to MW sizes for utility use. The molten carbonate fuel cell may be able to carve out a competitive position soon because of recent advances in development and because of its potential for superior cost and energy efficiency characteristics.

Capacity ranges of interest begin as small as several hundred kW but may range up to several hundred MW. Initial commercial applications will be fueled by natural gas, with sizes in the 2-MW range. Integration of this technology with coal gasification is a longer-term goal of the U.S. Department of Energy, the Electric Power Research Institute and some developers and potential buyers.

**Technology** -- The preferred carbonate electrolyte, solid at ambient temperature and liquid at operating temperature, is lithium-potassium carbonate. The chemical reactions are as follows:



#### Thermochemical

One advantage of molten carbonate technology is that a noble metal catalyst like platinum is not required for the chemical reactions, although one platinum supplier has suggested that the reaction could be improved with the addition of platinum. Nickel is commonly used instead.

Fuel cell power plants generally require a fuel processor (steam reformer) to convert a fossil fuel to hydrogen. The 650°C temperature of molten carbonate fuel cells is high enough that it is possible to convert methane (natural gas) directly to hydrogen in the cell itself, eliminating the separate fuel processor (steam reformer). This internal reforming concept promises greater system simplicity and offers higher system efficiency.

The research problems associated with this technology are scale-up of the technology, proving endurance (life) of the stacks, and testing mechanical and materials' stability associated with the high temperatures of the system.

Molten carbonate technology is suited for a wide range of fuels, including coal gasification. The internal reforming fuel cell is probably not the best fuel cell technology for hydrogen system applications since you have paid unnecessarily for the internal reforming capability.

**Commercial Availability** -- The earliest possible commercial availability of U.S.-developed molten carbonate fuel cells is late 1997. At the November, 1990 Fuel Cell Seminar in Phoenix, Arizona, a noted Japanese speaker predicted that the Japanese programs will not yield commercial application of molten carbonate technology until after 2000.

The largest molten carbonate stacks that have been tested are approximately 20 kW in size. Larger stacks will be tested in complete power plant systems beginning in late 1992.

The U.S. developers of this technology are:

- Energy Research Corporation, Danbury, Connecticut
- International Fuel Cells, South Windsor, Connecticut
- M-C Power, Chicago, Illinois

Several European and Japanese industrial and government organizations are also sponsoring significant product development programs in molten carbonate fuel cells.

**Energy Efficiency** -- The heat rate of molten carbonate power plants is shown in Table 8. As with most fuel cell technologies, the efficiency and heat rate curves for part load, and even overload conditions, is unusually flat for a utility generating technology. Thus, the technologies can be used over a wide range of applications and duty cycles, limited of course by overall economic considerations.

Type of System	Heat Rate (Btu/kWh)	Efficiency (%)
External Reforming	6,500	50
Internal Reforming	5,800	55

**Table 8:** Heat rate and efficiency of molten carbonate power plants (LHV).

**Cost** -- Molten carbonate fuel cell developers are predicting capital costs of below \$1,000/kWh. This data, combined with fuel cost and heat rate data, provide the basis for an economic evaluation. Traditional utility economics suggest that capital cost targets of \$1,000/kW are sufficient to achieve economic application of the technology.

Demonstrations planned for approximately 1994 are expected to cost approximately \$9,000/kW. Pre-commercial units are expected to cost approximately \$1,500/kW in the 1996 time frame.

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1. Appleby, A. J. and Foulkes, F. R., Fuel Cell Handbook, Van Nostrand Reinhold, London, 1989, pg. 540.
2. Bergman, M. K. and Serfass, J. A., *Report on APPA's "Notice of Market Opportunity (NOMO) for Fuel Cells" Initiative*, by Instar Community Systems and Technology Transition Corporation for American Public Power Association and Electric Power Research Institute, July, 1990, RP-1677-18, Final Report, January, 1991.
3. Serfass, J. A. et al, *APPA Market Study*, by Technology Transition Corporation for Electric Power Research Institute, RP - 1677-16, January, 1991

Hydrogen Application

## Hydrogen Application

### Solid Polymer Fuel Cell

Solid polymer fuel cells, sometimes known as proton exchange membrane (PEM) fuel cells, are low temperature devices that have several principal characteristics that differentiate them from other technologies:

1. The lower temperature allows more rapid start-up, making it useful for vehicle applications;
2. The technology has a higher energy density, producing more power per cubic meter; and
3. The solid electrolyte system is simpler than liquid electrolytes.

**Technology** -- The key to solid polymer fuel cells is the development of the electrolyte membrane. The Dupont Nafion™ membrane has been tested in a variety of systems but a newer Dow Chemical membrane is receiving much attention today due to the higher current density it provides. These membranes are acidic, consisting of a cross-linked organic polymer such as polyethylene, and therefore, conduct hydrogen ions. Hydrogen derived from natural gas or coal, containing CO<sub>2</sub>, is acceptable.

Water is required in the membrane for conductivity. Management of the water is critical for solid polymer fuel cells.

Temperature	Pressure
80°C	4 atm

The typical operating temperature and pressure are provided in Table 9.

**Table 9:** Operating temperature and pressure for a typical solid polymer fuel cell.

Solid polymer technology does require the presence of a noble catalyst like platinum. Some of the research is designed to reduce the platinum loading to minimize the cost impact of this expensive material.

**Commercial Availability** -- NASA's Gemini missions employed solid polymer fuel cells built by General Electric. The capacity of these devices was about 1 kW. Missions since 1970 have used the alkaline fuel cells of United Technologies Corporation.

Ergenics is commercializing solid polymer fuel cells in sizes up to 500 W.

General Motors, Ballard Power Systems and Dow Chemical have begun work under contract to the U.S. Department of Energy to develop a methanol reforming solid polymer fuel cell vehicle. The ultimate goal is a 80 KW prototype power plant in a vehicle in 1996.

***Energy Efficiency*** -- Conversion efficiencies over 50% are attainable.

***Cost*** -- No meaningful cost figures can be reported, yet. The platinum loading is still higher than it will be in commercially competitive products, and the cost of the membranes is still very high.

***References*** --

1. Appleby, A. J. and Foulkes, F. R., Fuel Cell Handbook, Van Nostrand Reinhold, London, 1989.
2. Creveling, H. F. and Sutton, R. D., *Research and Development of a Proton-Exchange-Membrane (PEM) Fuel Cell System for Transportation Applications*, presented at the November, 1990 Fuel Cell Seminar, Phoenix, Arizona.

### **3: Major Hydrogen Research Programs in the U.S.**

Most hydrogen research in the United States is funded by the federal government. Appropriations to the Department of Energy (DOE) and the National Aeronautics and Space Administration (NASA) provide the funds.

The DOE hydrogen program is directed to conducting research and development to investigate the production, storage, distribution and use of hydrogen in energy applications. Management of the DOE program is by the Solar Energy Research Institute (SERI) in Golden, Colorado. While SERI does some of its own in-house and contracted research, most of the research has been performed by the Renewable Hydrogen Consortium, comprised of the following four Centers at four Universities:

- University of Hawaii's Hawaii Natural Energy Institute (HNEI)
- Texas A&M's Center for Electrochemical Systems and Hydrogen Research (CESHR)
- University of Miami's Clean Energy Research Institute (CERI)
- University of Central Florida's Florida Solar Energy Center (FSEC)

These four programs are summarized in the following pages, as well as the research conducted by SERI itself.

Significant hydrogen research has also been funded by DOE in the past to two other universities:

- Syracuse University
- Stanford Research Institute

The Syracuse work is continuing under a recent transfer of management authority from Brookhaven National Laboratory to SERI. Current work is summarized in this chapter.

Several fuel cell research programs are also federally funded through DOE's Fossil Energy and Conservation and Renewable Resource offices. Fossil Energy programs are directed to large stationary applications, 40 kW to 100 MW in size. The following fuel cell technologies have sizeable research programs within Fossil Energy:

- Phosphoric Acid
- Molten Carbonate
- Solid Oxide

### Hydrogen Research Programs

The Conservation and Renewable Energy programs are directed to vehicular and smaller scale technologies. Solid polymer fuel cells receive significant funding in this office.

Hydrogen research is also conducted by NASA and Department of Defense centers and laboratories. The two principal programs, directed to aerospace applications of hydrogen, are:

- National AeroSpace Plane (NASP) program managed by the NASP Joint Program Office (JPO) at Wright-Patterson Air Force Base.
- Advanced Launch System (ALS) program managed by NASA.

Other smaller DOD programs are directed to specific applications such as mobile fuel cells or remote fuel power stations, although these are not necessarily directed to hydrogen-fueled applications.

Only the SERI managed work is reported in this phase of the Technology Assessment, although the chapter concludes with a brief discussion of NASA hydrogen research needs.



## Hydrogen Research Programs

### Texas A&M

Hydrogen research is being conducted by the Center for Electrochemical Systems and Hydrogen Research (CESHR), at Texas A&M University, College Station, Texas. The research is managed at SERI under SERI's contract with DOE.

The research program is entitled *Novel Methods of Solar Hydrogen Production*. The objective of this research is the use of solar energy in novel photoactive devices to split water in order to produce a storable hydrogen fuel.

The research is divided into four tasks:

1. Oriented Semiconductor Photodecomposition of Water
2. New Bioreplica Hydrogen Photocell Concepts
3. Hydrogen and Oxygen Evolution Photocatalyst Development
4. Biogenic Solar Hydrogen Production

#### **Task 1: Oriented Semiconductor Photodecomposition of Water**

The objective of Task 1 is the development of devices that, when immersed in aqueous solution in the presence of sunlight, will be capable of generating enough voltage at high enough currents to split water with high efficiency. The approach is to build a photoconversion device composed of two or three stacked photovoltaic devices.

The initial activity is to optimize the band energies of the mechanically stacked cells by connecting them in optical and electrical series. Initial efforts have focused on material selection and fabrication for the photovoltaic cells. On the basis of evaluation of materials with the desired band energies and efficiencies, the triple stack cell decided upon has  $\text{CuInSe}_2$  as the bottom cell, either GaAs or CdTe as the middle cell, and  $\text{GaInP}_2$  as the top cell. The principal methods of fabrication were "chemical spray pyrolysis" and "electrodeposition". Sprayed  $\text{CuInSe}_2$  films were examined by X-ray diffraction. The films had many pinholes which must be eliminated to ensure high efficiency cells.

Three electrodeposition approaches were considered to produce  $\text{CuInSe}_2$ :

1. Deposit binary compounds of the constituent elements ( $\text{Cu}_2\text{Se}:\text{In}_2\text{Se}_3$  or  $\text{CuSe}:\text{InSe}$ ) and heat treat to diffuse the materials.
2. Codeposition from a solution containing all three elements.
3. Deposit a Cu-In alloy on the substrate, and heat treat in an Se atmosphere.

Using the first approach, the deposited CuSe, showed a morphology under X-ray diffraction of  $\text{Cu}_3\text{Se}_2$  on a molybdenum substrate with good crystalline structure. InSe could not be deposited on the substrate, possibly because In and Se are not simultaneously stable at the same pH. Other approaches are being pursued. One step deposition of  $\text{CuInSe}_2$  has been unsuccessful on a molybdenum substrate. No work has been done on the effect of heat treatment on the crystal structure of codeposited materials.

Amorphous Silicon Alloys were prepared by plasma-assisted chemical vapor deposition. This is a parallel approach to creating a two or three stack photovoltaic device composed of low and high band gap materials. The deposited amorphous silicon alloy (a-Si:Ga:C:H; a-Si:Se:H and a-Si:S:H) materials were characterized with respect to their optical, electrical, and chemical properties. Alloy structures other than tetrahedrals were selected to decrease strain-induced defects. The bandgap energy as a function of increasing alloying gas concentrations of a-Si:Ga:C:H and a-Si:Se:H have been investigated, and the electrical properties of a-Si:S:H and a-Si:Se:H alloys are being studied. The composition of the a-Si:Ga:C:H films showed high carbon composition. The films were non-homogeneous with regions of low hydrogen concentrations. Films high in Ga had high O<sub>2</sub> concentrations. a-Si:S:H films showed more uniformity in S content.

## **Task 2: New Bioreplica Hydrogen Photocell Concepts**

The objective of this research mirrors that of Task 1 with the only difference being the use of organic semiconductors and dyes in thin films.

Combinations of organic conductors (OR), organic dyes (D), redox couples (R), and metals (M) are being investigated in the following combinations:

- OC/D/R
- M/D/OC + R
- M/OC + D/R
- M/D + R/OC

Experimental efforts focused on identifying the structure and maximum absorption of suitable dyes. Once suitable dyes with peak adsorption wavelengths of 430 nm to 540 nm were identified, electrode structures for these dyes were fabricated using printing, electrodeposition, immersion, and codeposition techniques. The measured open circuit photovoltages for the dyes tested were on the order of 200 to 300 mV. Voltages as high as 630 mV were achieved using codeposited phenosafranine and polypyrrole. These dyes irreversibly broke down. It is suspected that the dyes acted as electron donors, and the redox pairs as electron acceptors forming a molecule with a new structure.

Another approach is to couple dye systems together with an organic conductor. The structure in these systems is: OC/R1/D/R2. It is hoped that a proper combination of these structures optically connected in series on a metal substrate will yield a high photovoltage. An attempt using  $\text{SO}_4^{2-}$  as one of the redox couples yields a 200 mV photovoltage. Photocurrents have also been on the order of 50  $\mu\text{A}$ . This is probably due to the high resistance of the dye elements in the cells.

Theoretical models for organic dye-based photovoltaic cells were constructed for p- and n- type materials. These models developed an expression for the photocurrents from the transport equation for photoexcited electrons and the boundary conditions at the dye film/organic semiconductor interface. For the n-type semiconductor, no photocurrent maximum is observed, but at a critical thickness at the

dye layer, the photocurrent becomes limiting. As the diffusion coefficient or photoelectron mobility increases, the critical thickness increases. The p-type semiconductor shows no photocurrent maximum, but shows the same limiting effect at a critical thickness as in the n-type semiconductor case. Up to the critical thickness, the photocurrent is a function of the potential drop in the dye film.

### **Task 3: Hydrogen and Oxygen Evolution Photocatalyst Development**

The purpose of this activity is to investigate electrocatalysis in the photoelectrochemical splitting of water.

Previous work had shown that water could be split with a solar to chemical conversion of 2.93%. Experimentally a stack of three amorphous silicon cells were placed on a titanium substrate with ruthenium oxide painted on the back side of the substrate. Platinum islands of 1 nm to 10 nm were deposited on the top n-type layer. Aluminum was used to provide ohmic contact for the p-Si.

Studies were carried out using scanning tunneling microscopy. When the cell without electrical connections was immersed in 1 molar sulfuric acid, hydrogen was produced at the platinum/n-a:Si and oxygen was produced at the ruthenium oxide side of the cell. This was done under simulated solar radiation. The conversion efficiency was calculated from the incident light, the moles of hydrogen produced, the current density, and the water displaced.

Steady state efficiency is reported at about 5%.

### **Task 4: Biogenic Solar Hydrogen Production**

The objective of this task is to identify bacteria with high rates of hydrogen production among rumen bacteria and the impact of oxygen to those production rates.

Pure strains of rumen from beef cattle were isolated, diluted, and grown anaerobically. The gases evolving from the bacteria were measured with a chromatograph using a thermal conductivity detector and argon as a carrier gas. Repeated runs with various strains of rumen bacteria showed variations of up to 100 times in hydrogen production.

Very few strains of bacteria were shown to be good hydrogen producers. The best run produced hydrogen at the rate of  $1 \times 10^{-6}$  moles/min from a 100  $\mu$ l sample of bacteria ( $3.34 \times 10^5$  l H<sub>2</sub>/yr per liter of bacteria). The control for this research, *Clostridium pasteurianum*, showed a narrow range of hydrogen production rates. Whether these rates of production could be sustained on woody wastes, solid wastes, and sewage remains to be seen.

### **References**

1. Anani, A. and J. Appleby, et al., *Novel Methods of Solar Hydrogen Production: Annual Technical Progress Report*, College Station, Texas, Center for Electrochemical Systems and Hydrogen Research, August 1989.

Hydrogen Research Programs

## Hydrogen Research Programs

### University of Hawaii

The Hawaii Natural Energy Institute at the University of Hawaii has been funded by SERI since 1985. In 1988, under a SERI contract, the Institute completed an assessment titled *Hydrogen Production from Renewable Resources*. The main conclusion of this study was that while hydrogen production from renewable resources is feasible, it is too expensive to compete with fuels in today's markets. The study was heavily oriented to the energy needs of the state of Hawaii. Therefore, some of the findings of the study may not be applicable to the rest of the United States.

Four of the study's recommendations are relevant to SERI's subsequent national research program:

- Scale-up biomass gasifier technology for hydrogen and methanol production;
- Continue research on steam and carbon dioxide gasification of biomass to determine if they may be viable alternatives to partial oxidation;
- Continue to pursue active research on advanced concepts of electrolysis, with emphasis on commercialization of high pressure and high temperature systems; and
- Expand present research on photoconversion technology as a long term method of producing inexpensive hydrogen.

One final point is that the study found wind generation, although 50% more expensive than geothermal, to be much less expensive than the solar thermal options investigated for Hawaii. The study estimated the cost of wind power at about \$.075/kWh. It pointed out that Hawaiian Electric Renewable Systems, a subsidiary of the local electric utility, Hawaiian Electric Industries, was selling power to the utility for \$.06/kWh from wind systems on Oahu and Hawaii. It was not earning the 10% return contained in the study cost estimate of \$.075/kWh.

From this study emerged four activities that would be carried out, beginning in fiscal year 89, by the HNEI under SERI program management.

#### **Task 1: Hydrogen Production Through Pyrolysis of High Moisture Content Biomass in Supercritical Water**

The goal of this task is to demonstrate the production of hydrogen from biomass, with up to 50% moisture content. Biomass with high moisture content includes grasses and various types of aquatic biomass. The study also wishes to determine the parameters which influence the production of hydrogen from various biomass feedstocks.

In fiscal year 89, test runs were made using a supercritical fluid reactor, modified to accommodate a slurry feed reservoir. Pyrolysis was performed utilizing glucose, algae, kelp, and sewage sludge. In supercritical water with temperatures of 500°C or higher and residence times of 30 seconds, steam gasification of biomass was observed. The product ratio was 2 H<sub>2</sub> product for every CO<sub>2</sub> product produced, reactant product exceeding organic reactant. Both the CO<sub>2</sub> and hydrogen were available at high temperatures and 5,000 psi.

This Task was transferred to SERI's biomass program for fiscal year 1990. Since this transfer, kelp and sewage sludge were fed into the reactor. Yields from these biomass forms were lower than expected. This might be due to the feed system which has since been replaced with a high pressure stirred tank feeder.

## **Task 2: Photoelectrochemical Production of Hydrogen**

This activity is divided into three sub-tasks, each of which will be briefly described.

### **Sub Task 2.1: Photoemission and Photoluminescence Studies of Catalyzed Photoelectrode Surfaces for Hydrogen Production**

Micro-islands of metal deposited on semiconductor photoelectrode surfaces are known to catalyze reactions for hydrogen production in photoelectrochemical cells. The purpose of this study is to determine how the metal islands can be made to improve the photoelectrode efficiency. The efficiency of the photoelectrode depends on the rate of hydrogen production and reductions in the rate of recombination and leakage. The deposition of platinum catalyst in micro-islands can greatly increase the hydrogen generating current density of p-type semiconductor material, like InP photocathode. The size and spacing of the micro-islands must be small enough to minimize the loss of photons due to coverage of the semi-conductor surface by the metal. On the other hand, the separation must be ample enough to allow efficient collection of the photoexcited electrons.

Photoemission and photoluminescence studies were conducted on metal islands of various sizes to determine the optimum size of metal clusters for generating the photovoltage and reducing the surface recombination loss. Using X-ray photoemission the photovoltage as a function of the ratio of the thickness of the metal micro-islands of chromium and the photoelectron escape length.

Under X-ray photoemission, a shift in the Fermi level of the metal deposition relative to that of the semiconductor substrate was observed. The photoluminescence study focused on measuring emissions from the recombination losses at the semiconductor interface. Wafers of InP were doped with Sn. These samples were optically excited by a HeNe laser. This produced photoluminescence in operating photoelectrode. The emission intensity was found to depend on the bias voltage applied to the photoelectrode and the coverage of cobalt on the InP cathode.

Follow-on studies will use these techniques to determine optimum size and separation of micro-islands on semiconductor electrodes.

**Sub Task 2.2: Solar Energy Chemical Conversion by Means of PEC Methods Using Coated SI Electrodes**

The objective of this effort is the "optimization of stable, high efficiency photoelectrodes". Only inexpensive semiconductor materials such as Si, a-Si, CdSe, and CdTe are being considered.

Activities through July of 1990 included:

- Improved fabrication procedures for c-Si photoelectrodes
- Evaluation of the methods of improving photoefficiency
- Measurement and comparison of the current voltage behavior of Si photocathodes with different thicknesses of platinum

**Sub Task 2.3: Assessment of Impedance Spectroscopy Methods for Evaluation of Semiconductor-Electrolyte Interfaces**

The objective of this effort is to characterize type III-V compound semiconductors by impedance measurements to assess their photoelectrochemical performance.

The first year of the effort was directed to evaluating past work on impedance measurements and develop and configure the needed hardware and software, and begin experimental work on p-type InP. Results from this year's works included Mott-Schottky plots for indium phosphide using impedance spectroscopy for various pH values. The flatband potential was found to vary by 60 mV/pH unit. Mott-Schottky plots for gallium indium phosphide were found to be well behaved for capacitance measurements and show nonlinear and frequency-dependant behavior when measured using impedance spectroscopy. Gallium Aluminum Arsenide showed Mott-Schottky plots were linear at higher biases, but were nonlinear at lower biases and higher pH values. Photocurrent spectroscopy has just begun on Gallium aluminum arsenide.

**Task 3: Solar Energy Conversion with Cyanobacteria**

The purpose of this task is to develop a better understanding of the production of hydrogen in cyanobacteria.

The three basic enzyme systems involved in hydrogen metabolism by cyanobacteria are:

- nitrogenase;
- uptake hydrogenase; and
- reversible hydrogenase.

Nitrogenase...catalyzes the reduction of protons to hydrogen.... Uptake hydrogenase...is typically membrane-bound in cyanobacteria, and functions to recapture the hydrogen produced in nitrogenase. While the role of reversible hydrogenase is presently unclear, it is probably involved in hydrogen uptake.

The *Anabaena* species is being used as the model to study the molecular biology of cyanobacterial hydrogen production. A large number of the genes of this species have been cloned and sequenced, and methods for genetic manipulation of this species are well developed. Current efforts focus on identifying the structural gene for uptake hydrogenase. A single strand of DNA containing the 3-kb EcoRV fragment contains the DNA which hybridizes to a probe consisting of *B. japonicum* uptake hydrogenase structural genes. Characterization of this fragment is currently underway to determine whether or not this fragment contains the structural genes of uptake hydrogenase.

#### **Task 4: Nonclassical Polyhydride Metal Complexes as Hydrogen Storage Materials**

Metal hydrides are a promising method of hydrogen storage. A cobalt group of nonclassical polyhydride complexes have to be synthesized and characterized. "These complexes, which contain up to 1.6% available hydrogen have promising hydriding/dehydriding behavior." Ongoing efforts include synthesizing nonclassical polyhydride iron complexes from an iron half sandwich hydride complex. Most nonclassical polymetal hydride metal complexes undergo complete and reversible loss of hydrogen under mild conditions.

#### **References**

1. *SERI Biofuels Program Quarterly Technical Report*, Second Quarter FY 1990. SERI, Golden, Colorado, April 1990.
2. *Hydrogen from Renewable Resources Research: Annual Report to the Solar Energy Research Institute*, Hawaii Natural Energy Institute, Honolulu, Hawaii , August 1990.



## Hydrogen Research Programs

### University of Miami

The research program at the University of Miami's Clean Energy Research Institute is funded by DOE and managed as a subcontract by SERI. The objective of the effort is to investigate four hydrogen topics:

- System modeling,
- Biological hydrogen production,
- Liquefaction,
- Safety.

This is the only DOE/SERI research program addressing safety.

#### **Task 1: Hydrogen Systems Application Analysis**

The objective of this task is to develop a model for a renewable hydrogen system. The steps in this project are to:

1. Develop a data base on the energy systems of interest,
2. Perform a hydrogen systems analysis using those elements,
3. Compare the performance with fossil fuels,
4. Develop a dynamic model for renewable hydrogen systems.

Detailed information was developed and calculated for photovoltaic systems, wind systems, electrolysis, underground storage, and hydrogen-fueled automobiles with hydrogen engines. The report did not discuss how the electrolytic plants were sized in relation to the intermittent nature of the energy sources that they would be coupled to.

A materials and energy analysis of the conversion to a PV hydrogen system was performed with a common basis for all input requirements. The energy analysis indicates that the price of PV power must approach \$.40/kW<sub>peak</sub> before the ratio of energy input to energy output is less than one. The project estimates the cost of 1,000 MW of PV powered electrolysis facility at \$1.5 to 3 billion, and a similarly sized wind facility at \$1.3 to 1.6 billion.

The study assesses the environmental cost of coal, oil, and natural gas at \$10.90/MBtu, \$9.20/MBtu and \$4.46/MBtu respectively.

Component or System	Cost	Life (yr)
Solar PV Produced Electric Energy	\$.065 - .08/kWh	
Wind Produced Electric Energy (6m/sec wind)	\$.039 - .06/kWh	30
Electrolysis Systems	\$170 - 250/kW	20
Energy Value of Electrolytic Hydrogen	\$11 - 30/MBtu	
Underground Storage	\$1.74 - 3.33/MBtu	
Pipeline Transport	\$.39/MBtu	
Compression (200 - 400 bar)	\$.47 - .71/MBtu	
Liquefaction	\$4.27/MBtu	

Table 10: Selected cost estimates developed in modelling task.

As of August 1989, the date of the report, work was just beginning on the dynamic model. Further efforts will expand the range of hydrogen technologies evaluated, and continue model development.

## Task 2: Biological Hydrogen Photoproduction

This task is a five-year effort to investigate mechanisms associated with changes in *cyanobacterium Synechococcus sp. Miami BG 043511* metabolism during the cell cycle as it relates to hydrogen production.

The specific areas of concentration are changes in the following:

- In the activity levels of hydrogen producing enzymes, hydrogenase and nitrogenase
- In the activities of hydrogenase-mediated hydrogen recycling
- In phosphorylation and ATP content
- In the activity of photoevolved oxygen as it relates to hydrogen
- description of the electron donor system for hydrogen photoproduction.

Findings from these studies will be applied to hydrogen systems.

During the first year, it was determined that the biochemical activity of *Synechococcus* during synchronous growth are cell cycle events. It was necessary to separate hydrogen and oxygen production by the samples to avoid the possibility of explosion. This was accomplished by separating in time the hydrogen and oxygen production during the cell cycle. Test runs showed that hydrogen photoproduction is a nitrogenase-dependent activity.

Reductions in cell activities related to oxygen production were observed to be greatly reduce after 12 hours. The reason for this phenomena was investigated. Part of the decrease in activity was found to be caused by a decrease in PS I and PS II activities. Ongoing efforts will continue to explore cell metabolism and address the questions raised in the first year's activities.

### **Task 3: Hydrogen Liquefaction**

The purpose of the study is to identify new technologies that could improve hydrogen liquefaction. The study reviewed four conventional, five advanced, cooling technologies and eleven liquefaction systems.

The study concludes that a precooled, modified, Claude system offered the best characteristics of the conventional liquefaction systems. Magnetocaloric liquefiers have promise but are in the developmental stage.

The investigators present a liquefaction scheme that couples a helium modified Claude complex refrigerator with nitrogen precooling and a low-pressure hydrogen stream. An optimization study for this scheme would be the next step toward building a prototype. Three liquefaction systems were analyzed in the report. The report also analyzed cost, safety, and environmental concerns associated with liquefaction plants, as well as boil off associated with storage and transporting liquid hydrogen.

The major conclusions from the study are:

- The optimized precooled complex modified Claude cycle seems to possess better performance than other conventional systems;
- Investigators believe the helium modified Claude system mentioned previously offers the basis for an improved conventional liquefier;
- A magnetocaloric liquefier has the potential to have high efficiency;
- Two effective ways of reducing boil-off due to stratification and thermal overfill in a storage tank are by:
  - Providing vertical conductive plates,
  - Maintaining the liquid at subcooled or saturated conditions with magnetic refrigeration.

- Magnetic liquefaction is the most environmentally acceptable refrigeration system.

Follow on work should include the following:

- Fluid flow and heat transfer analysis of magnetocaloric liquefiers,
- Development of new mechanical designs and better magnetic field distribution systems,
- Materials research related to magnetic properties and temperature dependence.

#### **Task 4: Hydrogen Safety and End Use Characterization**

The purpose of this study is to investigate and develop solutions to safety problems associated with hydrogen production, storage, and distribution for large-scale energy systems. The initial effort consisted of developing three hydrogen leakage models and determining the proper model for various circumstances. The hydrogen pressure drop across the three leaks and volumetric flow rates were measured and compared to Reynolds number information. Comparisons of the rates of leakage and time required to form a burnable mixture were made for hydrogen, methane, and propane.

The results of these tests show that leak onset occurs at the same Reynolds number for each gas studied. At low pressures, hydrogen and propane showed the same volumetric flow rates across the leak. At higher pressures the onset of significant leakage occurs first with propane due to its high Reynolds number relative to hydrogen or methane. For constant pressure at residential natural gas pressures, the energy content of the hydrogen leakage rate was 38% to 46% of that for natural gas, and 15% to 25% of that for propane. Based on experiments, hydrogen forms a combustible mixture more quickly than methane but more slowly than propane under similar conditions.

A second part of the study investigated safety associated with large scale photoelectrochemical, photobiological, and photochemical splitting of water. The study evaluated creating conditions that made combustion impossible by avoiding a burnable concentration of fuel, avoiding sources of ignition, or avoiding concentrations of oxidant necessary for sustaining combustion. The avoidance of a source of ignition was viewed as impossible.

A review of the literature for photosynthetic sulfur bacteria, non-sulfur bacteria, cyanobacteria, and green algae showed that only filamentous non-heterocystous, single cell cyanobacteria is capable of producing hydrogen and oxygen in sufficient quantities to raise safety concerns. Since this form of cyanobacteria produces hydrogen and carbon dioxide during one part of its cycle and oxygen during the other, it is possible to mechanically separate the hydrogen and oxygen and eliminate the problem. Photochemical hydrogen production methods have potential safety problems unless designed to collect hydrogen and oxygen in separate locations.

Photoelectrochemical systems collect hydrogen at one electrode and oxygen at the other, posing no safety problem.

Other conclusions from the study are:

- Some photochemical and photoelectrochemical hydrogen production systems contain toxic substances. These systems must be thoroughly evaluated, if any of them show commercial promise;
- Plastic pipe used in today's gas distribution systems must be evaluated to determine their permeability to hydrogen. No information is available on whether these polyethylene pipes are more or less permeable for hydrogen than for natural gas.

**References:**

1. Veziroglu, T. Nejat, *Solar Hydrogen Energy System*. Clean Energy Research Institute, Coral Gables, Fl. October 1989.

Hydrogen Research Programs

## Hydrogen Research Programs

### University of Central Florida

The Florida Solar Energy Center at the University of Central Florida is under a SERI managed contract for DOE to perform research on photoelectrochemical hydrogen production, chemical storage of hydrogen, and evaluation of new thermochemical cycles for splitting water.

#### **Task 1: Photoelectrochemical Hydrogen Production.**

The Objectives of this task were to:

- Study the physical and chemical variables that effect efficient hydrogen production and stability for a semiconductor slurry irradiated by a filtered xenon lamp;
- Investigate the PEC reactions occurring for CdS/RuO<sub>2</sub> in various electrolytes (Na<sub>2</sub>S, Na<sub>2</sub>SO<sub>3</sub>, NaOH);
- Search for semiconductor-catalyst-electrode systems of higher efficiency and better stability.

The experimental apparatus consisted of a storage tank, mixer, a thermal bath in which sat the mixed reactor, a settling tank and metering pump. CdS powder was suspended in a dilute aqueous solution in which RuCl<sub>3</sub>·3H<sub>2</sub>O was assumed to be converted to RuO<sub>2</sub>. The experiments took place under positive pressure (6-8 psig), at 60°C, in a solution of 0.032 M Na<sub>2</sub>S, .1M Na<sub>2</sub>SO<sub>3</sub>, and .1M NaOH. Before use, reactors were filled with nitrogen to remove any trace of oxygen. The existing gases from the reactors were periodically analyzed using a gas chromatograph.

Three sets of experiments were performed: the rate of H<sub>2</sub> evolution in the presence of catalysts (Pt, RuO<sub>2</sub>), was determined; conditions which promoted photoanodic corrosion were studied; and stationary particle density tests to determine optimum loading were performed. Results from these experiments were:

- 2.5 times increase in H<sub>2</sub> production rate using RuO<sub>2</sub> catalyst and a 9 time increase in H<sub>2</sub> production rate using Pt catalyst;
- Chemical analysis of the electrolyte was underway although photoanodic corrosion proved more difficult than expected;
- Optimum hydrogen generation rate occurred at 1 mg/cm<sup>2</sup>.

The follow-on recommendations involve modifying the reactor system to eliminate the gas-liquid interface in the 5-reactor system, and reduce the large amount of gas-dead space. Studies on the catalyzed particle should been done to determine optimum size, catalyst loading and orientation for maximum hydrogen evolution.

#### **Task 2: Synthesis and Characterization of Nickel Doped Magnesium Hydride**

One method of hydrogen storage is within a metal hydride. Magnesium is an inexpensive and abundant element which, in the form of magnesium hydride, has a high hydrogen content (7.66% by weight). However, its direct production by combining hydrogen and magnesium at 570°C and 200 bar is slow and incomplete, and the MgH<sub>2</sub> produced has a high disassociation temperature. It has been shown that the doping of MgH<sub>2</sub> with a suitable

transition metal will create a compound with excellent storage, hydrogen disassociation and recombination characteristics, and cycling characteristics.

The objective of this effort is to prepare and analyze the structure of various doped, catalytically prepared, magnesium hydrides. Specific objectives include:

- hydrogen storage greater than 6% by weight;
- Fast hydrogenation/dehydrogenation kinetics;
- Insensitivity to impurities normally present in hydrogen gas; and
- Installed cost under \$5/MBtu.

A two-step catalytic process was used to produce  $MgH_2$  with magnesium anthracene as the intermediate product that is then reacted with hydrogen to produce  $MgH_2$  and anthracene. The  $MgH_2$ , which is pyrophoric, was heated in solution with bis-(cycloocta-(1,5)) - diene nickel to produce  $MgH_2(Ni)$  and cyclooctane. Doping with less than 1% nickel gives the compound stability in air.

Equipment to characterize the doped magnesium hydrides was constructed and calibrated during 1989 and the first half of 1990. The setups to analyze kinetic data from the samples included a thermovolumetric analyzer and a thermogravimetric analyzer. Other analysis to be performed is structure characterization using X-ray diffraction and SEM.

***References--***

1. T.-Raissi, Ali et al., *Hydrogen, Methane and Mixed Gas System Integration: The Transition to Hydrogen Power*, Florida Solar Energy Center, Cape Canaveral, Florida, November, 1990.



## Hydrogen Research Programs

### **Solar Energy Research Institute**

DOE funds a hydrogen research program through the Solar Energy Research Institute (SERI). The goal of this program is to produce competitively priced hydrogen for utility and transportation applications. To achieve this goal and sustain it, hydrogen must be produced at \$10/MBtu or less with renewable resources. The program has focused its efforts on reducing the cost of producing hydrogen.

The SERI hydrogen program funds research at four Congressionally mandated centers other universities, consulting firms, and within SERI. This section summarizes the research conducted by SERI in-house, and with consulting firms.

SERI research has focused on photoelectrochemical and photobiological hydrogen production.

#### **Bioelectrochemical Production of Hydrogen from water: Interaction of Surface-Modified Electrodes with Biological Materials**

The objective of this project is to reversibly adsorb biological materials on electrode surfaces using electrostatics. The advantage of this approach is that highly active enzymes from green plants and bacteria can be selectively used for water splitting. The disadvantages are that enzyme catalyst lives are sometimes short and require redox mediating groups to couple with solid electrodes.

Most enzymes and nearly all microbial cells have a net negative charge and are electrostatically attracted to positively charged surfaces, while being electrostatically repelled by negatively charged surfaces. The assumption for this research is that biological materials can be attracted to positively charged electrode derivatized with electrochemical active groups. When the redox groups are reduced, the biological material can be detached by making the electrode neutral or negative. The electrode can then accept new biological material. Slow progress has been made on this effort over the past year.

One approach involved the use of an electrochemically active quinone on the surface of the electrode. Bacteria are attached to the electroactive group which reduces to hydroquinone. Hydroquinone produces a negative charge of sufficient magnitude to repel the negatively charged bacteria from the surface. Some preparations bound the bacteria over 50% of the electrode surface area, showed nearly total release, and could be recycled several times. Reproducing the results was a problem.

Approaches using particles of activated charcoal in physical and electrical contact to increase the surface area for bacterial and enzyme adsorption are being pursued with some success. Work is focusing on optimizing net surface charge and charge densities on the derivized electrodes to promote better adsorption and desorption of the biological materials.

## Photoelectrochemical Hydrogen Production

The objective of this effort is to identify multiple bandgap photoconversion structures that yield solar photoconversion systems with conversion efficiencies of 15% to 25%.

Multiphoton photoelectrolysis systems consist of two or more photoactive semiconductors configured in such a way that when they are simultaneously illuminated; the energy of each of the illuminated semiconductors are additive to provide a photovoltage for doing useful chemical work greater than that achievable from either of the photoactive semiconductors. The objective of the current effort is to investigate the basic properties of these multiphoton systems and compare their technical promise.

The first system examined was p-InP/n-GaAs described in the literature as a self-driven system (operates without a bias) with a hydrogen conversion efficiency of 8.2%. The system produces hydrogen at the Pt-coated p-InP photocathode and oxygen at the Mn<sub>2</sub>O<sub>3</sub>-coated n-GaAs photoanode. Two concerns about this system arise from the band structure of the two semiconductors:

- The two materials are not lattice matched, so strain will be induced at the InP-GaAs interface.
- The unperturbed InP/GaAs system has band edges inconsistent with what would be required for a p/n self-drive system. (The n-GaAs conduction band lies above that of the p-InP conduction band.)

For the system to be a self-driven water splitting system, the surface treatment of these semiconductors must have induced large band edge movement. Examination of the Pt/InP interface and the GaAs/Mn<sub>2</sub>O<sub>3</sub> using Mott-Schottky measurements showed movement of the flatplate potential in the wrong direction for a self-drive system. The cell was tested directly and run in a .5 M NaOH solution. The results of the analysis of the run were as follows:

- There was no evidence of oxygen production at the GaAs anode.
- Mn<sub>2</sub>O<sub>3</sub> is stripped from the GaAs surface during photooxidation reaction.
- The cell is not splitting water as a self-driven cell, but photodecomposing GaAs in .5 M NaOH and producing hydrogen.

Current work includes developing new self-drive systems using layered metal dichalcogenides such as p-GaAs coupled with MoSe<sub>2</sub>. Work has begun on making single crystals of doped MoSe and MoS. Other work includes attempts to develop these multiphoton devices using Al<sub>x</sub>Ga(1-x)As are being investigated. The principal problem seems to be stabilizing the Al<sub>x</sub>Ga(1-x)As to prevent decomposition.

Effort in both the self drive systems and the use of III-V semiconductor alloys is continuing.

## Hydrogen Research Programs

### **Syracuse University**

The research funded by SERI at Syracuse University is directed to hydrogen storage.

#### **Hydrogen Storage on Superactivated Carbon at Refrigeration Temperatures**

The objective of this effort is to verify the feasibility of storing >4% hydrogen on activated charcoal. The technical requirements are to establish design and performance characteristics for use in an optimized design operating at refrigeration temperatures. Objectives include comparing the cost and performance of various storage systems.

Apparatus was constructed to measure by volume the amount of hydrogen (99.9999% pure) fed into activated charcoal placed in a pressure chamber. The system was tested at three refrigeration temperatures and pressures up to 55 atm. Voids and adsorbed hydrogen have been measured for different temperatures and pressures. As pressure increases, the difference between the adsorbed and void space increases until about 25 atm and then it decreases to 55 atm.

Performance evaluations of gaseous hydrogen storage (200 atm), liquid hydrogen storage, metal hydride storage, and hydrogen storage on AX-31-M activated charcoal at refrigeration temperatures showed liquid hydrogen was the most attractive storage medium. Metal hydride was more volume efficient at storing hydrogen than activated charcoal and had a higher hydrogen equivalency density, but activated charcoal was more weight efficient. The best results for the activated charcoal system was found at 150°K and 54 atm.

Activated charcoal was estimated to be the least expensive option per MBtu stored at a cost of \$6.96/MMbtu stored. Metal hydride storage was the next most expensive option at \$13.07/MBtu stored. Efforts to characterize hydrogen storage in activated charcoal beds is continuing.

#### ***References--***

Schwarz, J.A., *Carbon Storage: Modification-Assisted Cold Storage (MACs) of hydrogen on Activated Carbon*, Syracuse University, Syracuse, New York, report to SERI, January, 1991.

Hydrogen Research Programs

## Hydrogen Research Programs

### **NASA Needs**

NASA is not involved with earth-based energy systems, although current legislation may change this. However, NASA, has a mission interest in technology transfer of aeronautic and space information and products it develops to terrestrial applications, including those which relate to hydrogen. The following information was obtained from interviews with NASA Headquarters, research and field personnel.

Hydrogen remains NASA's fuel of choice for the foreseeable future; Therefore, NASA has two interests in hydrogen research:

- Solving near-term operational problems; and
- Longer-term research to provide a more economical and assured supply, transport and storage of hydrogen.

Recent leaks associated with the launching of the shuttle have heightened NASA operational personnel's continuing concern about safety and product loss. Concerns were expressed about hydrogen losses during storage and transfer, especially during cool down of the pipes and tanks. The safe use of hydrogen, which is essential to the further development of applications, underlies all of these concerns.

While hydrogen costs represent a small part of overall mission costs, its availability at a reasonable price is essential. NASA expects its requirements for hydrogen to increase many times if it is to perform the missions and develop the vehicles it has under design.

Research concerns about hydrogen revolve around its transfer, storage and use in space. Operating in a zero gravity environment creates unique problems for measuring hydrogen in a tank, transferring hydrogen between tanks, and metering the flow from one tank to another. Storage of hydrogen for years without loss in space will be necessary for NASA to perform a number of its planned missions.

Development of advanced engines for space vehicles and the National Aerospace Plane (NASP) which are hydrogen fueled, are other areas of NASA research interest. Coupled with this interest is the development of slush hydrogen technology to use in the NASP.

Another NASA concern is the development of energy systems for a moon base. Such a system could easily be hydrogen coupled with electricity.

The hydrogen-related R&D topics listed below arose out of the discussions with NASA personnel. They are divided into operational R&D and long-term research topics.

### **Operational R&D**

The following topics have a relatively near-term focus to solve today's problems:

- Equipment, material and practices to reduce losses during storage and transfer of hydrogen
- Improved materials compatible with the hydrogen operating environment of low temperature and high pressure
- Increased understanding of the safety issues surrounding hydrogen through experiments and simulations, from which operating practices can be developed that lead to reduced losses during hydrogen storage and transfer
- Continually improved and updated control systems and components used for hydrogen flow
- Test stand conversion, where possible, from manual control to remote control during tests
- Smart hydrogen sensors for non-air atmosphere and non-intrusive level detection of hydrogen in storage tanks
- Microprocessor-based control system which develops cloud maps from hydrogen detectors using dispersion models to trace leakages to point sources

### **Long-term Research**

The following longer-term research interests were expressed in the NASA interviews:

- Bearings that act as an airfoil using the gas being pumped
- Utility energy system for space, especially the moon -- hydrogen and oxygen with electricity is a natural choice
- Regenerative hydrogen storage in space -- tanks without boil-off for two-year storage
- Methods for transfer and metering hydrogen tanks and transfer in space
- Pressurization of tanks in space to make hydrogen slush
- Advanced cryogenic engines

Hydrogen Research Programs

NASA Needs

- Effective methods of producing slush hydrogen on earth
- Investigation of the infrastructure to be developed in the U.S. to provide the best insurance that, over the long-term, there will be sufficient hydrogen reliably available to NASA.

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## 4: Hydrogen Application Strategies

This chapter develops an estimate of the energy cost of hydrogen in two end-use applications compared with conventional alternatives.

The two applications studied were:

1. Energy delivered to the wheels of a vehicle through the use of hydrogen produced by various renewable resource technologies and electrolysis hydrogen; and
2. Busbar cost of electricity generated from hydrogen, produced from renewable resources, fueling a fuel cell.

The vehicle application compares the cost of hydrogen (per MBtu) delivered to the wheels of a fuel cell powered, electric drive automobile to that of a gasoline-fueled vehicle with an internal combustion engine. The electric utility example calculates the busbar cost of electricity generated by a fuel cell. Penetration of this market is assumed to occur at 10¢/kWh for peaking and about 7¢/kWh for base load power.

These examples are a measure of the status of hydrogen technologies, and the penetration thresholds they must cross.

## Application Strategies

Application Strategies

**Vehicles**

In this section of the report, current baseline renewable and hydrogen costs are established, and projected to reflect current increasing deployment of the technologies. Using these projected costs, the minimum conditions for a transportation application are developed.

The efficiency of the internal combustion (IC) engine over a normal driving cycle is assumed to be 20%<sup>1</sup> and the efficiency of the transmission and remainder of the drive train is assumed to be 75%. Then, the overall efficiency of an IC engine automobile is 15%.

Component	Efficiency (%)
Engine	20
Transmission	75
Overall Auto	15

Table 11: Efficiency of a gasoline IC engine automobile over a normal driving cycle.

A hydrogen fueled automobile could be powered by a fuel cell system having a driving cycle efficiency of 60%. Efficiency of the electronic controller, wires, and the motors could total 80%. The result would be a hydrogen fuel cell powered car with an overall efficiency of 48%<sup>2</sup>.

Assuming the price of gasoline is \$1/gal without taxes and assuming the Btu content of gasoline is 127,600 Btu/gal, the cost of energy delivered to the gasoline powered vehicle's wheels is \$52.24/MBtu. Hydrogen in the tank of a hydrogen fuel cell automobile at \$25.08/MBtu would deliver an equivalent energy cost at the wheels.

Component	Efficiency (%)
Fuel Cell	60
Motors, etc	80
Overall	48

Table 12: Efficiency of a hydrogen fuel cell powered automobile over a normal driving cycle.

It is known that hydrogen can be produced from fossil fuels with steam reforming, partial oxidation, and coal gasification for well under \$20/MBtu. A later phase of this study will explore whether pyrolyzed biomass can produce hydrogen at under \$20 per million Btu. The assumption is that it can.

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<sup>1</sup>Optimized internal combustion engines operate over a range of thermal efficiencies between 20% - 30%, depending on throttle setting and engine speed. For actual vehicle use, an average energy efficiency of 20% is assumed.

<sup>2</sup> Watson, H.C. et al. *Reduction of Cycle Variability and Limit Operation of Alternate Fuels by Pilot Hydrogen in Unmodified SI Engines*. Hydrogen Energy Progress VIII:Proceedings of World Hydrogen Energy Conference. Pergamon Press, New York City, July, 1990.

Can solar, wind, or geothermal energy lead to a cost of hydrogen that is no more than \$25/MBtu, the break even cost in comparison with a gasoline IC engine powered car?

### Photovoltaic Systems

The following analysis calculates the cost of dc power produced from solar PV arrays and the cost of the converted ac power. The analysis is based on the cost reductions experienced as a result of the deployment of other large scale technologies, the cost reductions inherent in the large scale use of PV and hydrogen systems for transportation applications. Dr. David L. Block and Ms. Ingrid Melody, in their World Hydrogen Energy Conference paper<sup>3</sup>, provide the present day figures in Table 13.

These figures result in costs of \$5,850/kW<sub>peak dc</sub>. Assuming utility economics for production of dc power, the averaged levelized carrying charge in constant dollars for a solar system with a tax and book life of thirty years is .108. Given that the average daily solar insolation in the southwest is 5.83 kWh/m<sup>2</sup><sup>4</sup>, then a 12% efficient system would produce 268.1 kWh<sub>dc</sub>/m<sup>2</sup> annually. The annual cost of the solar system, excluding power conditioning is \$657/kW, or 29¢/kWh. This compares with Dr. Block's estimate of 24¢ for the Desert Southwest. The principal difference is his assumption of a 7% discount rate with 4% escalation.

Component	Present
Module efficiency	14%
Balance-of-plant efficiency	90%
Power Conditioner Efficiency	95%
Module Cost	\$600/m <sup>2</sup>
Balance-of-plant Cost	\$100/m <sup>2</sup>
Power Conditioner Cost	\$800/m <sup>2</sup>
O & M Cost	\$3/m <sup>2</sup>

Table 13: Today's efficiency and cost figures for a flat plate PV system.

Learning curves have been used to estimate the ultimate cost of large factory-produced power generation systems<sup>5</sup>. Learning curves have been applied to project the cost improvements made to combustion turbines by General Electric and to fuel cells in numerous studies sponsored by EPRI and others. Given the nature of PV production, as modules are mass-produced in a

<sup>3</sup> Block, David L. and Melody, Ingrid. *Efficiency and Cost Goals for Photoenhanced Hydrogen Production Processes*. World Hydrogen Energy Conference. July, 1990.

<sup>4</sup> Block WHEC paper. Ibid

<sup>5</sup> Bos, Peter B. and Weingart, Jerome M. *Integrated Commercialization Analysis for New Energy Technologies*. Prepared by Polydyne Inc. for Energy Management and Utilization Division, Electric Power Research Institute. July, 1984.

factory, it would seem reasonable to apply a learning curve to PV modules that contains both improvements due to research and increased production volume.

For both combustion turbines and fuel cells, the learning curve applied to each technology is 85%. That is, for every doubling in manufacturing output, the cost of manufacturing the item decreases to 85% of the previous cost. In contrast to large equipment, the semiconductor industry has experienced learning curves between 60% and 90% for the same product in different decades. The learning curve for amorphous silicon solar cells on a cost/kW basis is 66.5% in Solar Hydrogen: Moving Beyond Fossil Fuels<sup>6</sup>, and one might assume that a 66.5% learning curve is appropriate for solar modules. Although that is a very attractive learning curve, we will use a more conservative figure of 85% since we are evaluating deployment of large numbers of large scale systems.

Production (MW)	DC Busbar Cost (\$/kWh)
20	.29
40	.246
80	.21
160	.178
320	.151
640	.129
1280	.109
2560	.093
5120	.079

If we assume current U.S. flat plate solar production is 20 MW/yr, half of world-wide photovoltaic production, then the busbar rates in the Desert Southwest would experience the 85% learning curve with data in Table 14, shown in Figure 19.

Table 14: Effect of learning curve on calculated PV electricity cost, based upon current U.S. production volume.

Using the amorphous silicon solar cells learning curve of .665 yields dc power costs of about \$.03/kWh for production levels of 5,120 MW of solar arrays deployed.

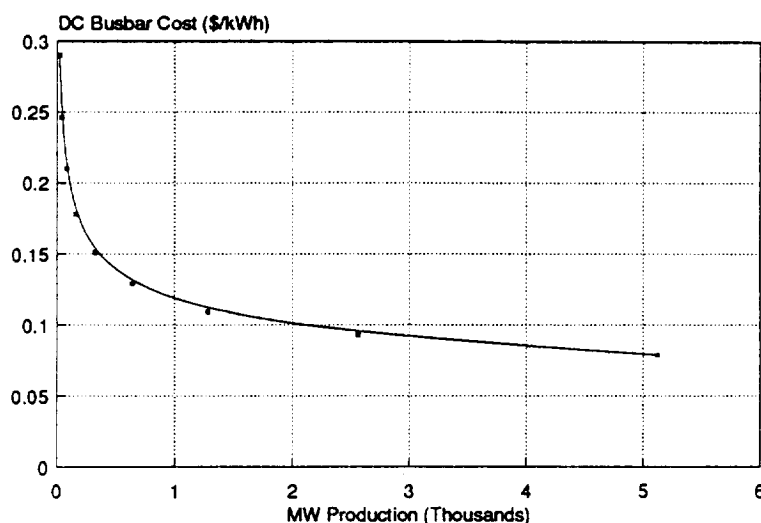
### Wind Systems

Wind energy systems can already produce cheaper power than this study projects photovoltaic technologies will eventually be able to do. In California in 1990, the busbar cost of many wind systems is under \$.07/kWh with a capacity factor of 35%<sup>7</sup>. In Hawaii in 1986, wind was being sold to the local utility for \$.06/kWh<sup>8</sup>.

<sup>6</sup> Ogden, J.M. and R. H. Williams, Solar Hydrogen: Moving Beyond Fossil Fuels, World Resources Institute, Washington, DC, 1989.

<sup>7</sup> *Favorable Forecast for Wind*, EPRI Journal, June 1990, p.15.

<sup>8</sup> Block paper, *ibid.*



**Figure 20:** Learning curve effect on the cost of electricity produced from solar PV.

and other forms of geothermal (volcanic heat) offer a continuous source of steam to use in a turbine for electricity generation for many years. Estimates by HNEI state that geothermal produced electricity could be produced on the island of Hawaii for \$.042/kWh<sup>9</sup>. Facilities such as those in California have operated for years as base load plants.

The cost of a large (>100 MW) electrolysis plant in the United States is not known. In 1983, EPRI conducted a study on the cost and performance of electrolytic cells<sup>10</sup>. The study found that a 1-MW electrolyser costs about \$320/kW (1989\$) of hydrogen produced, and a 10 MW electrolyser costs about \$185/kW of hydrogen produced.

A subsequent study by EPRI for NASA, of the supply of the hydrogen and oxygen needs of the Kennedy Space Center, showed the cost of the approximately 20 MW electrolyser facility to be about \$20 million<sup>11</sup>. This worked out to \$1,000/kW for hydrogen production, compression

<sup>9</sup> *Hydrogen from Renewable Resources Research: Annual Report to the Solar Energy Institute*, Hawaii Natural Energy Institute, Honolulu, HI., August, 1990.

<sup>10</sup> *Market Potential of Electrolytic Hydrogen Production in Three Northeastern Utilities' Service Territories*, EPRI, Palo Alto, CA, PR-1086-13, May, 1984.

<sup>11</sup> Fickett, A.P., and Kalhammer, F.R., *Water Electrolysis, Hydrogen: Its Technology and Implications, Production Technology Vol.1*, CRC Press, Cleveland, 1977, pp 3-44.

Modest improvement in wind systems such as increasing life, reducing maintenance costs, improving turbine designs, and increasing unit size will produce wind busbar power at under \$.05/kWh by 1995. By 2000, decreases in the cost of wind machines, and increases in production quantities should lower costs to under \$.03/kWh.

### Geothermal Power

For prime sites, the harnessing of geysers, water injection in hot rocks

(to 2400+ psig), and one day's plant storage. Annual plant and labor costs were estimated at 1.5% of the plant capital cost. Assuming a levelized carrying cost of 10.8%, refurbishment at 1.75% annually, the cost of pipeline hydrogen due to the electrolysis plant alone would be \$5.96/MBtu for steady state hydrogen production based on 8,600 hours of annual operation.

### **Hydrogen Production Systems**

The matching of the three renewable systems described above and a given quantity of annual hydrogen production (requirements from the previous section) yields very different results independent of the differences in the price of electricity.

In the Southwest, the capacity factor for solar is about 25%<sup>12</sup>. The electrolysis plant for a solar hydrogen production facility whose daily hydrogen volume output is designed to match the output of a utility/electrolysis grid-connected facility requires an electrolysis plant four times larger (except for the compressed hydrogen storage tanks) since it only operates one-fourth of the time. The electrolysis plant serving a solar facility would have a cost of, not \$5.96/MBtu as cited above for an 8,600 hr/yr facility, but about \$18.24/MBtu. The electrolytic cell refurbishment cost increases by four times to \$1.37/MBtu, and the labor and maintenance costs are assumed to double to \$.58/MBtu. The total cost of the electrolysis plant is \$20.19/MBtu of hydrogen produced, without even considering the large cost of the solar/electric equipment. To serve the fuel cell car competitively requires that the solar-produced electricity cost less than \$4.89/MBtu of hydrogen produced. It is estimated that 447 kWh/MBtu of hydrogen produced is required to convert ac to dc, electrolyze and compress the hydrogen. Thus the electricity would have to cost about 1¢/kWh, without considering the cost of transporting the hydrogen to the filling station.

The situation is somewhat better with a wind electrolytic system. With a 35% load factor at the best wind sites, the size of the electrolytic plant would have to be 2.86 times that of a comparably-sized grid connected electrolytic hydrogen plant. This yields a capital cost of \$13.76/MBtu assuming a cost factor of 2.31. The refurbishment cost is 2.86 times that of the grid connected plant or \$.97/MBtu, and the maintenance and labor costs are assumed to be 1.43 times the grid connected cost or \$.41/MBtu. The total facility-related cost is \$15.14/MBtu, leaving \$9.94/MBtu for the input electricity to electrolyze and compress the hydrogen in order to compete with the gasoline IC engine car. Thus, the electricity would have to cost no more than \$.022/kWh.

The situation is much more attractive for geothermal electrolytic hydrogen production. If one assumes an isolated operation with the geothermal plant on line at full capacity 8000 hours per year, then the capacity factor is 91% for the geothermal plant, and the match between the electrolytic plant and geothermal plant is 93%. This yields a capital cost of the electrolytic plant

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<sup>12</sup> Block, *ibid.*

that is 1.071 times the cost of a comparably-sized grid connected facility or \$6.11/MBtu. The refurbishment cost, and maintenance and labor costs are respectively \$.31/MBtu and \$.36/MBtu. The total plant cost is \$7.05/MBtu, leaving \$18.03/MBtu for the electric input energy. This corresponds to \$.04/kWh for geothermal production of electricity, close to the projected cost of geothermal energy in Hawaii. If hydrogen fuel cell cars exist and are inexpensive enough, then geothermal-produced electricity coupled with electrolysis appears to be the most attractive near term renewable hydrogen vehicle option.

## Conclusion

As was mentioned earlier, a fuel cell powered automobile could be expected to have an overall energy efficiency three times as great as a gasoline IC engine automobile. Unfortunately, it is also certain that a fuel cell vehicle will be more expensive than a gasoline IC engine auto. Let us consider what interim hydrogen strategies exist given the combination of the following factors:

- high cost of fuel cells today;
- high cost of PV-produced hydrogen today;
- available technology to put a hydrogen vehicle on the road today;
- growing recognition of the pollution cost of driving an IC engine car.

One possible interim strategy for the introduction of a hydrogen fuel cell auto would build, in the near-term, on the fuel processor (steam reforming) technology for producing the hydrogen-rich (with CO<sub>2</sub>) gas. The reformer could be modified for use at service stations to supply hydrogen for vehicles. Natural gas, available by local distribution pipelines at the service station, would be the fuel to be reformed. Dr. Appleby in his paper *Hydrogen as a Transportation Energy Vector* estimates that natural gas can be steam reformed to provide compressed hydrogen for \$6.80/MBtu with natural gas at \$2.00/MBtu<sup>13</sup>. This could be used in a vehicle with a hydrogen engine with higher efficiency than conventional gasoline engines until a fuel cell car is designed and built.

The storage system for a hydrogen powered vehicle is a major consideration. Estimates of the cost of hydrogen storage for a heavily used vehicle with a range equal to today's gasoline powered vehicles has been calculated for refrigerated superactivated charcoal storage by Dr.

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<sup>13</sup> Appleby, A. John. *Hydrogen as a Transportation Vector*. Presented at NHA's 1st Annual U.S. Hydrogen Meeting, March 1990.



Schwarz<sup>14</sup> for DOE at \$7.46/MBtu/cycle. The storage capacity of the system studied was 880,000 Btu, larger than would be necessary for a fuel cell powered car with a 300-mile range. This cost includes the storage system, utilities (compressor, refrigerator, etc.), and energy cost. A similar study was done by Dr. Schwarz for DOE on stationary applications of liquid hydrogen storage. The storage costs in that case for the entire system, including utilities and energy were: \$10.93/MBtu/cycle for pressurized hydrogen (5000 psig); \$17.94/MBtu/cycle for liquid; \$13.07/MBtu/cycle for metal hydride (FeTiH<sub>2</sub>); and \$6.96/MBtu/cycle for superactivated carbon storage<sup>15</sup>.

The cost of pollution from gasoline, excluding global warming and greenhouse considerations, is estimated at \$9.00/MBtu<sup>16</sup>. The pollution costs of gasoline are estimated to average \$1.10/gal at the pump. This corresponds to \$5,500 over the average 10-year life of an automobile. Add to that the fuel cost saving for a fuel cell powered automobile of about \$15.00/MBtu for using steam reformed hydrogen on a near term basis (about \$1,053/yr), and there may be sufficient incentive to switch to hydrogen. The problem is to determine what should be the long term renewable source of hydrogen.

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<sup>14</sup>Written communication from Dr. J.A. Schwarz.

<sup>15</sup>Amankwah, K.A.G., Noh, J.S. and Schwarz, J.A., *Hydrogen Storage on Superactivated Carbon at Refrigeration Temperatures*, National Hydrogen Association's 1st Annual U.S. Hydrogen Meeting, Washington, DC, March, 1990, pp. 15-1 - 15-12.

<sup>16</sup> Appleby, *ibid.*

Application Strategies

## Application Strategies

### **Electric Utility**

If transportation is one of the most expensive energy markets, then electric utilities are one of the least expensive.

The long-term target cost for the electric utility multi-megawatt fuel cell is \$700/kW<sup>17</sup>. The fuel cell operates on hydrogen and air to produce electricity at 5,600 Btu/kWh (61% net efficiency) using one of several fuel cell technologies. For 6,000 hours of operation (base load, not peaking duty) the fuel cell operation and maintenance and stack replacement costs would have to be 17.4 mils/kWh<sup>18</sup>.

Today's projected capital and operation and maintenance costs of a molten carbonate fuel cell operating on hydrogen, are \$700/kW - \$800/kW and 25 mils/kWh when commercial. Reduction to the targets mentioned above is possible. This leaves 7¢/kWh for fuel, or about \$12.50/MBtu, taking into account the efficiency of the fuel cell. No near term renewable technology has a chance of meeting this fuel target price.

### **Potential Renewable Technology for Producing Low Cost Hydrogen**

Other than inexpensive biomass, the only technology that could meet a target price of \$12.50/MBtu hydrogen fuel is direct water splitting by one of three processes:

- photoelectrochemical
- photobiological
- photochemical

The long term goals for each of the processes are the same, including:

- photocatalyst that lasts at least 5 years;

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<sup>17</sup>Serfass, J.A., *The Market for Fuel Cell Power Plants Within Municipally Owned Utilities*, Prepared by Technology Transition Corporation, Washington, DC for EPRI, Palo Alto, CA. RP-1677-16, January, 1990.

<sup>18</sup> Serfass, *ibid.*

- cost of no more than \$10/m<sup>2</sup> for the photoactive material<sup>19</sup>;
- installed structural cost for the collector system cost of \$125/m<sup>2</sup>; and
- efficiency of 10% to 16%.

The targeted costs for such a system are in Table 15.<sup>20</sup> Other costs are listed in Table 16.

System	Long-term Goal
O & M Cost	10% of facility cost
Indirect Costs	\$.2/MMBtu
Storage	\$.2/MMBtu
Primary Distribution	\$.5/MMBtu
Oxygen Credit	\$1.3/MMBtu
Photocatalyst Life	5 yr
System Efficiency	13%
System Losses	8.75%

Table 16: Other performance R&D goals for photolysis system.

MBtu, if the first commercial facility met the SERI goals and produced hydrogen at \$23.18/MBtu. The market would need to expand 1000 fold to stimulate hydrogen production approaching \$6/MBtu. At this price for hydrogen, 6 to 7¢/kWh power can be produced.

The technology must be developed to produce hydrogen at \$12.51/MBtu. This would assure a long term supply of affordable hydrogen for the auto market to replace steam reformed

Component	Cost (\$/m <sup>2</sup> )
Collector	45
Balance of System	27
Support & Installation	43.8

Table 15: Component costs of a photolysis system meeting overall system cost target of \$125/m<sup>2</sup>.

The net effect of meeting these goals is hydrogen produced at \$23.18/MBtu for one large facility producing hydrogen at the rate of 10 million scf/d.<sup>21</sup> Running this technology down a learning curve would require approximately a 20 time (200,000,000 scf/d) expansion in the market to achieve a price of \$12.51/

<sup>19</sup>Copeland, Robert, *Photochemical Hydrogen Production System*, Hydrogen Energy Progress VIII: Proceedings of the 8th World Hydrogen Energy Conference, Honolulu, HI, July, 1990, Pergamon Press, New York, p. 207.

<sup>20</sup>Copeland, Robert, *Photochemical Hydrogen Production System*, Hydrogen Energy Progress VIII: Proceedings of the 8th World Hydrogen Energy Conference, Honolulu, HI, July, 1990, Pergamon Press, New York, p. 207.

<sup>21</sup>ibid, and private discussion, September, 1990.

natural gas. Dominance of that market by hydrogen vehicles will cause the price of hydrogen directly produced by photoprocesses to decrease dramatically as more hydrogen for vehicles is produced. However, progress in this technology is slow. It is problematic whether such stringent goals will be achieved because at this time, efficiencies have not exceeded 3% in sunlight for any of these technologies.

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## **5: Conclusions and Recommendations for Future Work**

This initial review of hydrogen technology and DOE research has provided some insight into the current state of technology and the paths that would be required for hydrogen to play a role in our energy future.

To develop hydrogen as a fuel, comprehensive energy systems must be developed from production to use. As far as possible the current infrastructure for energy production delivery, transportation, and use should be utilized. Early niche markets for hydrogen will appear as direct substitutes for other fuels. Once hydrogen is established in the market niches, the system using hydrogen will slowly be modified to optimize its use, and new technologies developed specifically for hydrogen will be introduced. The orientation of the conclusions in this report are presented with this thought firmly in mind.

## Recommendations

### **Technology Summaries**

Only about 20 hydrogen technologies are examined and summarized in this report. There are at least as many technologies that were not covered in this initial report that will be addressed in future years.

Subsequent phases of this report must also develop missing cost information and update the information that is presented as additional research results on commercial activity is reported.



## Recommendations

### **SERI's Hydrogen Research Program**

SERI's hydrogen research budget of approximately \$2.5 million is inadequate to address the range of technologies that would constitute a robust hydrogen program. The program is forced to pick and choose technologies to support, without the resources to establish and maintain a strategic direction on a broad front. The principal hydrogen activity for SERI funding has been the four university research centers at Texas A&M, University of Hawaii, University of Miami, and University of Central Florida. In-house research has also been funded in biological hydrogen production and photolysis. There is also research at Syracuse University on hydrogen storage on superactivated charcoal at refrigeration temperatures.

Given its limited resources, the SERI hydrogen program has the correct strategic focus. It has avoided commitment to large demonstration projects which it could not sustain and to projects that are inappropriate, given the state of development of most hydrogen technologies. Based on preliminary analysis in the study, it is performing basic research in the most promising hydrogen technologies - biomass, biological hydrogen production, and photoelectrochemical hydrogen production - at a sustainable level for the resources at hand. The storage technologies that it is funding seem to be the appropriate ones for those categories of hydrogen storage.

Strategically the SERI hydrogen program has two problems. First, to continue to be effective, the SERI Hydrogen Program must decide whether its principal activity is a mission-oriented program, or if it is principally a funder of basic and applied university research. Since it is the national focus for hydrogen research, either role is appropriate. However, the program can not continue to write a mission-oriented program plan *and* implement a university-based pure and applied research program. Second, the program needs a vision of the future for hydrogen technology to which it can tie its research and other activities. Only the University of Hawaii has the type of balance between mission, research activity, and practical goals that should be the foundation of the national hydrogen program directed from SERI. A large part of the second problem is that DOE has not articulated national energy goals that include hydrogen as clearly as has been done by the State of Hawaii. Without that level of commitment and resources, a strong case can be made for a hydrogen program oriented toward basic and applied research.

The tactical effect of the confusion over whether the program is mission-oriented or not is one of emphasis. This is most clearly illustrated in the area of photolysis. There are photolysis activities at three of the four university hydrogen centers and at SERI. These are parallel activities aimed at the same basic objective with commercialization dates in the 2010 to 2020 time frame at the earliest. The projects are applied and basic research, which are important and should be supported, but not as a mission-oriented program at four different locations. However, a mission-oriented approach is probably justified in the case of biomass gasification, particularly if hydrogen production from biomass can be added as a task to existing biomass projects managed by the Biomass Program. There is one biomass pyrolysis activity at the University of

## Recommendations

Hawaii. This activity is being run out of the biomass program. The emphasis of the Hawaii program on biomass is on alcohol production, not hydrogen.

Finally, industry university partnerships should be fostered. Ultimately industry, not the universities, are going to make these technologies work. Early on industry and universities should be working hand in hand on developing and fabricating these technologies. For instance, Texas A&M should be trying to work with Texas companies like Texas Instruments on photoelectrochemical conversion technologies. The annual reports to SERI from the university laboratories are full of fabrication failures some of which might be avoided with closer industry-university cooperation. The universities should be developing the ideas, designing the systems and having industry fabricate them with university technical support. NHA recognizes that given the political nature of federal hydrogen funding, many of these problems have been beyond the control of SERI.

## Recommendations

### NASA

NASA needs have been previously addressed beginning on page 91. However, several observations are worth stating. The NASA hydrogen program needs a breakdown in operation and long-term research. The near-term research needs to revolve around availability, cost, safety, leak detection and reduction in hydrogen losses. Sometime in this decade, NASA will have to build new facilities using state-of-the-art technology, or refurbish its existing facilities and upgrade its aging systems. NASA researchers are concerned with NASA's ability to carry out its long term mission. This includes the transfer, storage and handling of hydrogen in space; developing techniques to produce slush hydrogen for the aerospace plane; and developing energy systems for a moon base. Spinoffs from technologies developed for these applications are likely to find their way into terrestrial applications in the future. Beginning a dialogue on this question in the near future is a worthy consideration.

## Recommendations

### Application Studies

#### Vehicle

The application study for vehicles reached several conclusions.

- Wind is an economically viable alternate technology today for electric production.
- Photovoltaic technology will likely become a viable technology for electric production in the Southwest by approximately the year 2000.
- A preliminary analysis indicates that a break-even cost for hydrogen in a fuel cell powered automobile is \$25/MBtu if gasoline is \$1 per gallon.
- Intermittent sources of electricity (PV, wind, solar thermal) combined with an electrolysis facility can not produce hydrogen for much under \$25/MBtu even if the electricity is "too cheap to meter". To produce the same quantity of hydrogen as a grid connected unit, the PV and solar thermal electrolysis facility must be four times its size, and the wind energy electrolysis facility about three times its size. This is not true for the geothermal unit which is a base load facility.
- Geothermal power coupled with electrolysis can just meet the \$25/MBtu price, with an electricity price of just over 4¢/kWh.
- Gasified biomass is likely to be a cost-effective renewable resource that could be produced for well under \$25/MBtu. This needs to be investigated in depth.

#### Electric Utility

- To produce 10¢/kWh electric energy from \$12.50/MBtu hydrogen almost certainly requires a fuel cell because of its high efficiency.
- As a practical matter, a fuel cell would have to operate for 6,000 hours annually for the 10¢/kWh electric price to be achieved with \$12.50/MBtu hydrogen.
- The only technologies with a possibility of supplying hydrogen at roughly \$9/MBtu the requirement to justify 6,000 hours of utility fuel cell operation on economic dispatch are photoelectrochemical, photobiological, or photochemical technologies that may be competitive in the 21st century.

## Recommendations

- The photolysis technology(ies) must meet their long term SERI program goals (\$125/m<sup>2</sup> for collector system with a 30 year life, 10/m<sup>2</sup> for photoactive material with a 15 year life), and then, have the technology mass produced to drive down costs.
- Saturation of the vehicle fuel market by hydrogen would probably be necessary to drive cost down sufficiently in order to allow penetration of the utility market.
- The energy utility vision is to integrate hydrogen with electricity which will provide new challenges and opportunities for a transportation market. Appropriate economic paths need to be identified for utilities to be hydrogen suppliers in the future

## Recommendations

### **Technology Assessment Phase III**

Continuation of the Technology Assessment will both expand the base of technologies covered and probe more deeply into the analysis of the applications examined in this Phase I effort. While the work plan has not been developed yet, the following tasks are anticipated. Phase II will be supported by both NASA and the Department of Energy's hydrogen program managed by the Solar Energy Research Institute.

The following tasks are planned for 1991 under NASA sponsorship:

Task 1: Develop approximately ten additional technology summaries. The list of technology summaries to be added will include those recommended by the NHA Technology Review Committee or the NASA/SERI sponsors. These might include:

- Geothermal hydrogen production
- Ocean thermal hydrogen production
- Solar thermal hydrogen production
- Cavern hydrogen storage
- Phosphoric acid fuel cell for hydrogen applications
- H<sub>2</sub>-O<sub>2</sub> storage
- Space applications of hydrogen
- Catalytic steam reforming hydrogen production
- Magnetic refrigeration for H<sub>2</sub> liquefaction

Task 2: Revise and enhance the Technology Assessment Report. The following activities are anticipated:

- Modification of existing summaries to include new information
- Updating other elements of the report to include new technologies assessed
- Incorporating the findings of 1991 SERI-sponsored tasks into report
- Develop an assessment of NASA-funded hydrogen research similar to that prepared for DOE/SERI

## Recommendations

- Develop a preliminary assessment of hydrogen applications in subsonic aircraft, and water heating and space conditioning

The following tasks are planned for 1991 under SERI sponsorship:

Task 3: Assess industry's hydrogen technology interest and R&D capabilities through targeted meetings and discussions. Identify preliminary interest in cooperative government/industry research projects.

Task 4: Develop detailed energy and economic paths to technology development for hydrogen applications. In 1991, describe the technically possible and economically promising options for hydrogen vehicles and utility hydrogen generation and storage. Determine the technology development steps necessary to achieve the technical goals.

Efforts beyond 1991 will assess subsonic aircraft and space and water heating applications of hydrogen, eventually leading to an integrated vision for hydrogen as an energy carrier and fuel.

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## Appendix A: Hydrogen Data

Chemical Formula .....	H <sub>2</sub>
Molecular Weight .....	2.0159
Normal Boiling Temperature (NBT) at Atmospheric Pressure, °F .....	-422.97 (20.39K)
Freezing Temperature at Atmospheric Pressure, °F .....	-434.5 (14.0K)
Critical Temperature, °F .....	-399.95 (33.18K)
Critical Pressure, psia .....	190.75
Critical Density, lb/cu ft .....	1.88
Density of Liquid at NBT, lb/cu ft .....	4.43
Specific Volume of Saturated Vapor at NBT, cu ft/lb °F .....	12.032
Specific Heat of Liquid at NBT, Btu/lb °F .....	2.3
Specific Heat Ratio (c <sub>p</sub> /c <sub>v</sub> ) of Vapor at 86°F and One Atmosphere Pressure .....	1.4
Thermal Conductivity, Btu ft/sq ft hr °F:	
Saturated Liquid at NBT .....	0.069
Vapor at Saturation Pressure at NBT .....	0.0092
Vapor at One Atmosphere Pressure at 86°F .....	0.105
Viscosity, Centipoises:	
Saturated Liquid at NBT .....	0.0131
Vapor at Saturation Pressure at NBT .....	0.0011
Vapor at One Atmosphere Pressure at 86°F .....	0.009
Color .....	Clear/water white
Flammability Limits (Vol. % in air) .....	4.1 - 74
Toxicity, Underwriters' Laboratories Classification .....	Group
Calorific Value:	
LHV Btu/SCF* .....	274
HHV Btu/SCF* .....	324
* 60°F, 14.696 psia	

**Table 17: Hydrogen Data Sheet**

Hydrogen Data

List Prices for Hydrogen		#/MMBTU
Liquid Hydrogen (Bulk at Plant)	\$15 - \$20 (25 TPD to 5 TPD)	
Liquid Hydrogen (Dist. by trailer)	\$0.60 - \$0.70 (per 100 mi RT)	
Liquid Hydrogen (Dewar Size)	\$30 - \$50 (500 liters to 10 liters)	
Gaseous Hydrogen (Bulk/pipeline)	\$10 - \$15 (25 TPD to 5 TPD)	
Gaseous Hydrogen (Tube Trailer)	\$200 - \$300 (100 psig short haul)	
Gaseous Hydrogen (Cylinder)	\$600 - \$800 (manifold pallet to cylinder)	

NOTE: 1) Assume product derived from steam methane reforming and using lower heating value.  
2) TPD = Tons Per Day; R/T = Round Trip

Table 2: Price data for hydrogen (1991 NASA Calculations).

Weight of Liquid or Gas Hydrogen		Volume of Liquid Hydrogen @ NBP		Volume of Hydrogen Gas @ 70°F & 1 ATM	
lbs	Kg	liters	gallons	ft <sup>3</sup>	m <sup>3</sup>
1.000	0.454	6.409	1.693	191.96	5.436
2.205	1.000	14.130	3.733	423.26	11.984
0.156	0.071	1.000	0.264	29.95	0.848
0.591	0.268	3.785	1.000	113.37	3.210
0.521	0.236	3.339	0.882	100.00	2.832
0.184	0.083	1.179	0.311	35.31	1.000

Table 3: Hydrogen Measurements

Hydrogen Data

1 kWh = $3.6 \times 10^6$ Joules
1 Btu = 1,055 Joules
1 GJ = .9479 MBtu

Table 4: Energy Conversion Table

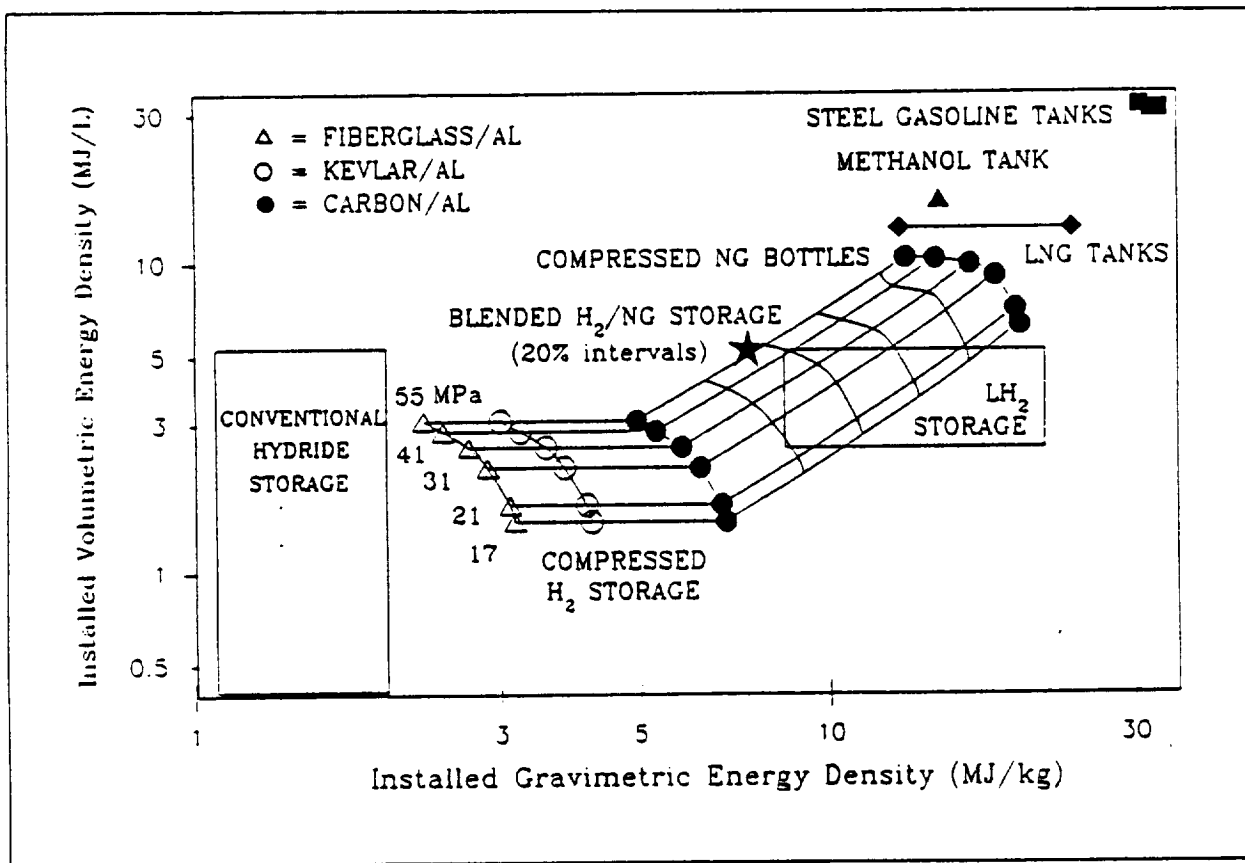


Figure 1 Comparison of several hydrogen and other on-board fuel storage system energy densities. (Block, et al. 1988).

<sup>1</sup> " Baseline car: 400 mile range, 40 mpg, 1 ton curb weight. CH<sub>2</sub>, compressed H<sub>2</sub>; LH<sub>2</sub>, Liquid H<sub>2</sub>; CCH<sub>4</sub>, compressed methane; LCH<sub>4</sub>, liquid methane." Included in Florida Solar Energy Presentation of "An Overview of Hydrogen Research at the Florida Solar Energy Center," DOE/SERI Hydrogen Program Review, January 23-24, 1991, Washington, DC.

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