SOLAR HYDROGEN CHRONICLES

edited by

Walt Pyle

Solar Hydrogen Chronicles

A Hands-On Guide to Solar Hydrogen Fuel:

Production
Purification
Storage
Utilization

A Collection of Articles about Hydrogen from *Home Power* Magazine

edited by Walt Pyle

TOC
▶

Wheelock Mountain Publications
Wheelock VT USA

Solar Hydrogen Chronicles

Version 1-03. Publisher, Wheelock Mountain Publications, 324 Minister Hill Road, Wheelock VT 05851, USA.

This booklet is sold for information use only. The buyer assumes complete personal responsibility for the use or misuse of the information contained in this booklet.

The articles in this e-book were originally published in Home Power magazine in the period 1991-1998.

Although care is taken to present accurate information, the authors and publisher will not retro-actively inform or re-imburse buyers if [or when] there are corrections or updates and revisions to this e-book.

TOC

How to use this e-book

Text links

Click on **maroon colored text** to go to a link within the e-book.

Click on **blue colored text** to go to an external link on the internet. The link will automatically open your browser. You must be connected to the internet to view the externally linked pages.

Buttons

The **TOC** button will take you to the table of contents.

The left facing triangle will take you to the previous page.
The right facing triangle will take you to the next page.

Table of Contents

Introduction

Production of Solar Hydrogen

Purification of Hydrogen

Storage of Hydrogen

Utilization of Hydrogen: Cooking

Utlization of Hydrogen: Space Heating

Making Electricity with a Fuel Cell

Transportation (Fuel Cells and Engines)

Future Developments

Click the chapter title or number to go to that chapter.

TOC

Acknowledgments

The editor gratefully acknowledges the following authors, who shared their experience and knowledge about small home-sized applications of hydrogen technology, through Home Power magazine articles.

David Booth

Reynaldo Cortez

John Dabritz

Mark Hayes

Jim Healy

Dr. Conrad Heins

Clifford W. Mossberg

Mark Newell

Richard Perez

Amanda Potter

L.E. Spicer

Alan Spivak

Dr. Robert Wills

TOC

Forward

Solar Hydrogen Chronicles includes all of the articles about hydrogen that were published in **Home Power magazine issues #1 to # 59** during the 1990s. We wanted to get all of the "hands-on" Home Power articles on hydrogen together in one booklet to improve the access for those with an interest in this topic.

Hydrogen is a **non-carbon fuel**, as defined below. And, **hydrogen is an energy carrier** as well. It is referred to as an energy carrier because the energy required to obtain hydrogen from water, or from a hydrocarbon, must be an input to the process. When combined with air or oxygen, hydrogen can be used as a fuel for many human needs, such as **cooking, water heating, space heating, electricity generation, and transportation**. Hydrogen can also be used with air or oxygen in a torch for the welding, cutting, and heat-treating of various materials.

> **Fuel: A material that is bumed to release heat energy,**
> **for example, hydrogen, coal, oil, or uranium.**

TOC

Solar hydrogen is a **non-carbon fuel** made from sustainable, renewable resources: sunlight and water. Our nearest star, the sun, produces radiant energy that constantly reaches our planet. We experience this radiant energy as heat and light. The arriving solar radiant energy can be converted directly into electricity by photo-voltaic [solar electric] cells, and indirectly by windmills, and hydroelectric turbines. The electricity produced by these renewable resources can then be used to make hydrogen and oxygen from water by electrolysis. It is also possible to concentrate solar energy and use it in thermal processes that produce hydrogen and oxygen from water.

The **emissions** from a hydrogen flame contain **no carbon oxides [no carbon dioxide, CO_2 , and no carbon monoxide, CO]**. The emissions from a hydrogen air or hydrogen-oxygen flame do not contain hydrocarbons.

Hydrogen is a gas at ambient temperature and pressure. Hydrogen is the lightest gas known. It is much lighter than air, and is very buoyant in our atmosphere. It has a Specific Gravity at 75° C and 1 atmosphere pressure of 0.06952 [air = 1.00000].

At a very low temperature, 20.1° Kelvin [-252.9° C, or -423.2° F] and atmospheric pressure, hydrogen may be liquefied. Below O.l° K, hydrogen may become slush or even solid.

The hydrogen atom [H] is the simplest atom, consisting of one proton and one electron with atomic weight 2.0l6. The electrons on hydrogen atoms possess spin and the hydrogen molecule [H_2] is formed from two hydrogen atoms only when two hydrogen atoms with opposite spin are combined. Two isomeric forms of hydrogen exist at equilibrium: ortho-hydrogen [parallel spin] and para-hydrogen [antiparallel spin]. At or above ambient temperature, the equilibrium ratio is 75:25 ortho-para.

Advantages of hydrogen as a fuel include:

- clean-burning nature
- sustainability
- versatility as a chemical feed-stock

Burning hydrogen with oxygen produces only water and heat as the combustion products. The water can be re-cycled by a solar hydrogen production process to make more hydrogen and oxygen. This cycle can be repeated essentially forever in human terms.

Disadvantages of hydrogen as a fuel include:

- lack of existing distribution infra-structure
- difficulty of storage due to low energy density
- wide flammable and explosive limits

The existing fuel distribution infra-structure consists of pipelines, tankers [ships, trains, trucks, airplanes] and service-stations that provide gaseous and liquid hydrocarbon fuels to homes, motor vehicles and industry. At this time there is only a very limited bulk hydrogen distribution infra-structure. A few short industrial hydrogen pipelines can be found in petro-chemical corridors. Most of the largest hydrogen production plants use the gas at the site of manufacture [for example, petroleum refining, fertilizer production]. Small

TOC

merchant supplies are often handled as compressed gaseous hydrogen using heavy high-pressure steel cylinders, with a high associated unit cost. Hydrogen supplies for intermediate sized sites, such as rocket propulsion or metallurgical processing plants, are usually handled as liquid hydrogen, and delivered in tankers.

The hydrocarbon fuels provide excellent energy-storage-density. Hydrogen does not enjoy a high energy storage density, and other ways must be found to overcome this limitation. Section 4 on Hydrogen Storage gives the details

Flammability limits and detonation limits are wider with hydrogen than with hydrocarbon fuels. Whereas hydrocarbons can be stored safely over a wide range of "rich" air-fuel ratios that are not flammable, the strategy for hydrogen storage is to store only pure gas [>99+% hydrogen].

At this juncture, most of the hydrogen used worldwide is produced by a process called "steam-reforming of hydrocarbons." Production of hydrogen at the present time, using the steam-reforming method, is not considered sustainable. This is because the hydrocarbons now used [natural gas, oil, coal, etc.] come from finite fossil resources that are being rapidly depleted. In the future, steam-reforming of bio-mass hydrocarbons may be used to produce hydrogen and hydrocarbons.

TOC
◀ ▶

Forward

In the near future, fuel cells, based on electro-chemical combustion of hydrogen with air, can be expected to replace existing stationary and mobile power plants. Those power plants now based on internal combustion engines and gas turbines will have poorer emissions and fuel economy performance than fuel cells. Fuel cells are now targeted for the transportation and distributed power generation sectors.

As we go to press on this First Edition of Solar Hydrogen Chronicles we have recently witnessed tremendous political and environmental concern over Global Warming, that has been brought to focus by the Kyoto Conference. We believe hydrogen will play an important role in reducing our man-made atmospheric contaminants and reaching the emissions reduction goals that have been set.

Walt Pyle
Editor
March 2, 1998

TOC
◀ ▶
x

Forward from the first edition

Hydrogen As A Potential Fuel

by Conrad Heins

Originally published in Home Power #21 • February / March 1991

In a world facing the real possibility of disastrous global warming, a fuel that does not produce carbon dioxide would appear to be a real godsend. Carbon dioxide is the ubiquitous by-product of all other combustion processes and the most important greenhouse gas responsible for that warming. Hydrogen is a potentially attractive replacement for both coal and oil as a fuel source because it produces no pollutants when it is burned. Only water is formed.

$$2\ H_2 + O_2 \text{ ---------> } 2\ H_2O$$

Although it will most likely play a role as a fuel in a renewable energy society, I believe that at the present time it is a mistake to push the use of hydrogen as a substitute for non-renewable carbon based fuels. Let me explain why.

TOC

Conservation

First and most importantly, the proposal to substitute hydrogen for other fuels is addressing the problem from the wrong end. We should be concerned far more with reducing the need for fuel, through conservation and improved energy efficiency, than with replacing a "dirty" fuel with a "clean" one. In the United States we use about twice as much energy as the Germans or Scandinavians to accomplish the same tasks, whether they be heating homes or driving to work. We need to focus not on the supply-side but on the demand side of the energy equation.

Application

A second, related point is that by addressing the problem in terms of supply we tend to ignore how the energy is being used, We fail to ask the critical question, "Is this particular kind of energy the best answer for this particular application?" Only when this question is posed are we able to to make judicious choices, especially if we want to take into account the second law of thermodynamics efficiency considerations, which deal with energy quality as well as energy quantity, or environmental impacts.

Reaction

Third, hydrogen is a far more reactive chemical than any of the materials that are currently used as fuels. I am not talking about flammability or explosiveness, but rather hydrogen's ability to undergo chemical reactions with other compounds. It is a good reducing agent; it adds to double bonds, causing embrittlement of plastics and elastomers; and, because it is such a tiny molecule, hydrogen can even work its way between the atoms of metals such as steel, causing hardening and embrittlement.

TOC
◀ ▶

Unrenewable

Fourth, hydrogen is not made from a renewable energy source. Virtually all of it is produced from natural gas, methane, by an endergonic reforming process that uses steam.

$$\mathbf{CH_4 + 2\ H_2O \text{-------------}> CO_2 + 4\ H_2}$$

It might be argued that because part of it comes from water we are obtaining the hydrogen, at least partly, from a renewable resource. However, the energy captured in the hydrogen will always be less than the energy in the methane plus the energy required to drive the reaction. And carbon dioxide is still produced; as much, in fact, as would be formed if the methane were burned as a fuel in the first place! Why waste energy to produce an energy storage material that is far more difficult to store and handle than the fuel it is made from, especially when the starting fuel is the cleanest burning of any of today's primary energy sources.

It must be emphasized that hydrogen is made from natural gas because this is the least expensive way to make it - considerably less expensive, for example, than of using electrolysis of water using electricity at off-peak rates. It is unrealistic to assume that, at least for the near term, hydrogen would be made in any quantity from anything but methane. We are left with the likelihood that the "hydrogen economy", like today's "hydrocarbon economy", would be based on a non-renewable resource.

TOC
◀ ▶

Solar Hydrogen

Of course, it is possible to break apart water and obtain hydrogen in other ways. The formation of hydrogen and oxygen from water using electricity is the one that is most often touted. If the electricity is provided by PV panels, we are talking about using a renewable energy resource, sunlight, to provide hydrogen in a non-polluting way. Such a proposal, when first heard, sounds attractive. However, a little further examination indicates that is not a good answer.

The biggest problem is the prodigious amount of electrical energy that would be required to replace even a portion of the hydrocarbon fuels we now use. Wilson Clark, in his classic book, Energy For Survival, makes his point very clear.

"The amounts of hydrogen that would be required in a hydrogen economy are enormous. For instance, according to Dr. Gregory, to produce enough hydrogen to fully substitute for the natural gas produced in the United States at the present time [1974] - i.e., 70 trillion cubic feet of hydrogen - would require more than 1 million megawatts of electric power to produce. Total electric generating capacity in the United States is only 360,000 megawatts. To meet the projected hydrogen requirements for natural gas alone would call for a fourfold increase in generating capacity, which would mean building 1,000 additional 1,000-megawatt power stations! This does not provide for increased electric power demand for other purposes, nor does it take into account the generation of hydrogen for transport fuel or as an additive in chemical and industrial processes."

By way of comparison, world production of photovoltaic generating capacity was about 50 megawatts (peak sun) last year. Even if this capacity were to be increased a 100-fold and all of it used to produce hydrogen, we would still be making a fraction of 1% of what would be needed to replace the natural gas consumed in the U.S. In addition…

Storage

Why use electricity, the most versatile form of energy available, to produce a material that is not easily stored (the boiling point of hydrogen is -435°F, about 22°K above absolute zero) or handled and that will probably be burned to produce mechanical energy in a process that will be less than 30% efficient… when the electricity might be used directly?

If energy storage is needed, why do it through such a difficult-to-store material for which large scale storage technologies do not even exist, when electricity can be stored in batteries, flywheels or pumped storage systems far more effectively?

Efficiency

If it is to be used for transportation, why select a process that will operate at no more than 30% efficiency (an internal combustion engine) when an electric motor can be used that is at least 75% efficient? And why select a fuel that is so difficult to deal with in a mobile situation? (Wilson Clark, one of the early proponents of hydrogen fuel, includes a good discussion of the hydrogen powered automobile in Energy For Survival. He points out that a Dewar flask type container for liquid hydrogen that would that would hold the energy equivalent of 15 gallons of gasoline would have to be about 37 gallons in size and would cost (1974 prices) about $1,800. The use of metals, such as magnesium, to store hydrogen as a metal hydride would require an even larger volume).

Why Photovoltaics

Finally, why photovoltaics? As pointed out earlier, photovoltaics is not a good choice for generating vast amounts of electricity. It is much more suitable for smaller scale applications where grid power is not available. Although it will probably be used to generate utility power as well, utilities have never considered using it in any other capacity than for peaking power. In addition, these systems presently produce electricity at a cost of from $.25 to $.75 per kilowatt hour (20 year life cycle cost). Even were the cost to

TOC
◀ ▶

be cut in half, which is what we expect to happen during the next decade, we are talking about a much more expensive kind of electricity than could be produced by other renewable sources, such as the LUZ concentrating solar thermal facility that is presently supplying peaking power to the Los Angeles basin at about $.08 per kilowatt hour.

If these questions are answered primarily by, "because photovoltaics is renewable and non-polluting, and the burning of hydrogen produces no pollutants", I suggest that a much more thorough analysis of the situation needs to be carried out.

Access

Dr. Conrad Heins teaches a course in renewable energy, including photovoltaics, at Jordan College, 155 Seven Mile Rd, Comstock Park, MI 49321

Hydrogen Basics

by Amanda Potter and Mark Newell

Originally published in Home Power #32 • December 1992 / January 1993

Home Power is gearing up to use hydrogen fuel for cooking. We've been hoping to eliminate or at least reduce our propane use for a long time now and have been encouraged by the interest and enthusiasm in hydrogen that we've seen in our readers.

Hydrogen is not a source of energy; rather, it is a non-toxic means of storing and transporting energy. Any energy source can be stored in the form of hydrogen. Solar, wind and hydro power can be used to break down the molecular bonds which bind hydrogen in hydrocarbons and water. Hydrogen, unlike electricity, is efficiently transported over long distances (through pipelines, for example). It enables energy produced in areas where renewable energy resources are abundant to be safely transported to areas with high energy use. Part of hydrogen's virtue as an energy storage medium is the fact that energy stored in the form of hydrogen can be converted into different forms of usable energy without producing pollutants. Heat or electricity can be produced, with water as the primary by-product.

TOC

Catalytic Combustion

Hydrogen can be recombined with oxygen to produce heat in the normal combustion process or it can be recombined in a fuel cell to produce electricity. In both cases the primary by-product is water. Burning hydrogen produces some nitrous oxides because of the high burning temperature. However, using a catalyst (such platinum or nickel) lowers the temperature and decreases the surface area of the reaction, which increases efficiency and reduces the nitrous oxides to a negligible amount. Pure catalytic combustion uses a catalyst to cause the hydrogen-oxygen recombination to occur without the input energy of a flame. There is a 100% efficient conversion of hydrogen to heat when temperatures are kept below 100° Celsius or 212° Fahrenheit.

Converting a propane stove to run on hydrogen is a fairly simple process. Low tech, inexpensive catalysts such as stainless steel wool (3%-22% nickel) work well and are easy to use. However, stainless steel wool is not as effective in eliminating nitrous oxides as more expensive catalysts. For more information on these operations see Fuel From Water by Michael Peavey. Also look in your local library under hydrogen.

TOC
◀ ▶

The Electrolyzer

An electrolyzer is a device that uses electric current to electrolyse or split water (H_2O) into hydrogen and oxygen. (See Electrolyzer Physics, p.17) Electrolysis is currently the cheapest, simplest, and most efficient method of home scale hydrogen generation. Well-made and relatively inexpensive electrolyzer cells are available from Hydrogen Wind in Iowa. Each electrolyzer cell requires 2 Volts; the current determines how much hydrogen they produce. (See Hydrogen Fuel, p.32 and Water Electrolyzers, p.38.)

How Much Hydrogen Would We Use?

We plan to use electrolyzers to produce hydrogen, but how much hydrogen do we need? Ideally we would like to supply the gas needs for the eight of us that live here on Agate Flat. That, however, is no small feat! In order to determine how much hydrogen we need to produce and store, we calculated how much hydrogen we would use on a daily basis. Here's how much hydrogen we would need to run the cookstove, our only gas appliance: there are 82,000 British thermal units (BTU) per gallon of liquid propane. A 5 gallon tank of propane lasts us approximately twenty days. We therefore use:

$$\frac{82{,}000\,\text{BTU}}{\text{gal}} \times 5\,\text{gal} = 410{,}000\,\text{BTU every 20 days}$$

$$\text{or } \frac{410{,}000\,\text{BTU}}{20\,\text{days}} = 20{,}500\,\text{BTU every day}$$

How much electricity do we need to run through electrolyzers to produce 20,500 BTU of hydrogen? We have a number for converting BTU into kilo-

TOC
◀ ▶

watt-hours (kW-hr) of electricity but it assumes 100% efficiency. With the kind of electrolyzers we are looking at, we expect the efficiency to be about 50%.

$$1\,\text{BTU} = 2.9287 \times 10^{-4}\,\text{kW–hr}$$

$$\frac{20{,}500\,\text{BTU} \times \left(2.9287 \times 10^{-4}\,\frac{\text{kW–hr}}{\text{BTU}}\right)}{0.5\,\text{efficiency}} = 12.0\,\text{kW–hr}$$

This means we would need 12 kW-hr input to the electrolyzers each day to produce hydrogen for our daily cooking needs. This is a lot of electricity! There are a lot of us up here now, but we are going to need to find more efficient ways of our cooking and heating hot water if we hope to power our entire stove with hydrogen. We are planning on installing a solar hot water heater. We presently use our solar oven almost every sunny day and we are planning on building a larger one to further cut down on our propane use.

A Realistic Approach

We can begin by supplementing our propane use with hydrogen. The next question is how much hydrogen can we produce. Home Power will soon be adding two trackers to test. With our additional loads, this will add about 1.5 kW-hr surplus power per day. We use the following conversion factors to

TOC

determine how many cubic feet of hydrogen (at atmospheric pressure, 1 atm.) 1.5 kW-hr will produce and how much energy in BTU this amount of hydrogen will give us.

$$1\ \text{ft}^3\ H_2\,(\text{at } 1\ \text{atm}) = 0.0791\ \text{kW–hr}$$

$$\text{or } 1\ \text{kW–hr} = 12.6\ \text{ft}^3\ H_2\ (1\ \text{atm})$$

$$1\ \text{ft}^3\ (1\ \text{atm}) = 270\ \text{BTU}$$

Using the above conversion factors,

$$\frac{1.5\ \text{kW–hr}}{\text{day}} \times \frac{12.6\ \text{ft}^3\ (1\ \text{atm})}{\text{kW–hr}} \times 0.5\ \text{eff} = \frac{9.45\ \text{ft}^3\ H_2\ (1\ \text{atm})}{\text{day}}$$

$$\frac{9.45\ \text{ft}^3\ H_2\ (1\ \text{atm})}{\text{day}} \times \frac{270\ \text{BTU}}{\text{ft}^3\ H_2\ (1\ \text{atm})} = \frac{2551.5\ \text{BTU}}{\text{day}}$$

We will be able to produce 9.45 cubic feet of hydrogen at atmospheric pressure (or 2550 BTU hydrogen) each day from our 1.5 kW-hr/day surplus energy. This will only run our cookstove burner (assuming 10,000 BTU/hour) for a little more than 15 minutes.

TOC

Storage

Now that we have the hydrogen, how do we save it until we need it? Hydrogen storage can be complicated and costly. Hydrogen can be stored as a liquid, in a metal hydride, or as a pressurized gas. Liquid hydrogen at -253°C requires costly and complex storage containers and the energy required to liquify hydrogen is 20-40% of the energy being stored. Certain metals like magnesium, titanium, and iron absorb hydrogen when cooled and release it when heated. In these metals, hydrogen remains a gas but is confined in the spaces between molecules in the metal. When the metal is “charged” with hydrogen, it is called a metal hydride. Metal hydrides are the safest way to store hydrogen, especially in transportation applications, but are also more costly and complex than pressurized gas. Hydrogen can be stored as a gas at high or low pressures. High pressure systems allow smaller tanks but require expensive compressors. We are considering relatively low pressure storage options because we would like to keep our storage system as simple as possible.

To determine the size of our storage container, we’ve converted cubic feet into gallons.

$$9.45\ \text{ft}^3\ H_2\ (1\ \text{atm}) \times \frac{7.5\ \text{gal}}{\text{ft}^3} = 70.88\ \text{gal}\ H_2\ (1\ \text{atm})$$

TOC

The Ideal Gas Law

When we talk about storage, we also need to talk about the pressure. The above equation assumes we are storing the hydrogen at just above atmospheric pressure.

Hydrogen, stored as a gas, follows the ideal gas law, $P_iV_i = P_fV_f$. The law states that the initial pressure times the initial volume of a gas is equal to the final pressure times the final volume of the gas.

Pressure in the ideal gas law must include atmospheric pressure. When we inflate a tire to 35 pounds per square inch (psi), we are actually inflating it to 35 psi above atmospheric pressure. Atmospheric pressure is the pressure per square inch exerted on us by the atmosphere above us. It varies according to elevation and temperature but is about 14.5 psi. Anything less than that is a vacuum; anything more is pressurized. So, the tire we inflated would actually be at 35 + 14.5 psi or 49.5 psi. The tires walls only “feel” 35 psi because atmospheric pressure presses on it.

We have 70 gallons of hydrogen at just above atmospheric pressure, at say 0.25 psi above atmospheric, or 14.75 psi. If we choose to store the

TOC

hydrogen at 50 psi above atmospheric pressure or, 64.5 psi we can the resulting volume by applying the ideal gas law:

$$P_i \times V_i = P_f \times V_f$$

$$V_f = \frac{P_i \times V_i}{P_f} = \frac{14.75\ \text{psi} \times 70.88\ \text{gal}\ H_2}{64.5\ \text{psi}}$$

$$= 16.2\ \text{gal}\ H_2\ \text{at}\ 64.5\ \text{psi}$$

The 70 gallons of hydrogen we produce can be stored in a 16 gallon storage tank at 64.5 psi. The advantage of the higher pressure is the low volume storage tank. Hydrogen at 64.5 psi could be stored in a propane tank. Propane tanks, however, are expensive and a compressor might be necessary to increase the pressure of the hydrogen. Since hydrogen storage becomes more expensive and complicated as we increase the amount of hydrogen stored, we decided to start our system with only one day’s worth of storage. Our options are to either store 16 gallons of hydrogen in an empty 10-20 gallon propane tank at 64.5 psi or store the 70 gallons of hydrogen in two 55 gallon drums at slightly greater than atmospheric pressure (see “Hydrogen Fuel,” p.32 and “Hydrogen Storage,” p.94).

TOC
◀ ▶

Hydrogen For Home Power Users

Hydrogen offers many possibilities for home power users. Indefinite, long term storage becomes possible with hydrogen. Many home power systems produce more power than can be used during only one season. PV's produce surplus power in the summer; micro-hydro systems produce surplus power in the winter. Hydrogen allows for the storage of the surplus energy produced during one season to be used in another. Hydrogen can be combusted to produce heat for cooking or space heating with no pollutants. It gives home power producers the option of eliminating the last of their fossil fuels. Hydrogen can also be added directly into an existing propane supply. Hydrogen mixes with propane and can be used in a propane appliances year-round, without any modifications, to conserve propane (see "Hydrogen Fuel," p.32).

In the foreseeable future, we may see fuel cells become a cost-effective method of producing electricity with stored hydrogen. Hydrogen could then be used as an alternative to batteries, which require proper maintenance and employ toxic heavy metals which eventually need to be disposed of or recycled.

This exercise has given us a good idea of what it will take to replace all of our propane use with hydrogen. It's brought home the importance of con-

TOC

servation; our solar oven and solar hot water heater will determine if our transition will be possible. There is little information on “home scale, home budget” hydrogen systems. We welcome any advice or experience.

Electrolyzer Physics

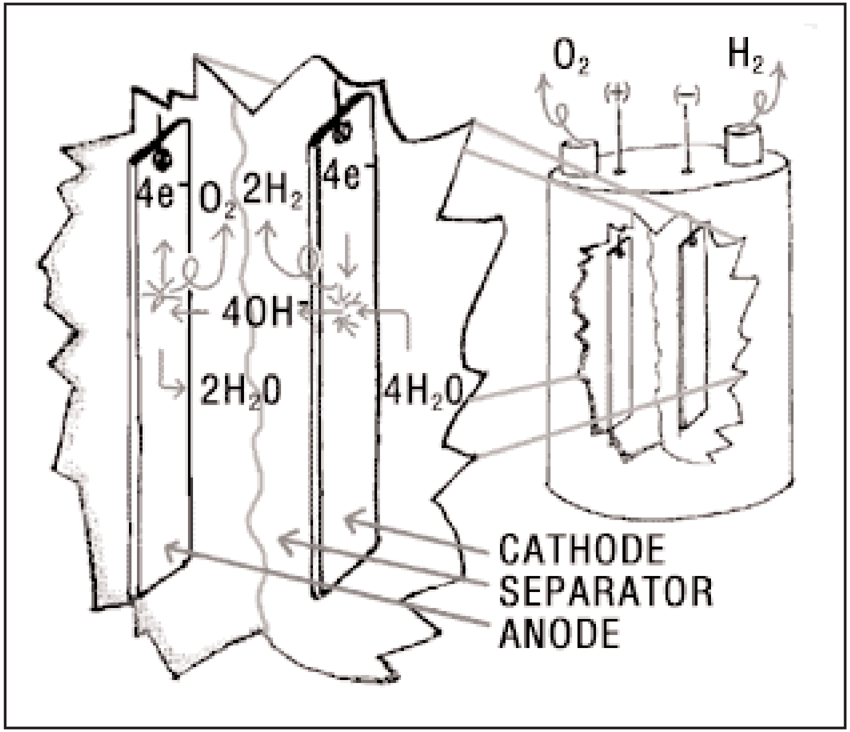
An electrolyzer is a device that uses direct current electricity to break the bonds holding together water, H_2O, into its components hydrogen, H, and oxygen, O.

An electrolyzer has three main components: an electrolyte, two electrodes and a separator. The electrolyte solution consists of distilled water and a salt, acid, or base, and is held in a chamber. The electrodes are pieces of metal which sit in the electrolyte and pass current through the electrolyte. The separator is a barrier that physically separates the electrodes from each other yet allows current to flow between them.

The Process

The following reactions occur when the electrolyte is a 30% solution of potassium hydroxide, KOH. If another electrolyte is used the results will be the same although the reactions will be different.

When DC electricity is connected to the two electrodes, current passes through the solution (H_2O and KOH), decomposing the chemical bonds of



the H_2O molecules. Electrons enter into the chamber via the negative terminal, called a cathode, and cause a reaction. In this reaction four water molecules, $4H_2O$, are broken into eight positively charged hydrogen ions, $8H^+$, and four negatively charged oxygen ions, $4O_2^-$. Since the four oxygen ions are unstable in this state, each one quickly re-attaches to one hydrogen ion, forming four hydroxyl ions, $4OH^-$. The four remaining hydrogen ions, $4H^+$, combine with four electrons at the cathode to form hydrogen gas, two molecules $2H_2$.

This half reaction is:

$4e$ - + $4H_2O$ –» $4OH^-$ + $2H_2$

The negative hydroxyl ions that were generated at the cathode are attracted to the positive electrode, called the anode. The electrolyte increases the

TOC

conductivity of the water, allowing the hydroxyl ions to be pulled to the anode. At the anode another reaction takes place in which the four hydroxyl ions give up four electrons and form oxygen gas, O_2 , and two water molecules, $2H_2O$. These electrons leave the chamber via the anode to complete the circuit. The oxygen and hydrogen gas, kept separate by a barrier, bubble up through the electrolyte into separate pipes and off to their points of use or storage. This reaction looks like:

$4OH$ –» $O2 + 2H_2O + 4e^-$

The overall result of the two reactions looks like this:

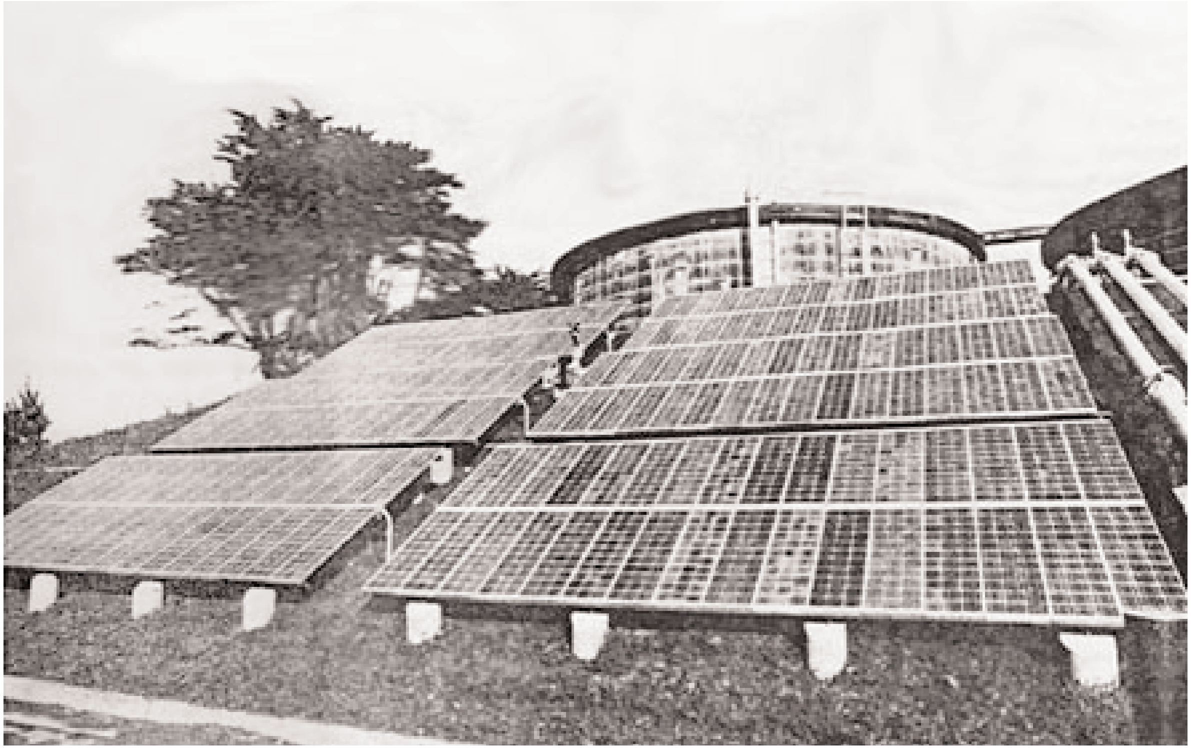
$2H_2O$ –» $O_2 + 2H_2$

Access:

Mark Newell and Amanda Potter, c/o Home Power, POB 520, Ashland, OR 97520 • 916-475-3179

Fuel From Wate by Michael A. Peavey, (ISBN 0-945516) Merit Products, Inc., Box 694, Louisville, KT 40201. Also available from Alternative Energy Engineering.

The Schatz PV Hydrogen Project



192 PV panels make electricity which is converted into hydrogen, and then back into electricity by fuel cells.

by Richard Perez

Originally published in Home Power #22 • April / May 1991

TOC

The Schatz PV Hydrogen Project

Many of us dream of more efficient ways to store the power we make from renewable energy sources. Here's a system that uses sunlight to make hydrogen and oxygen gas. These stored gases are converted directly into electricity by a fuel cell. Sound futuristic and impossible? Well, it's happening at Humboldt State University in Arcata, California.

An opportunity we couldn't refuse

I recently attended a conference on energy conservation at Humboldt State University. One of the conference's organizers, Michael Welch of the Redwood Alliance, suggested we visit an experimental PV/Hydrogen project at the school. It was an opportunity that we couldn't pass up. So, Bob-O Schultze and I saddled up and headed for the Humboldt Hydrogen.

The People

Renewable power systems are born because someone decides to build them. It is the interest and intelligence of the system's inventors/designers/users that makes it a reality. The hardware is secondary to the human desire to do it. We have technology coming out of our ears and we still fight wars over the oil that is slowly killing us. Renewable energy is worthless if we don't use it.The PV/Hydrogen project is the work of Dr. Peter Lehman and the crew of the Environmental Resources Engineering Dept. at Humboldt State. Bob-O and I were prepared for an ivory-tower tour focusing on the age encrusted ideas

TOC

chiseled indelibly in stone. What we found was entirely alive, open, and growing. These folks' project is as real as a physics book, but their feet are dangling over the edge of energy reality, just like those of every home power producer. We instantly found ourselves at home with folks that shared the same dreams, concepts, and fears that we have. It was enough to make me want to go back to college.

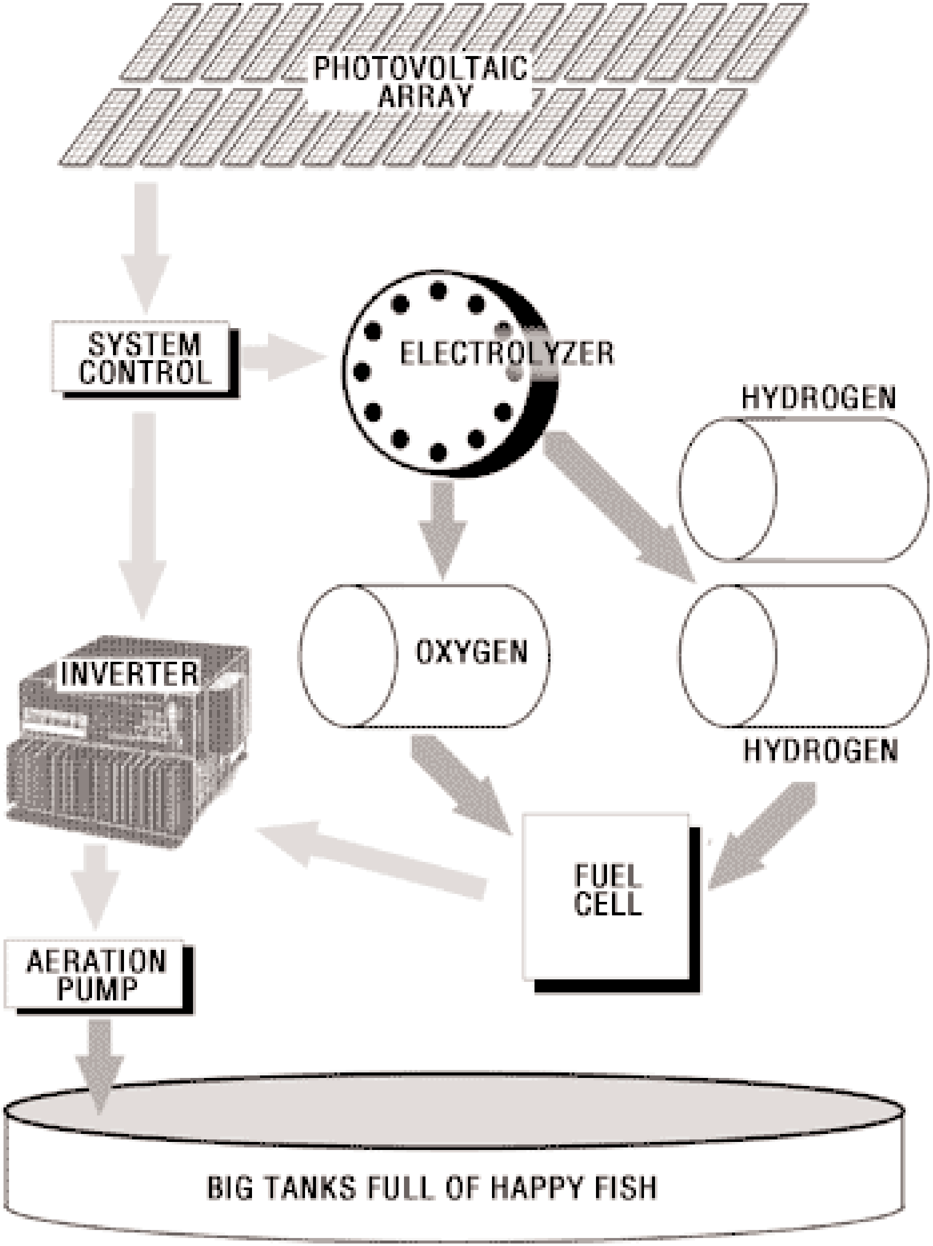
The Concept

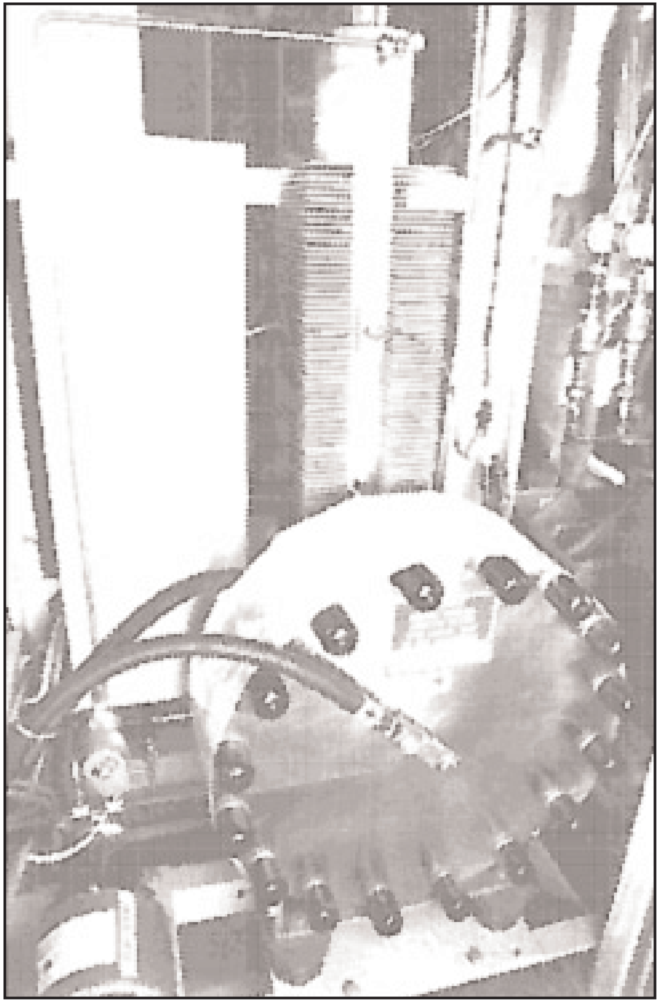
Sunlight makes hydrogen that makes electricity.

The concept of the Schatz Solar Hydrogen Project is not very different from home power systems, with one exception. The power here is stored as hydrogen and oxygen gases rather than in a battery.

An 8,000 Watt photovoltaic array directly converts sunlight into electricity. The power of the array feeds an electrolyzer cell. The electrolyzer converts the array's power into hydrogen gas and oxygen gas by electrolysis of water. These gases are stored in tanks for use at night or on overcast days. The hydrogen and oxygen gases are fed into a fuel cell for direct conversion into DC electric power. The DC electricity, either from the array direct or from the fuel cell, is converted into 120 vac by an inverter. The load supplied by this system is the aeration compressor bubbling air into the Marine Lab's fish tanks. Talk about happy fish! They have an uninterruptible solar power supply to provide their air.

While the fish are happy, so are the folks working on this project. They are learning, hands-on, to apply hydrogen storage in a PV system. This learning experience is the real reason for the Schatz Solar Hydrogen Project. High-tech R&D projects and backwoods home power systems both learn about renewable energy the same way - by doing.





The electrolyzer

The PV Array

The photovoltaic array contains 192 ARCO M75 modules wired for 24 VDC use. The array is broken into sub-arrays that are each individually controlled. Each module in the array is grounded and wired with #10 gauge, USE insulated copper wire. The output of each sub-array connects to the main system by #2 wire. Each sub-array is isolated from the rest of the array by a 60Ampere Schottky diode.

The Electrolyzer

The electrolyzer is a high pressure, bipolar, alkaline type. The electrolyzer contains 12 individual cells connected in series, each with a working voltage around 2 VDC. The electrolyzer cells use a 25% solution of potassium hydroxide (KOH) in water. The plates of the cells are made from stainless steel. This electrolyzer is made by Teledyne Energy for manufacturing processes that require pure hydrogen. It produces about 20 liters of hydrogen gas per minute and is between 75% and 80% efficient.

The gas output of the electrolyzer is metered by a mass flow calorimeter, a visual flow meter, and mechanical pressure gauges.

The oxygen gas is far from pure as it leaves the electrolyzer's cells. The oxygen output of the electrolyzer still contains small amounts of hydrogen gas and vast amounts of water vapor. The oxygen gas is first run into a tube-in-tube condenser that turns the water vapor into a liquid that is removed. The dryer oxygen gas then passes into a catalytic scrubber that combines the minute amounts of remaining hydrogen gas with the oxygen gas and produces water. The water is drained off and then the whole process of condenser/catalytic scrubber is repeated. The net result is very pure, very dry oxygen gas that is stored in the tank.

The electrolyzer requires only minimal maintenance - the replenishment of its electrolyte about every six months of continuous operation.

The Storage System

Both the hydrogen and oxygen gases produced in the electrolyzer are stored for later use in the fuel cell. These gases are stored in three 500 gallon LPG tanks with a rated working pressure of 250 psi. Two red tanks hold the hydrogen and one green tank holds the pure oxygen. Working pressure in these tanks is 100 psi to 125 psi. These tanks use all the hydrogen accouterments of pressure relief valves, stainless steel piping and connectors, and thermocouples that act as "gas gauges" determining the amount of gas in the tank.

Peter Lehman stands beside the oxygen storage tank. Behind him are two hydrogen tanks

The Fuel Cell

The fuel cell reverses the process carried on in the electrolyzer and converts the stored hydrogen and oxygen gases back into water. This process also releases DC electricity at the same time. On the day we visited the Schatz project, the fuel cell had been returned to its manufacturer for testing. When installed in the system, the fuel cell will enable the stored gases to be directly and silently converted into electric power. The combination of the storage tanks and the fuel cell are roughly equivalent to the battery in a home power system. In contrast to batteries, fuel cells have no finite capacity. A fuel cell will produce power as long as it is fed hydrogen and oxygen. The storage capacity of the system is limited by the size of the hydrogen and oxygen tanks, not by the size of the fuel cell.

The outputs of the fuel cell are DC electricity and water. That's it. The entire system produces no polluting byproducts - no carbon dioxide, no sulfur dioxide, and no radioactive waste. The entire process is totally symmetrical. Water molecules are transformed into their elemental components of hydrogen and oxygen. The hydrogen and oxygen atoms are recombined into water molecules. The system's creators bank the solar energy in tanks and retrieve it when needed.

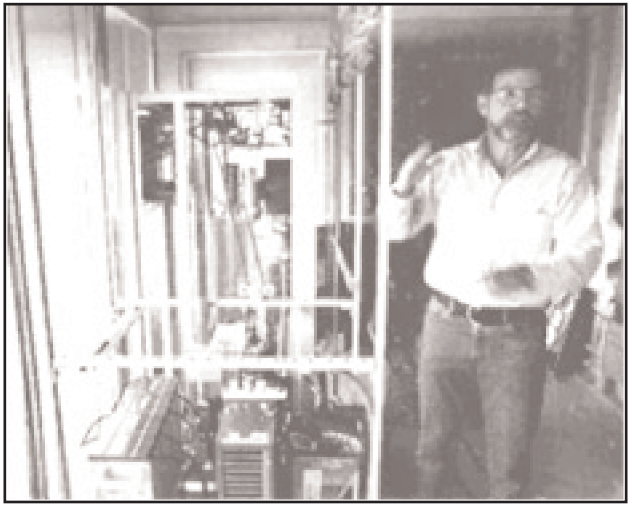
This particular fuel cell is made by Energenics of Ringwood, New Jersey. This fuel cell is a proton exchange membrane type that is capable of making effective use of the pure oxygen made by the electrolyzer. This fuel cell is an "instant-on" version that runs at lower temperatures (70°C.) than other versions (like the phosphoric acid version at 150°C. & the molten carbonate version at 800°C.). This Energenics version puts out 750 Watts continuously. The Energenics Company is working hand-in-hand with the Schatz project in research and development of retrieving energy stored in hydrogen.

The Inverter

We expected to find a high-dollar, super inverter in such an advanced system. Instead, we found the same garden variety Trace Inverter used in thousands of home power households. A Trace 2032 Inverter hummed happily on the wall. It doesn't care if its DC power comes directly from the PV array during the day, or from the fuel cell at night. The Trace is very democratic, and very reliable; it keeps the fish alive & happy.

System Control and Instrumentation

The instrumentation and control on the Schatz project are extensive. After all, the major product here is information. The system is monitored by computers at every stage of the process. Seven optoisolated, analog to digital converter boards talk to the system's two Macintosh computers. System control is accomplished by shorting out individual sub-arrays. This is accomplished by computers controlling 30 Ampere relays. A bank of NIFE Sunica nickel-cadmium cells is floated on the array to act as a "flywheel" to prevent constant relay switching during power surges.



Peter Lehman explains the system. The vacant space in the rack holds the fuel cell.

The System's Safety

A clear Lucite cage contains all hydrogen handling components. This cage vents outside and operates at less air pressure than the room in which it lives. Any hydrogen leaks are instantly detected by ultra sensitive hydrogen sniffers and the system is automatically shutdown. All piping within the system is stainless steel. The electrical components are protected with every known fuse, breaker, and disconnect. The entire system will not only meet the NEC, but it will make the most paranoid electrical inspector feel safe. This PV/hydrogen installation is safer than your kitchen stove or hot water heater.

The Reasons Why

The first reason is to learn how to store PV produced power as hydrogen. The second reason is to learn how to retrieve this stored energy through a fuel cell. The Schatz project is research and development in the use of solar hydrogen. The project is funded by Mr. L.W. Schatz, president of General Plastics Manufacturing Company of Tacoma, WA. My compliments to Mr. Schatz for looking far beyond the next quarter's profits and into an energy future we can all share.

Hydrogen Home Power?

Well, not yet. But, Peter Lehman and his compatriots are working on it. This system is far too costly and complex for basic home power right now. That's what Peter and the crew are working on. In the future, when we're using hydrogen for power storage, then it will be because folks like the Humboldt crew did their work right now.

Hopelessly Hi-Tech?

Not on your life. After a morning of sunshine hydrogen flowing through polished stainless steel, we visited another project at Humboldt State - the Campus Center for Appropriate Technology (CCAT). CCAT makes renewable energy real right now. The CCAT building uses PVs and wind for power (battery storage here), solar hot water, efficient appliances, a solar greenhouse providing space heat as well as fresh veggies, and even composting toilets. The CCAT building houses students in the Environmental Resources Engineering program and gives them the same hands-on experiences lived by home power producers. These students get to live on renewable power on a daily basis, learn about the systems involved, and create their own variations. They are an intense crew. I could see their commitment from the well-thumbed copies of Home Power on their bookshelves. The students at CCAT were not only learning new things, but are willing to share what they have learned. They have promised to write about their experiences in the next issue of Home Power.

TOC

Conclusion

Hydrogen storage is coming. The students and faculty at Humboldt State are joyously pushing the edge of the energy envelope. When I was in school the only things under discussion were building better bombs and nukes too cheap to meter. To find an established center of learning with a heart and an eye to our future gives me great hope. As I said, "It makes me want to go back to school."

Access

Dr. Peter Lehman, Director of the Schatz Solar Hydrogen Project,
Environmental Resources Engineering Dept.,Humboldt State
University, Arcata, CA 95521 • 707-677-0306 or 707-826-4231.

Richard Perez, c/o Home Power, POB 130, Hornbrook, CA 96044
916-475-3179.

Hydrogen Fuel

by L.E. Spicer

Originally published in Home Power #22 • April / May 1991

Hydrogen is an abundant fuel and it is simple to make. Above the initial cost of the generating equipment, the hydrogen produced can be free. The only substances used up in making hydrogen are water and electricity. My electricity comes from a wind generator and the water I use is rainwater. By using solar cells, the entire process can be done without one moving part.

Hydrogen's Traits

I consider hydrogen to be a much safer fuel than gasoline or propane. Hydrogen has a built-in safety factor because it is the lightest element. Upon release it disperses very rapidly, rising straight up, and is lost as soon as it is released. Hydrogen disperses so quickly that a gas welding torch will not light unless the spark is next to the gas outlet. An ordinary acetylene welding torch can be used with hydrogen. The hydrogen flame is clear and to adjust the flame you will need to look at the glow coming from the metal. In bright daylight the hydrogen oxygen flame cannot be seen.

TOC

Adjustments

A few simple adjustments can be made to your propane cooking stove to make it operate on hydrogen. Fill any large venturi cavity with steel wool to prevent a popping noise. Nex, adjust the jet size, regulate the pressure, and close off all air at the jet.

Gasoline engines can also be adjusted to run on hydrogen. I have adapted a propane/air mixer to a gasoline carburetor with success using hydrogen as a fuel. A standby gas generator set adapted to hydrogen would be a good arrangement.

A better use of hydrogen that I would like to see, rather than wasting it on a low efficiency gas motor, would be the use of a hydrogen-oxygen fuel cell. A fuel cell can be used for electricity or to run a vehicle with good efficiency.

Storage

I store my hydrogen in a 500 gallon propane tank. Propane and hydrogen are compatible in the same tank. In fact, propane can be conserved by bubbling hydrogen into it. Another advantage to putting hydrogen in propane tanks is to add smell to it, and to avoid mixing your hydrogen with oxygen from the air. Propane tanks also have a pressure release valve set at 250 PSI. I have had no problems with storing hydrogen below this pressure. Hydrogen and oxygen must be stored in separate tanks. The only time to

TOC
◀ ▶

combine oxygen or air to hydrogen is at the burn site. Hydrogen and oxygen mixed and ignited is explosive, same as any hydrocarbon fuel.

Electrolysis

In my electrolyzer cell, the hydrogen evolves off the negative potential; the positive potential releases the oxygen. It is important to maintain the same polarity on an electrolyzer cell. If the polarity is switched, your gases will be mixed. I use nickel on the positive side along with potassium hydroxide as an electrolyte. Nickel electrodes in potassium hydroxide do not electroplate away. Pure water is a non-conductor of electricity. Therefore, a potassium hydroxide electrolyte is necessary. The potassium hydroxide is not used up is the process of electrolysis. I purchase my potassium hydroxide from a chemical warehouse.

I use the hydrogen gas for combustion. I use the oxygen gas produced for welding, especially for cutting which uses lots of oxygen. I haven't bought oxygen for my cutting torch since I installed the hydrogen setup.

Homemade Electrolytes

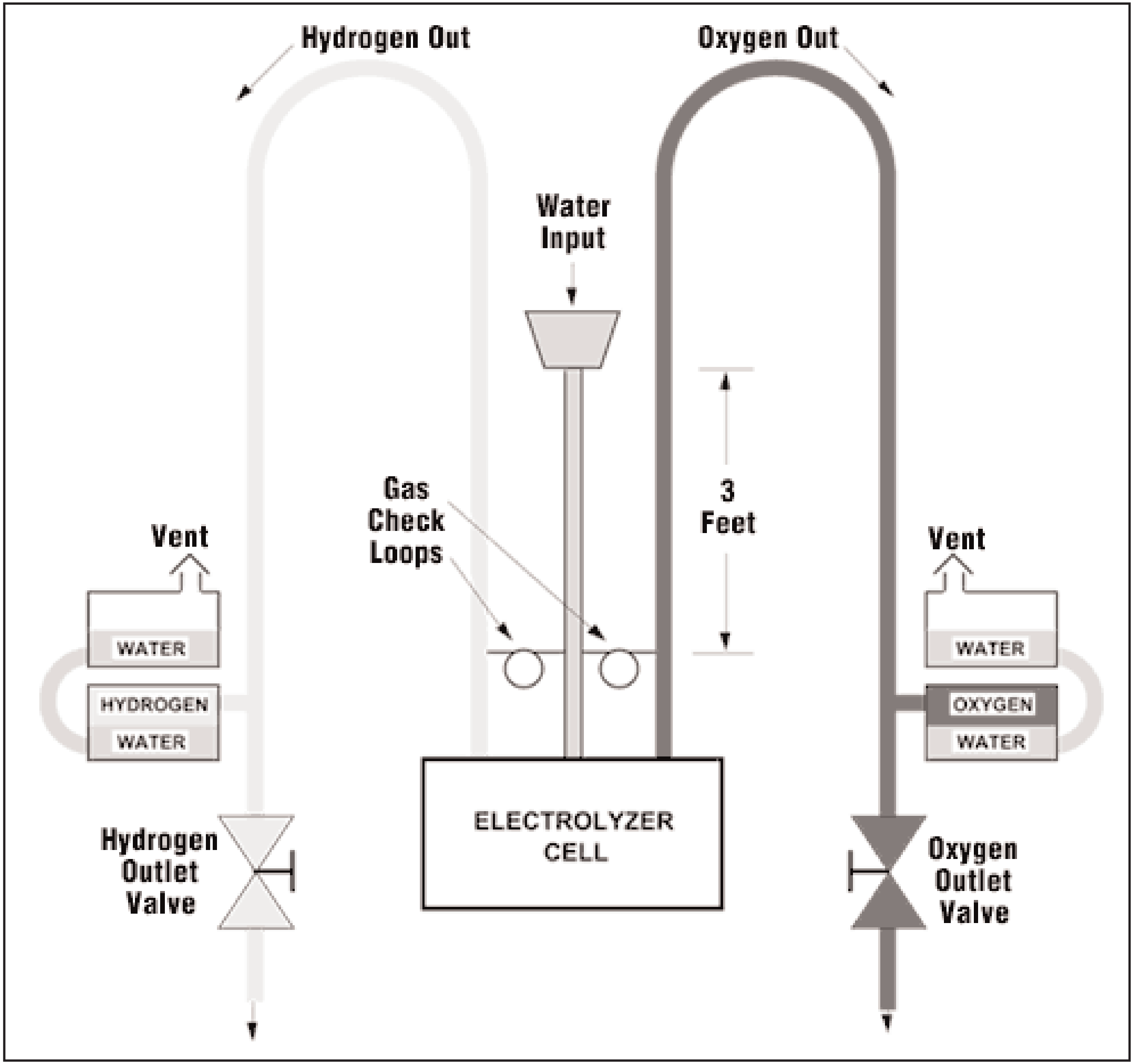
If you want to make your own electrolyte, it can be made from wood ashes. First, soak your wood ashes for a period of time, depending on how concentrated you want your solution. Remove the clear solution off the top of the wood ashes, then evaporate down to the specific gravity you want your electrolyte to be at. A weak solution works fine, and is not as caustic as a stronger solution.

Gas Pressure

Hydrogen and oxygen gas will evolve from the electrolyzer under pressure. This can be taken advantage of by using a hydrostatic column to obtain pressure. See the illustration, next page. This one cell electrolyzer along with this simple three foot hydrostatic control will give pressurized storage of both hydrogen and oxygen with no moving parts. The pressure is obtained from the weight of the three foot water column. This is sufficient pressure to displace the water from the bottom 55 gallon barrel to the top barrel. The water in the top barrel in turn puts pressure on the gas. A series of 55 gal. drums can be lined up in this fashion to store larger quantities of gas. There is no need for gauges as the liquid level can readily be seen through the clear tubing. There are no pop-off valves to be concerned with. After adding the electrolyte to the system, only water and electricity are needed for continued operation. A fail-safe feature of this control is that the hydrogen and oxygen go into storage or are vented into the air.

Controls & Power Sources

I also build a 50 PSI control that operates three electrolysis cells in series which operate at 12 Volts DC and 40 Amperes.


Hydrogen Out
Oxygen Out
Water Input
3 Feet
Gas Check Loops
Vent
WATER
HYDROGEN
WATER
Vent
WATER
OXYGEN
WATER
ELECTROLYZER CELL
Hydrogen Outlet Valve
Oxygen Outlet Valve

My larger control is a 100 PSI control which can handle six or more electrolyzer cells in series. I presently have a six cell unit with a 100 PSI control in my shop. It is powered by a Jacobs wind generator. Each cell requires 4 Volts DC. These are wired in series and operate at 24 Volts DC and will load to 40 amps with each cell delivering $^1/_2$ cubic foot of hydrogen per hour on a windy day.

A good power source to drive a one cell electrolyzer is a high amperage six Volt wind generator. Another good source would be a permanent magnet motor driven by water.

Access

L.E. Spicer, Hydrogen Wind, Inc. RR#2 Box 262, Lineville, Iowa 50147 • 641-876-5665.

TOC
◀ ▶

Water Electrolyzers

by L. E. Spicer

Originally published in Home Power #26 • December 1991 / January 1992

The wind blows freely over the hill behind our house, turning an old Jacobs wind charger. This is the power source that we use to split the rain water that flows off our roof. Above the set-up cost and maintenance, making hydrogen is a free ride. For wind and water are free and nothing else is used up in the process.

Inside the Electrolyzer

Electrolyzers make hydrogen and oxygen from water by electrolysis. In the previous chapter, Hydrogen Fuel, our hydrostatic column was explained. Here I would like to give drawings that more clearly show the water electrolyzer and the arrangement of multiple electrolyzer cells in a common liquid electrolyte as brought forth by patent #4,382,849 and used by Hydrogen Wind, Inc.

Figure 1 (next page) is an exploded view of the basic one cell electrolyzer. You can see in the drawing that it is simple in construction. It consists of a positive and negative electrodes #44 and #20, a separator box #16, within a pressure retaining housing #22.

TOC

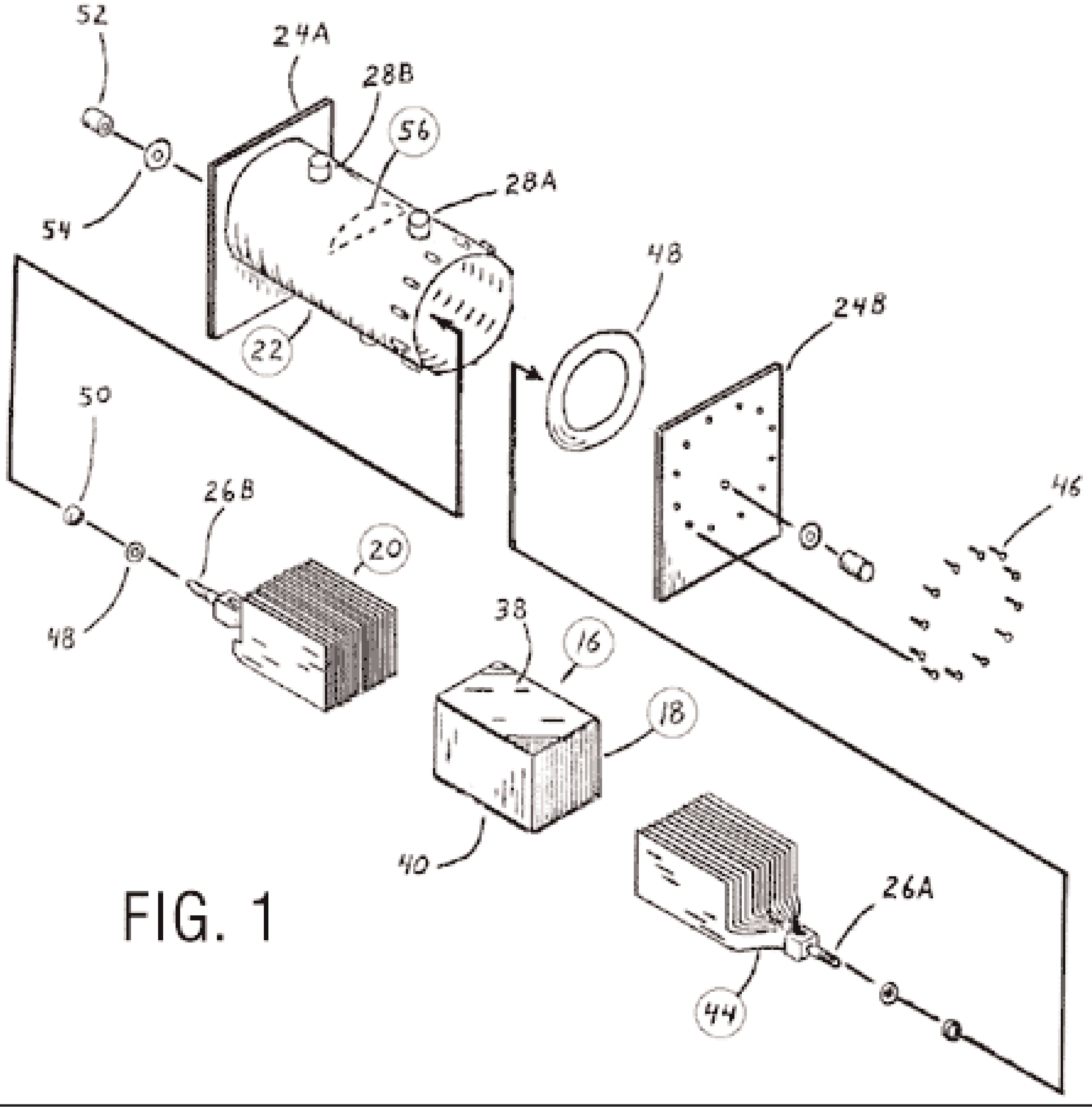


FIG. 1

TOC

Hydrogen and oxygen are divided out of the water by the use of a microporous membrane #18 configured into the separator box illustrated by Figures 2 and 3. The hydrogen and oxygen as separate gasses rise out of this box and separation is maintained by the divider plate (#56 in the upper part of Fig. 1).

A multiple of these cells can be wired together to equal an available DC power source. This, however, must be done in a certain way. If a number of electrolyzer cells were just wired together in a common electrolyte, the electricity would simply enter on the first positive electrode and pass through the electrolyte and exit on the last negative electrode, ignoring all the cells in between.

FIG. 2

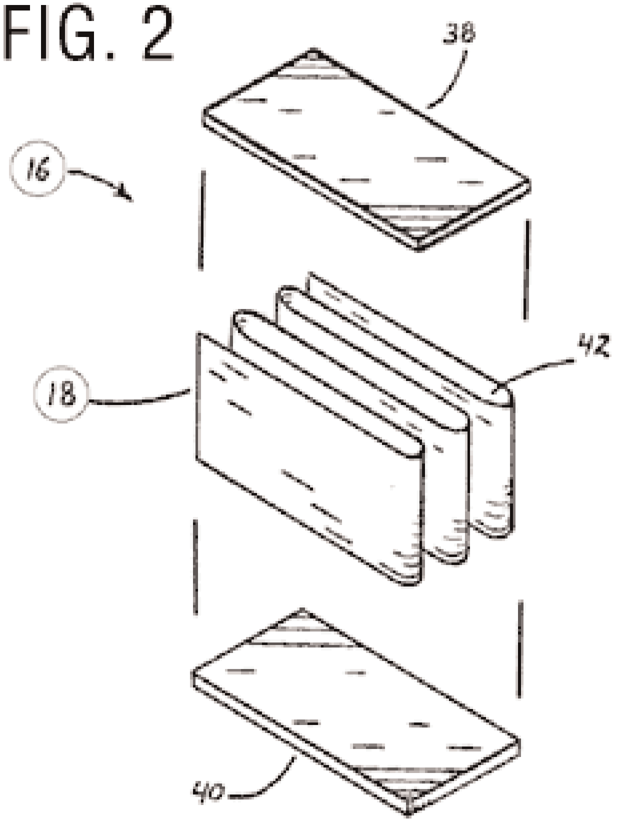
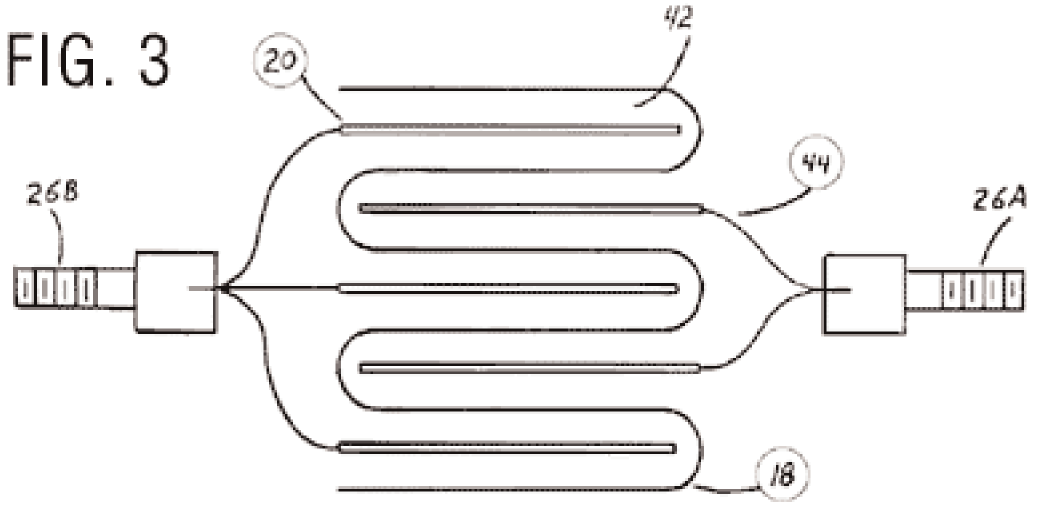


FIG. 3



Gas Traps

This shunting of the current can be avoided by using gas traps and electrolyte channeling as shown by Figure 4 and 5. The gas traps (#30 of Figure 4, next page) consist of plastic tubing that hold a pocket of gas to prevent the flow of an electric current.

Electrolyte Channeling

The electrolyte channeling (#60 of Figure 5) is also plastic tubing arranged so that the greatest resistance to shunt current through these

FIG. 4

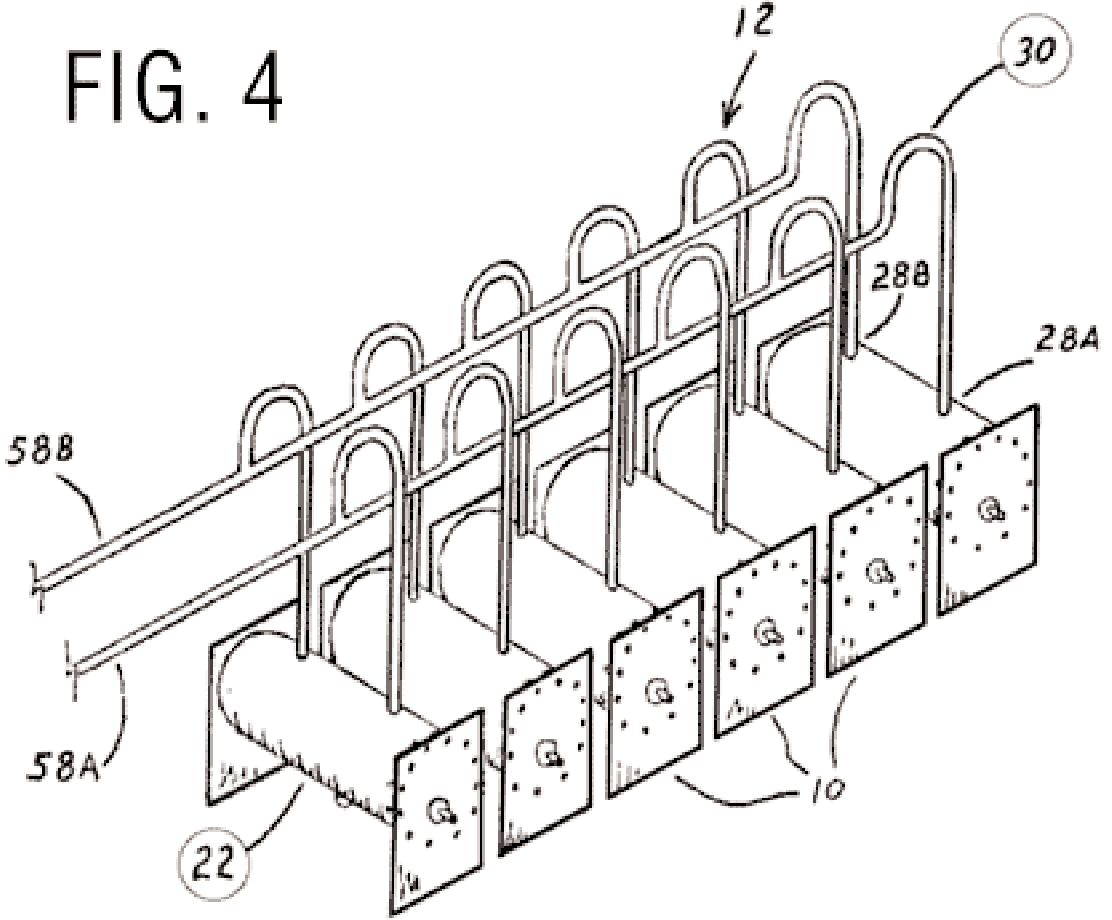
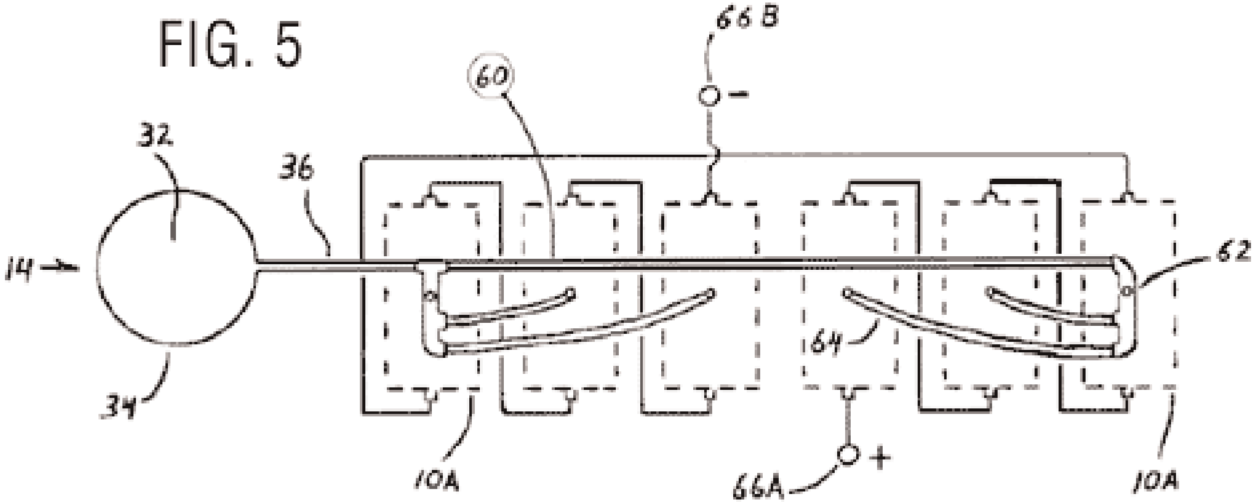


FIG. 5



tubes is at the cells of the highest potential. Electricity therefore, will take the path of least resistance, which is straight through each cell.

In addition to this, each electrolyzer must be spaced apart from each other to avoid electrical contact, and must rest on a plastic or non-electrical conducting surface.

Access

Author: L. E. Spicer, Hydrogen Wind, Inc., Rte. 2 Box 262, Lineville, IA 50147 • 641-876-5665.

TOC
◀ ▶

Solar Hydrogen Production by Electrolysis

by Walt Pyle, Jim Healy, Reynaldo Cortez

Originally published in Home Power #39 • February / March 1994

Why would anyone want to produce hydrogen at home? Hydrogen can be used as a non-toxic energy storage and transport medium. Hydrogen that is made from water using solar energy is a sustainable and renewable home energy supply. Make hay (or hydrogen) while the sun shines. Then use the stored hydrogen to produce heat and electricity on demand, day or night! We got excited about solar hydrogen production during the seventies and the first oil shocks.

What happened between the seventies and nineties? For the most part we worked with thermolysis (splitting water with concentrated solar heat) and photoelectrolysis (splitting water in a liquid solar cell). We also followed the work of other hydrogen pioneers, such as Roger Billings and his associates, who produced and used hydrogen in home appliances and vehicles. The article by Richard Perez about the Schatz PV Hydrogen Project (p. 20) and a subsequent visit to Humboldt State University's Trinidad Marine Laboratory launched us into designing and making a "home-sized" system based on electrolysis of water. Electrolysis is the competition for thermolysis and pho-

TOC

toelectrolysis at this juncture. Hydrogen and oxygen can be produced from water using electricity with an electrolyzer.

This article describes the installation and operation of a 12 cell Hydrogen Wind Inc. 1000 Watt electrolyzer. This electrolyzer can produce 170 liters/hour (6 cubic feet/hour) of hydrogen and 85 liters/hour (3 cubic feet/hour) of oxygen (at standard temperature and pressure). In addition, we describe a homebrew purification and storage system for the hydrogen and oxygen produced by the electrolyzer. With proper after-treatment, the gases produced can be stored safely. The purified hydrogen and oxygen can be used in fuel cells (to produce direct current electricity) and catalytic burners (for heating and cooking) without poisoning or damaging the noble metal catalyst materials. The gases can also be used for welding and cutting, as well as for motor vehicle fuel.

!!!!Safety First!!!!

Making and storing hydrogen and oxygen is not kid’s stuff - this is “rocket fuel”! Use flashback flame arrestors on the hydrogen and oxygen outlets from the electrolyzer. Secure dangerous caustic from small prying hands. Make sure your gases are pure before storing them. More on safety follows.

How Much Hydrogen Do I Need?

This varies tremendously from household to household, depending on how well the Demand Side Management job has been done. We can run our Platinum Cat space heater for about three hours on a cubic meter of hydrogen. The amount of gas needed can be estimated from the energy consumption of any appliance. Amanda Potter and Mark Newell's article (Hydrogen Basics, p.8) describes the operation of an electrolyzer and shows how to calculate the amount of gas needed to run appliances. See the chapters on hydrogen space heating (p.143), hydrogen cooking (p.118 and 129), and making electricity from hydrogen with a fuel cell (p.169).

How Much Power Does It Take?

A cubic meter (35.3 cubic feet) of hydrogen gas takes about 5.9 hours to produce in this electrolyzer, when operated at its rated input power of 1000 Watts. This means the energy required to produce a cubic meter of hydrogen and 0.5 cubic meter of oxygen is about 5.9 kW-hr. This translates to an efficiency of 51%, where 3 kW-hr/m 3 equals 100% efficiency at 20°C. Typical industrial scale plants operate at about 4.5 kW-hr/m 3 or 67% efficiency at high current density. The efficiency is better at lower current density.

TOC

What Is Needed to Produce Hydrogen at Home?

Our system includes the following components and sub-systems (see the block diagram next page):

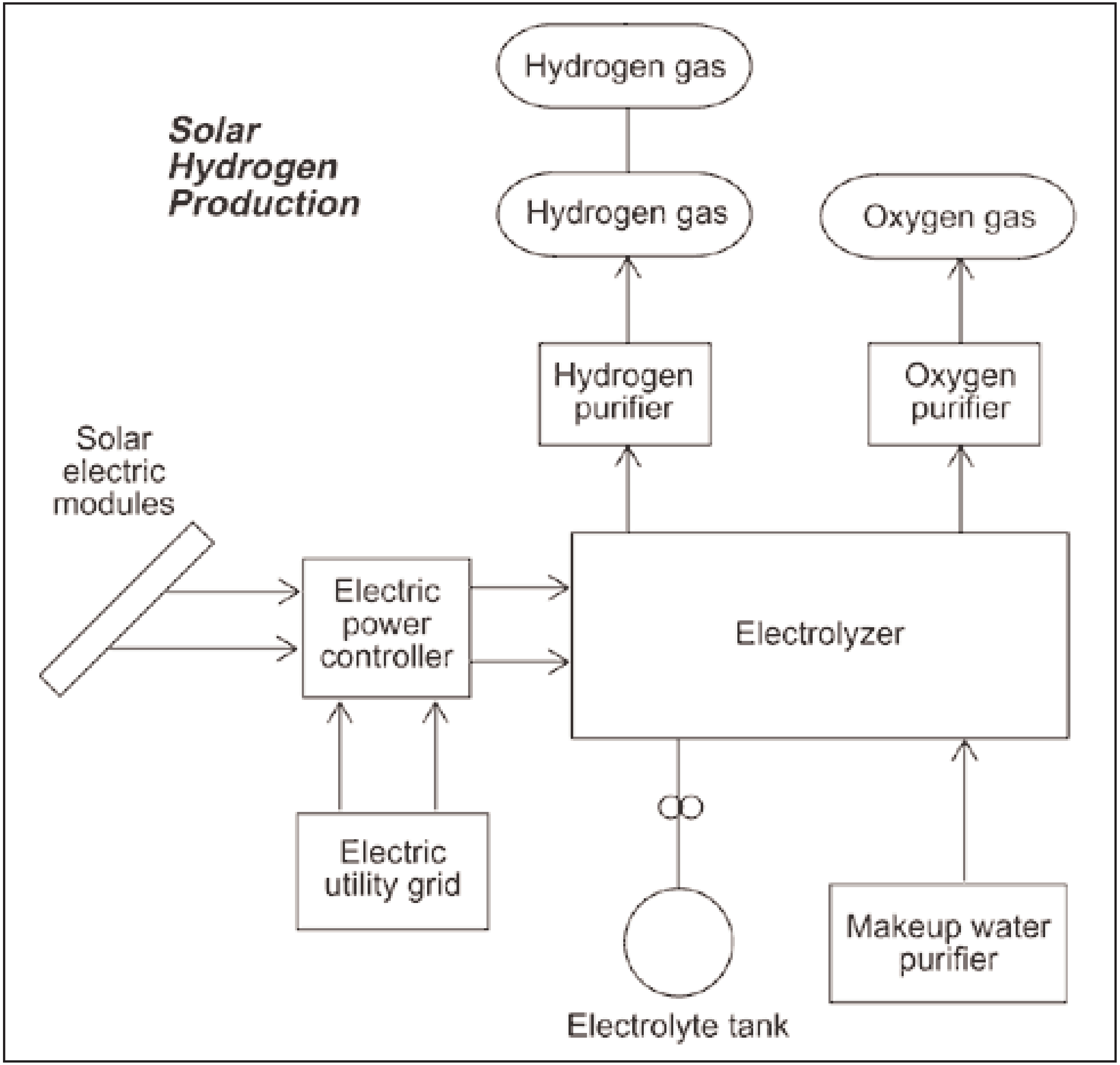
- Solar electric power and/or utility grid power
- Power Controller
- Electrolyzer
- Hydrogen Purifier
- Oxygen Purifier
- Hydrogen and Oxygen Storage Tanks
- Electrolyte Storage Tank and Transfer Pump
- Makeup-water Purifier

Where Can I Get An Electrolyzer?

The Hydrogen Wind electrolyzer is introduced by its designer Lawrence Spicer in the previous chapters “Hydrogen Fuel” (p.32). Hydrogen Wind Inc. electrolyzers are available in single cell units for small demand or educational use, and in multiple cell configurations which provide higher gas production rates.

We purchased a 12 cell 1000 Watt system with the gas pressure controls and electrical metering. Larger systems with up to 24 cells or smaller three cell and six cell systems are available. Another article by Spicer, “Water Electrolyzers,” (p.38), describes the individual cells in more detail along with an introduction to cell arrays.

TOC


Solar Hydrogen Production
Hydrogen gas
Hydrogen gas
Oxygen gas
Hydrogen purifier
Oxygen purifier
Solar electric modules
Electric power controller
Electrolyzer
Electric utility grid
Makeup water purifier
Electrolyte tank

The cell electrodes are fabricated from rectangular metal plates with tabs on one end. Both the anode and the cathode metal plates are made from porous, sintered nickel. Two clusters of nickel electrode plates, 14 for the anode and 14 for the cathode, are separated by porous plastic sheets folded accordion style within a separator container.

The plastic separator container is open at the horizontal ends, and closed at the top and bottom. This lets the larger hydrogen gas bubbles (which escape from the negative electrode or cathode) rise in the electrolyte, due to their buoyancy, and exit the separator container on one side. The hydrogen remains separate from the smaller oxygen bubbles which evolve from the positive electrode (anode) and exit on the opposite side.

The micro-porous polypropylene separator container and the electrode clusters are housed inside sections of steel pipe with flat steel plates welded on one end and bolted on the other end. The steel cell housings hold the water and potassium hydroxide electrolyte, and keep the hydrogen and oxygen gases apart after they rise from each end of the separator container. We installed our electrolyzer inside a small weather-protected shelter made from box tubing and sheet metal. We chose stainless steel sheet metal for its corrosion resistance to caustic electrolyte and long-lasting “perma-culture” value. The photograph on the next page shows an overview of the system.

Solar Power and Utility Grid Backup Power

Our solar electric power is produced by two 16-panel Carrizo Solar "Mud" photovoltaic arrays and a gaggle of other smaller panels. On a good summer day we get up to 75 Amperes at 14 Volts for charging the house batteries. When the two house battery banks are fully charged, our two 50 Amp SCI charge controllers disconnect the PV power, and the PV voltage rises. An Enermaxer controller senses the voltage rise and transfers the PV

An overview of the electrolyzer system. The power supplies and electrical controls are on the far left. Purification equipment is to the right of the power controls. The electrolyte reservoir and hydrogen and oxygen float valves with pressure gauges are to the right of the purification equipment. Twelve electrolyzer cells are shown on the far right. A feedwater purification system is just below the twelve electrolyzer cells. The caustic electrolyte storage tank is on the ground below the float valves.

Photo by Reynaldo Cortez

power to the electrolyzers to make hydrogen and oxygen during the remainder of the day. A utility grid electrolyzer power supply is used to make hydrogen and oxygen when there is insufficient solar power available.

How Do We Purify the Gases?

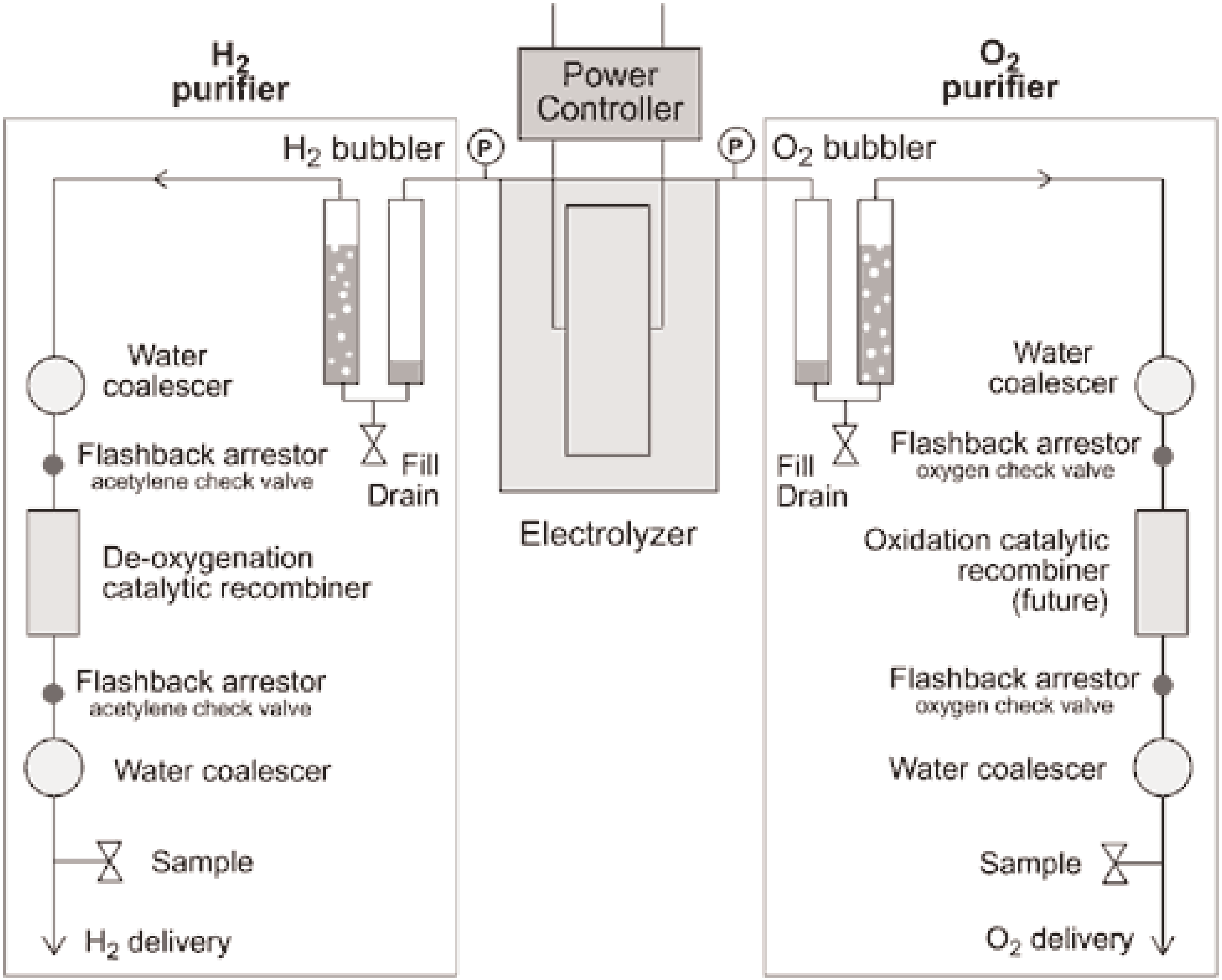
The gas purification system is shown in more detail in the diagram on next page. The hydrogen gas and the oxygen gas are purified by two different systems.

Bubblers

First, each gas is scrubbed by passing it through a water bubbler column. Each of the gas scrubbing bubblers is made from two vertical plastic tubes with end caps. A pair of fish-aquarium type bubbler frits was glued into holes drilled in the inside bottom caps of each acrylic plastic tube, using methylene chloride solvent. Flow of gas into or out of a bubbler can then be seen by the operator. The bubblers are filled about one-third full with distilled water using the drain and fill valves on the bottoms. We call these “Bi-directional Bubblers”. The bubblers are tolerant of flow in any direction, without letting the scrub-water into the product storage system or the electrolyzer. We got the idea for making these bubblers from Dr. Peter Lehman and his associates at Humboldt State University (Schatz Solar Hydrogen and Fuel Cell Laboratory.)

TOC
◀ ▶

Gas Purification System



TOC

The gases entering the purifier are saturated with water vapor and may contain minute amounts of caustic electrolyte aerosol and particulates like rust. After passing through the bubblers the gases are still saturated with water vapor, but virtually caustic- and particulate-free. Installing another coalescer before the bubbler would prevent particulates and some aerosol from entering the bubblers.

Coalescers

Next, the gases are partially dried by passing them through coalescing filters. Special materials were required for the oxygen coalescer filter to prevent spontaneous combustion, and no oil or hydrocarbons can be present.

The bi-directional bubblers and purification systems.

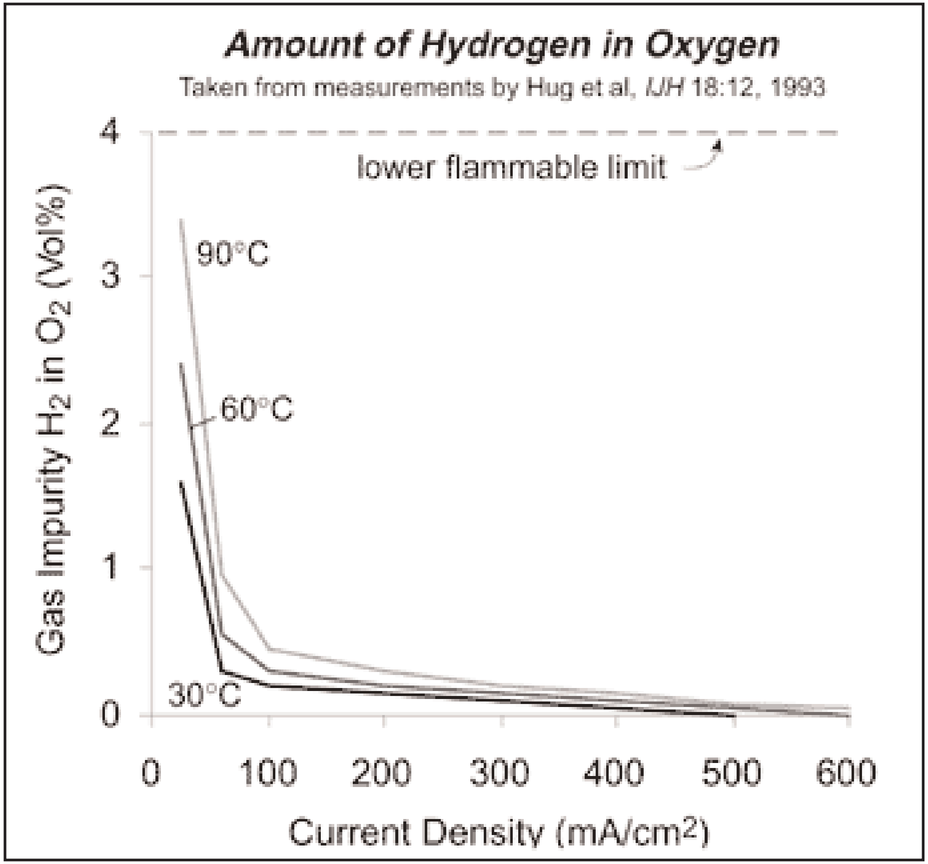
Photo by Reynaldo Cortez

Recombiners

The hydrogen gas purifier treats the hydrogen gas in a catalytic recombiner. The purpose of the recombiner is to recombine any oxygen impurity in the hydrogen product, and make water. The noble metal catalytic recombiner removes the oxygen impurity to make the hydrogen gas safe to store and handle. As a safety measure, we installed flashback arrestors between the first and second coalescers and the recombiners. The flashback arrestors prevent flashback of poor purity gases (oxygen impurity in the hydrogen produced) when they reach the recombiner and ignition source. The recombiners must be installed with their major axis vertical and the entry at the top.

Some data recently published by W. Hug et al from the German Aerospace Research Establishment (International Journal of Hydrogen Energy, Vol. 18 No. 12, pp. 973-977) shows that purity of the gases produced by an alkaline electrolyzer is affected by the current density and temperature of the cells. From the graphs (next pages) we see that the purities of the hydrogen and oxygen gases are poorer at low current densities (such as when a cloud covers the sun for example). This is because diffusion of the gases through the liquid electrolyte is a more significant fraction of the total production at low current densities.

The data also imply that there is more danger of having hydrogen impurity in the oxygen than the reverse. Note that the lower flammable limit, 4% for hydrogen impurity in bulk oxygen, is approached at low current densities.

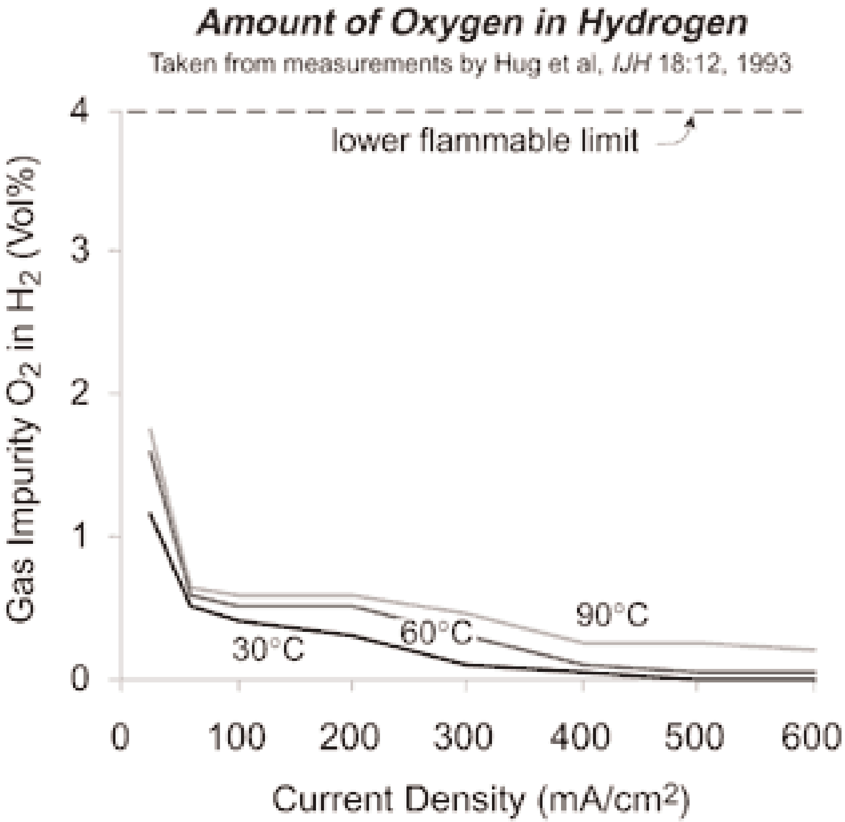


How Does One Store the Gases?

The hydrogen will be stored in two 0.47 cubic meter (125 gallon) propane tanks, and the oxygen will be stored in one propane tank.

REMEMBER: hydrogen gas is safe to store – hydrogen/air or hydrogen/oxygen mixtures are NOT safe to store! Put safety first!

Safety is your responsibility. It is our intention to give you the information you need to follow safe practices.



Each of our used propane tanks was cleaned thoroughly and hydrostatically tested to 13.8 bar (200 psig.). Pressure relief valves on each tank are set for 10.3 bar (150 psig.). A pressure switch is installed on the hydrogen tank feed line to shut off the electrolyzer power supply when the pressure reaches 6.9 bar (100 psig.), the rated maximum output pressure of the electrolyzer.

The produced hydrogen gas is pressurized by the electrolyzer to its maximum rated pressure of 6.9 bar or less. Our two hydrogen tanks hold the equivalent of: 6.9 bar x 2 tanks x 0.47 cubic meter = 6.5 cubic meters (at standard temperature and 6.9 bar pressure).

Makeup-water Treatment System

As hydrogen and oxygen are produced in the electrolyzer, water is consumed and it must be replaced. We produce our makeup-water using the local Utility District water, which is piped into the home. We want to prevent the formation of “mineral scale” on the surface of the electrodes inside the electrolyzer because we want them to last a long time. First, the water is passed through a 20 micron interference filter to remove particulates like rust and sand. Second, the water passes through a charcoal drinking water filter to remove organics and chlorine. Third, the water passes through a de-ionizing column to remove metallic ions. The water before and after the purifier was analyzed. The results are shown in the table below.

Water Purification Results

Element	Before Purifier, ppm	After Purifier, ppm
barium	0.009	nil
calcium	7.3	0.006
potassium	0.37	nil
magnesium	0.7	nil
sodium	1.8	nil
silicon	3.8	3.8

As you can see, we removed some scale-forming material. Other elements were below the lower detectable level of the instrument (approximately one ppb). Our water before the deionizer and charcoal filter is not very “hard” at this location; it does not contain very many dissolved minerals. After the deionizer there is a marked reduction in elemental concentrations of everything except silicon.

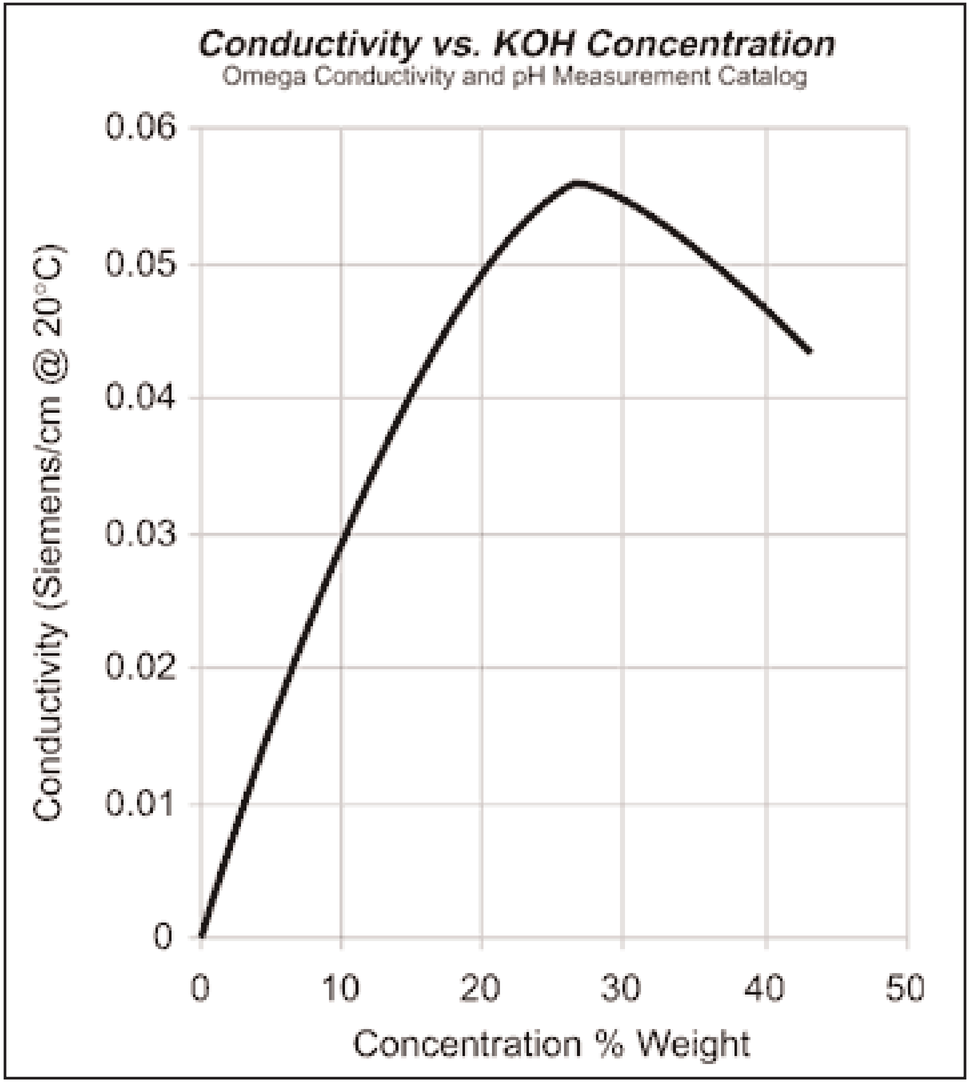
Why Conduct a Hydrostatic Test on the Electrolyzer?

Prior to filling the electrolyzer with caustic electrolyte, we conducted a hydrostatic leak test by filling the cells with purified water and pressurizing the cells and electrolyte reservoir to 6.9 bar (100 psig) using utility line pressure. Several tubing fittings leaked until tightened. Fixing water leaks during the initial hydrostatic test is much better than fixing leaks when they involve caustic electrolyte! Getting caustic on your tools, gloves, safety glasses, and clothes is a real drag. Plan ahead! When installing the tubing clamps, position them so you can tighten them later when the cells are tied together. An improvement would be to mount the cells higher to allow for access to the clamps from below.

TOC

Why Do You Need the Caustic Electrolyte?

Potassium hydroxide (KOH) in the water makes it electrically conductive, so that ions can be transported through the electrolyte during electrolysis. See graph at right showing the conductivity of the KOH electrolyte as a function of weight percent KOH in water. We have chosen KOH as the caustic. The twelve electrolysis cells and the electrolyte reservoir hold



TOC

about 61 liters (16 gallons) of water plus 15 kilograms (33 pounds) of KOH. This solution is about 23% KOH

Safety is a Must When Handling Caustic Electrolyte!

DANGER!! Potassium hydroxide is very corrosive and hazardous to handle. KOH deserves great respect. Goggles or safety glasses with side protectors, and plastic or rubber gloves are absolutely necessary when handling KOH. When caustic comes into contact with the skin, the natural oils of the skin are chemically converted to a soap, which initially gives a slippery feeling. Prolonged contact will dissolve the skin and give a chemical burn similar but more severe than that given by handling lime or fresh wet concrete with bare hands. The best treatment for any accidental spill is flushing with copious amounts of water, or neutralization with a weak acid such as vinegar. Always have a water hose hooked up and operational before handling KOH caustic. Keep the electrolyzer outdoors and locked so only qualified people can service it. A cyclone fence with top and sides might be the solution.

DANGER!! The mucous membranes of the eye are especially susceptible to caustic damage. It has been estimated that 15 seconds of contact to the eye with concentrated KOH caustic is enough to produce permanent blindness. If any KOH comes into contact with the eyes, the best treatment is to flush the eyes immediately with pure water for at least 15 minutes and seek medical attention.

TOC
◀ ▶

What Provisions Need to be Considered When Handling Caustic?

To service any of the cells, we need a way to drain the electrolyte and store it for re-use. We have a drain valve and line on the bottom of the electrolyte reservoir that allows the KOH solution to gravity drop into a stainless steel tank at a lower level on the ground. A tubing roller pump is used to refill the electrolyzer cells with KOH after the maintenance is completed. Our KOH tank was previously used as a swimming pool filter case.

We mixed the water and KOH in the ground level caustic storage tank. Water and KOH mixing produces chemical heat, the “heat of solution”, which is surprisingly high. After we mixed in all of the KOH flakes, the water temperature rose from 20°C (68°F) to about 82°C (180°F).

At this point we made our first big mistake. After the KOH and water electrolyte solution was mixed (and hot), we immediately started pumping it into the electrolyzer reservoir and cells, using the tubing pump. Within minutes, the tubing pump began leaking. We stopped the pump and drained the KOH back to the ground level tank. After cleaning up the mess, we found that the silicone tubing had split open. We let the KOH solution cool overnight. The next day we replaced the tubing in the pump, and tried again. This time the transfer proceeded without pump tubing problems.

By the time the caustic was about half pumped into the cells, we found that six of the tubing fittings on the first two cells were dripping KOH onto the floor of the shelter. The hot KOH the night before had damaged some of the pipe thread seals which were made with five minute epoxy. The threads in cells further away from the caustic KOH entry point were not damaged, presumably because the caustic KOH solution had cooled by the time it reached those points. We drained the caustic KOH back to the ground storage tank, removed the affected fittings and replaced the epoxy thread sealant. The next day we filled the cells back up with KOH solution for the third try.

More caustic KOH leaks! This time we had leaks on the tubing fittings on the gas-trap tubing loops where the hydrogen and oxygen come out of the cells at the top. Additional tightening of the tubing clamps with a 12 point box wrench stopped some leaks. Other fittings had to be removed and thread epoxy had to be reapplied. When will solid polymer electrolyte electrolyzer cells be available at a reasonable price so we won't have to hassle with KOH???

What Were the Cell Operating Conditions?

The cells require about 1.7 volts each to begin operating; at higher currents there is a greater voltage requirement. The direct current requirement is about 40 Amperes for each cell at rated gas output. In a twelve-cell system the cells are wired in series, so that all of the cells get the same current and the voltages add up to 12 x 1.7 V or 20.4 Volts total at 20 Amperes of current. The cells can also be wired in series-parallel for 10.2 Volts total.

Our solar photovoltaic system and grid back-up power supplies can only produce about 25 Amperes at the moment, so we cannot yet achieve full gas output. The 20.4 Volt operating voltage was not a problem with our Carrizo solar electric arrays, however, since they have an open circuit voltage of about 25 Volts.

Strange and Unusual Behavior?

When operating the electrolyzer the first day on direct current power, the power controller behaved predictably. We measured about 22 Volts and 25 Amperes flowing into the electrolyzer cells. We had gas flow only through the oxygen bubbler however!! And occasionally, the oxygen float valve “burped” some KOH solution upward with a release of gas. The fix for this problem was to raise the electrolyte level from about 5 cm (2 inch) on the reservoir level gauge to 20 cm (8 inch).

At first startup, the gas comes out after a delay of about an hour while the cells are “charging” and the gas bubbles on the electrodes get large enough to break away. Voltage across the cell array gradually rises during “charging” from 18 to 19 to 20 Volts before gas comes out.

On restart, hydrogen comes out later than oxygen since it must first fill the top of the electrolyte reservoir tank to pressure-pump the system. When both gases were coming out of the electrolyzer pressure control float valves, the pressure on the reservoir was 2.5 bar (36 psig) when discharging to atmospheric pressure.

The next day we may have had our first personal demonstration of William Grove’s astonishing observation that an electrolyzer can run backwards and become a power source. Grove discovered in the early 19th century that the reverse reaction - supplying oxygen and hydrogen to electrodes - causes an electrolyzer to produce direct current electricity and act as a fuel cell.

Before we turned on our power supply the next day, the voltmeter showed about 16 Volts DC on the electrolyzer terminals indicating it was acting as a “source”. After that we put a resistive load on the electrolyzer leads and generated about 16 Volts and 10 Amps for several hours (160 Watts) before it “ran out of gas”. Was the cell acting as a fuel cell, as an alkaline nickel-iron battery, or a combination of both?

TOC

Grunting and Wheezing Sounds are Normal!

Inside the Hydrogen Wind gas pressure control system there are three float control valves. Two float valves are used for the oxygen and one is used for the hydrogen. When the float valves are filled with gas (vertical acrylic tubes with top caps), they float on the electrolyte in the chambers. As each chamber fills with gas the electrolyte is gradually displaced and the the buoyancy of the float decreases. When the buoyancy is low enough, the float falls, which releases the elastomer plug from the exit passage and allows the gas to leave the system. The float valves cycle over and over again to release “bursts” of gas to the purifiers. You can hear grunting and wheezing sounds when standing alongside the unit. A little back pressure on the discharge lines makes the release less violent and quieter. With 1 bar (14.5 psig) back pressure we had good results.

Budget & Economics for Gas Production & Storage

The approximate cost for the solar hydrogen system equipment is listed on the next page, broken down by sub-system. The labor used for this installation was our own and was not tallied. Normally, for a “first time” system such as this, a rule of thumb is that the labor costs will about equal the capital equipment costs. Labor on any future clone would be significantly less.

Hydrogen System Cost

Equipment	Cost	%
12 cell electrolyzer system (incl S&H)	$2,300	34%
Photovoltaic modules (used)	$1,500	22%
Gas storage tanks, relief valves, tubing	$1,100	16%
Hydrogen purification system	$950	14%
Oxygen purification system	$350	5%
Caustic storage and transfer	$300	4%
Feedwater purification system	$275	4%
	Total $6,775	

Capital equipment costs could have been reduced by using fewer stainless steel and more plastic components. We didn't work out the "payout" or ROCE for this system before going for it. We made it because we thought it was nifty stuff! It would probably take quite a while to pay for this system. However, don't forget, it's a prototype. Mass production has a way of cutting costs by factors of ten. How does a cloned system capital cost of $678 sound?

Status and Future Direction

Startup of this system occurred during the first week of December 1993. Our next task is to measure the purity of the hydrogen and oxygen product gas streams before we attempt storage.

Eventually, when we have a use for the oxygen gas product in a large fuel cell, we plan to add an oxidation recombiner to the oxygen side. This will remove any hydrogen impurity from the oxygen side and make it safe to store and handle. For now, we are not storing the oxygen. Instead, we will supply the oxygen to the root system of vegetables in some experiments with a horticultural friend of ours, but that's another story...

A future article will focus on safe storage of hydrogen and oxygen (see "Hydrogen Storage," p.95 and "Hydrogen Purification," p.69). We plan to cover compressed hydrogen and oxygen gas storage and hydrogen storage in metal hydride.

Acknowledgements

Alternative Energy Engineering, David Booth and David Katz, for the upgrade to our Enermaxer power controller.

Jim Robbers and Mike Robbers for the used stainless steel swimming pool filter cases which we use for electrolyte storage.

TOC

◀ ▶

Access

Walt Pyle, WA6DUR, Richmond, CA • 510-237-7877

Jim Healy, WH6LZ, Richmond, CA • 510-236-6745

Reynaldo Cortez, Richmond, CA • 510-237-9748

Electrolyzer

Hydrogen Wind Inc. RR 2 Box 262, Lineville, IA 50147 • 515-876-5665

Purifier and Storage Components

Hydrogen Coalescer (Coilhose 27C3-S): Weill Industrial Supply Inc. FAX 510-235-2405

Bi-directional Bubbler: H-Ion Solar Co. • FAX 510-232- 5251

Flame Arrestors: Check valve flashback arrestor, flash arrestor body with female inlet check valve. Part # FA-3CV. Western Enterprises • FAX 216-835-8283

Purifier and Storage Components (continued)

Oxygen Coalescer Finite Housing S2M-2C10-025: A F Equipment Co. 408-734-2525

Hydrogen Recombiner Deoxo Purifier D50-1000: GPT Inc. FAX 908-446-2402

Pressure Relief Valves (Nupro 177-R3A-K1-A): Oakland Valve & Fitting Co. • FAX 510-798-9833

Power Sources

Solar arrays: Carrizo Solar Corp. • 800-776-6718

Enermaxer controller: Alternative Energy Engineering • 800-777-660

Hydrogen Purification

Electrolyzers driven by photovoltaics

by Walt Pyle

Originally published in Home Power #67
October / November 1998

Hydrogen gas (H_2) can be used for cooking, water heating, space heating, electricity generation, welding and cutting, and the synthesis and purification of other chemical materials. When hydrogen is made from water and renewable energy resources such as PV, wind, or micro-hydro, we refer to the produced gas as "solar-hydrogen." Solar-hydrogen is a sustainable carbon-free gas. It can release heat when burned with air or oxygen, or produce electricity when combined electrochemically with oxygen in a fuel cell. When solar-hydrogen is made or burned, there are no carbon monoxide, carbon dioxide "greenhouse gas," or hydrocarbon pollutants produced.

Hydrogen Purification

This article discusses hydrogen purification as a prerequisite to storage or utilization, and covers safety considerations in home power applications.

Where Does Hydrogen Gas Come From?

1. RE Electrolysis of H_2 Gas

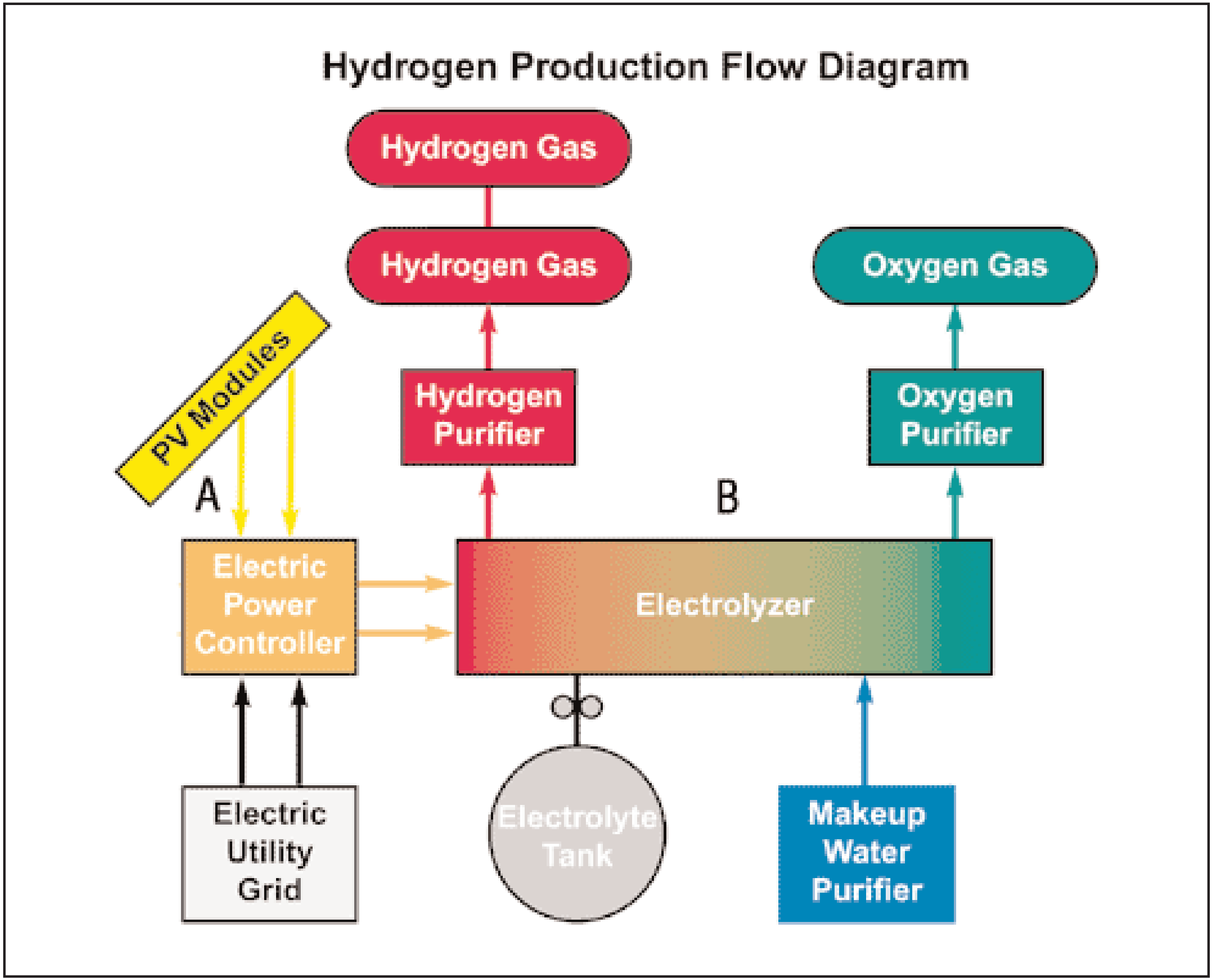
We use PV electricity to run an alkaline electrolyzer to produce hydrogen gas. Unfortunately, we do not have a creek or other water resource nearby for micro-hydro electricity production. We could really use it during the rainy season when there is less solar insolation. Since we are located on a hillside in an urban area, a wind generator tower would not be a welcome addition to our neighbors' view. With this in mind, we use PV electricity as the exclusive renewable power source for our hydrogen plant.

Solec 50 peak-Watt PVs (A, see diagram on next page) are arranged in eight panel arrays. They are wired in series-parallel for 24 Volts. Three of these arrays, totaling 24 panels, will produce sufficient power to run our Hydrogen Wind twelve-cell electrolyzer at nearly its rated 1 kW capacity.

Our Hydrogen Wind electrolyzer (B) is shown in the diagram with its associated purifiers and storage tanks. For more information on the production of hydrogen by electrolysis and hydrogen storage, see p.44 and p.94, respectively.

TOC

Hydrogen Purification



2. Industrial Cylinder H_2 Gas

We can buy hydrogen gas in high pressure cylinders from a welding supply house. The industrial grade is about 99.5+% pure hydrogen. It may have a few parts per million of hydrocarbons, water vapor, helium, oxygen, and nitrogen contaminants present. These cylinders come in four volumetric sizes, and have 120 to 240 bar (1800 to 3500 psig) pressure ratings. The most common cylinder size is six cubic meters (215 cubic feet). Most industrial hydrogen is made by steam-reforming natural gas.

In the past, we bought hydrogen cylinders and used them in our shop. Now that we make our own gas, we rarely have to purchase it.

3. High Purity Industrial H_2

There are several higher purity grades of hydrogen available for research and metallurgical processing purposes, when contaminants must be minimized. One is the “pre-purified grade” with minimum purity of 99.95%. This grade contains less than 20 ppm oxygen with a dew point of less than -59°C (-75°F). This quality of hydrogen is often referred to as “3-nines.”

Another high-purity hydrogen, the “ultra-high purity (Gold Label) grade,” provides 99.999% molecular hydrogen. Sometimes this is called “5-nines” purity. For those who demand the best, there is “Research Grade”. This grade has even fewer impurities, and is available in small lecture bottles.

4. Cryogenic Liquid H_2

Liquid hydrogen is primarily used as rocket fuel or for large industrial sites. The only significant impurity is helium. We have never used liquid hydrogen for home applications, because special tanks are required. The cryogenic tanks have dual walls. The space between the walls is evacuated and filled with radiation reflective multi-layer insulation. Some experimental cars have been run on liquid hydrogen.

6. Common-duct Hydrogen-Oxygen

Common-duct hydrogen-oxygen welding gas is commonly referred to as either Rhodes' gas or Brown's gas. This gas consists of hydrogen that comes from a "common-duct" electrolyzer, mixed with oxygen. It is VERY dangerous. $H_2 + O_2$ mixtures should NEVER be stored. Common-duct electrolyzer hydrogen is not suitable for use in hydrogen fuel cells, catalytic heaters, or diffusion burners.

The only sensible application for common-duct hydrogen is to run welding and cutting torches. When it is used in this manner, there is no storage and the gas is consumed as it is made.

TOC
◀ ▶

What Contaminants May Be Present in H_2?

1. Solid Particulate Contaminants in H_2 Gas

It is possible to find entrained particles of dirt and rust in a hydrogen electrolyzer's product stream. Some electrolyzers have steel or iron alloy containers, valves, and piping. This metal may produce low levels of rust particles over time. Electrolyzers frequently use high surface area electrode materials such as nickel that may lose small particles into the electrolyte. Sometimes, particles of either plastic or sealant will enter the electrolyte system. This happens due to poor housekeeping during manufacturing or repair. These particulates can be removed from your hydrogen gas stream with an appropriate scrubber or filter.

2. Liquid Contaminants in H_2 Gas

Electrolyte is the normal liquid contaminant in an alkaline electrolysis system. In this case, it is water plus potassium hydroxide (KOH). A small amount of KOH and water escapes from the electrolyzer with the flow of hydrogen. An aerosol of fine electrolyte droplets is produced as bubbles of hydrogen gas rise to the surface of the liquid electrolyte and then pop. The same thing happens on the oxygen side of the electrolyzer.

TOC

In our Hydrogen Wind electrolyzer, there is another source of KOH/water aerosol hydrogen contamination: electrolyte-wetted float valves that control the discharge of gas from the unit. Any other liquid contaminant in the hydrogen gas would be unexpected. A coalescing filter can remove solids and liquid KOH/water aerosol droplets.

3. Gaseous Contaminants in H2 Gas

Under certain conditions, we find gaseous contaminants such as oxygen, nitrogen, argon, and water vapor in our hydrogen gas.

Oxygen, nitrogen, and argon are present in normal air. When all three of these gases are present in the normal proportions, an air leak into the electrolyzer or its piping has occurred. However, this is rare. Usually, this is seen only at startup of the electrolyzer when purging or evacuation is imperfect. It also can happen when there are significant leaks in either the cells or in the interconnecting piping. Once the electrolyzer is operating above atmospheric pressure, no outside air will leak inside. However, some hazardous electrolyte may leak out if there are any poor seals. See the chapter “Solar Hydrogen Production by Electrolysis” p. 44 for safety information about handling alkaline electrolyte, as KOH is very corrosive to skin and eyes. Nitrogen and argon are not a safety concern, as they are inert gases. Oxygen is the contaminant of primary concern.

Water vapor is always present in a KOH/water electrolyzer. The gas vapor space of each cell is saturated with water above the electrolyte. The concentration of water saturation is governed by the temperature and pressure in that environment. The objective in a purifier system is to remove excess water vapor. This prevents condensation from occuring downstream, with subsequent flooding of other components. The presence of some water vapor in hydrogen that has been purified for storage in pressure tanks is not harmful - as long as a compressor is not used. The presence of water vapor in stored hydrogen gas slightly reduces its flammable limits in oxygen or air. Our electrolyzer produces gas under pressure, between 0.1 and 4 bar (1 to 58 psig), depending on storage tank pressure.

What are the Methods for Purifying H_2 ?

1. Scrubbers for Particulate and KOH Removal

Hydrogen gas that is contaminated by KOH/water electrolyte can be scrubbed by passing it through a water column in a Double-Bubbler TM (photo next page, and C in the diagram on page 85) to remove the KOH.

2. Catalytic Recombination Purifier to Remove O2 Impurity

The **catalytic recombination of hydrogen and contaminant oxygen** is usually accomplished at room temperature or higher, and **results in**

TOC
◀ ▶

the formation of water vapor, which is easily removed if necessary. These gases are recombined in a ratio of two parts hydrogen to one part oxygen. Complete removal of the undesirable oxygen impurity can be done in the presence of a stoichiometric or greater quantity of hydrogen.

The larger the volume of oxygen impurity present, the higher the catalyst temperature will be for a given flow. This happens because the formation of water releases heat.

Double Bubbler™ removes particulate matter and KOH from the hydrogen gas by passing it through a column of water.

Usually, the catalysts that are used for removal of the oxygen impurity from hydrogen (or vice versa) are based on platinum group metals (PGM). Thin films of PGM are supported on the surface of alumina pellets. The catalyst pellets are contained by screens in a section of pipe. The hydrogen gas flows through the pipe as it is being treated.

The **catalyst will not work while wet.** Care should be taken to avoid water condensation on the catalyst. If it becomes wet, simply dry it out before using. Removal of oxygen from hydrogen is called deoxygenation. Our catalytic recombiner (D, p.85) was designed to be capable of removing up to 3% oxygen from a hydrogen production stream, reducing the oxygen content to less than 1 ppm.

3. Polymeric Hollow-fiber Membrane Purifiers

Polymeric membranes employ the principle of selective permeation to separate gases. Each gas has a characteristic permeation rate. This rate is a function of the ability of a gas to dissolve and diffuse through a membrane. This **allows "fast" gases like hydrogen to be separated from "slow" gases like oxygen**. Some membrane separators use bundles of tiny hollow fibers inside a containment vessel or pipe.

During the process, a differential pressure develops across the fibers. This pressure drives the flow of the faster gas through the wall of the fiber. In this example, the faster gas is hydrogen. This results in the production of a purified hydrogen stream called the "permeate." To accomplish an efficient separation, the differential pressure must be 8 bar (100 psig) or greater. Monsanto makes this type of purifier for industrial hydrogen recovery under the Prism and Permea trademarks. At this time, they do not offer a purifier small enough to be used in a home-sized hydrogen plant.

4. Palladium-Silver Membrane Purifiers

Ultra-pure hydrogen can be obtained by diffusion through palladium alloys. Palladium is unique: it is extremely permeable to hydrogen, and it can store up to 1000 times its own volume of hydrogen! The mechanism of hydrogen diffusion through palladium alloy has six steps: adsorption, dissociation, ionization, diffusion, reassociation, and desorption. Johnson-Matthey, Inc. and Teledyne Wah-Chang manufacture membranes of this type.

Almost no hydrogen will flow through the membrane at room temperature. **Operating conditions** required for palladium alloy membranes include temperature of approximately **200 to 800°C** (392 to 1472°F) and differential pressure across the membrane of **3 to 12 bar** (44 to 180 psig).

In our renewable energy system, we did not have energy to spare for heating the purifier. In addition, our electrolyzer did not produce sufficient pressure to operate a palladium membrane separator. A solar thermal source could be used to heat a palladium membrane purifier and reopen this option.

This a very attractive method for **simultaneously removing water and oxygen from hydrogen**. It is also the most expensive hydrogen purification option reviewed. We priced one for our 1 kW hydrogen generation plant and found a small lab-sized palladium-alloy membrane purifier for about $2000. This is the **purest hydrogen gas available, 99.999999%** purity. Yes, that's

TOC

◀ ▶

"8-nines." Oxygen cannot pass through the membrane, so **safety is increased for hydrogen gas storage when these membranes are used for purification**.

5. Hydrogen Dryers for Removing Moisture

Water contamination of hydrogen can be reduced by coalescers, refrigeration dryers, membrane dryers, molecular sieve dryers, and desiccant dryers.

Coalescers (E, p.85)) are designed to cause combining of smaller aerosols into larger droplets, susceptible to the effects of gravity. Coalescers remove sub-micron solids and aerosols by three different mechanisms. First, particles in the range from 0.001 to 0.2 microns collide with the filter media and are subject to diffusion coalescing. Second, particles in the range of 0.2 to 2 microns are intercepted by 0.5 micron glass fibers. The efficiency of the interception mechanism increases as the pore size decreases. Third, particles 2 microns and larger are removed by direct inertial impacting, because of their larger mass and momentum. A coalescer is one of the most cost-effective water aerosol removers.

Refrigeration dryers cool the gas and dry it by condensation to a low dew point. These dryers use electric motor compressors and refrigeration fluids in a conventional Joule-Thompson expansion scheme. We did not choose a refrigeration dryer for our solar-hydrogen plant because of energy

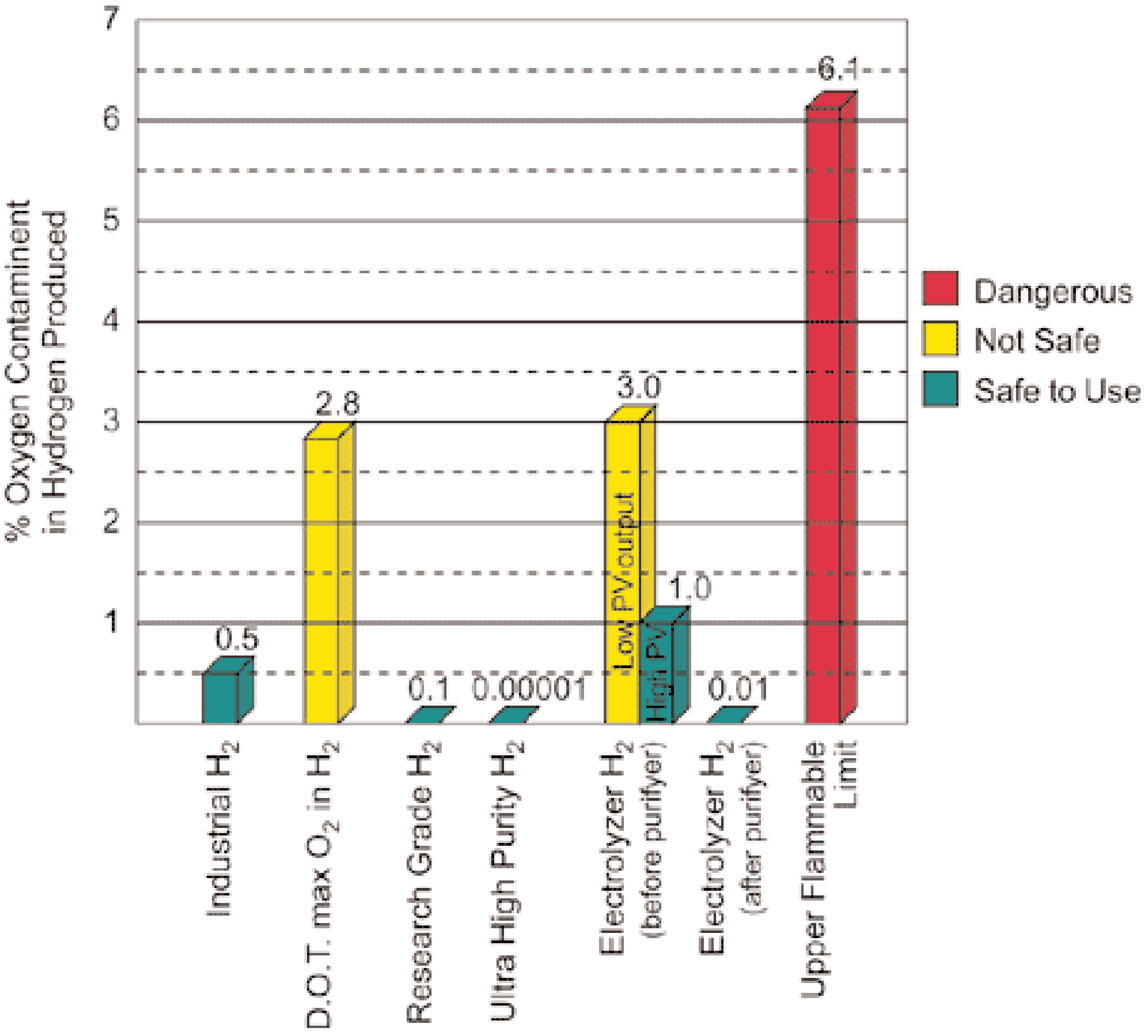
TOC
◀ ▶

consumption, cost, and reliability concerns. Perhaps an absorption refrigerator could be applied to this process with solar thermal energy to reopen this option.

Membrane dryers utilize a hygroscopic ion exchange membrane to selectively remove water vapor from mixed gas streams. It can be thought of as a desiccant in tubular form. Tubes are bundled together inside a pipe shell so that the wet feed gas stream flows through the tubes and wets the inside walls. A counter-current dry gas stream flows on the outside of the tubes and purges water from the shell. A disadvantage of this type of dryer is that the dry purge-gas flow rate is greater than the wet product feed rate. Perma Pure Products, Inc. makes this kind of gas dryer.

Another substance used for drying gas is zeolite. Zeolites are alumino-silicate mineral particles that absorb and desorb large quantities of water reversibly. Water absorption on these so-called molecular-sieve dryers is by way of a physical rather than chemical reaction. **Zeolite dryers** are regenerated thermally in their piping containers by heating them up to 550°C (1000°F) while purging with a dry gas. For continuous operation, two units are used. One is drying gas while the other is regenerating. RSI, Inc. makes small molecular-sieve zeolite dryers for hydrogen. We did not select a zeolite dryer for our solar-hydrogen plant because of concerns about energy consumption for the heat regeneration cycle. A solar heated regenerator would reopen this option.

Safety Levels of Oxygen Contamination



TOC

Desiccant dryers absorb water vapor from the gas by contact with a chemical substance like calcium chloride. One popular lab gas desiccant is called Drierite. It includes a color indicator to show when the desiccant must be regenerated. The color turns from blue to pink when water is absorbed. The desiccant is dried by heating or evacuation for recycle.

Safe H_2 Storage

You are responsible for the purity of the solar-hydrogen to be stored. Hydrogen and oxygen mixtures are not safe to store. Make sure that your gas is at least 99% pure hydrogen before storing it in a tank. Measure your hydrogen gas purity with a quality instrument to be sure it is safe.

Oxygen is the impurity of concern, so measure for it in your hydrogen on a regular basis. The strategy for safe hydrogen storage includes using 99+% pure gas, and eliminating the oxygen impurity.

Homebrew Purification System

A hydrogen purifier was constructed for our 1 kW home-scale alkaline-electrolysis hydrogen production plant. We chose a catalytic recombination process to remove the oxygen impurity. Details are shown.

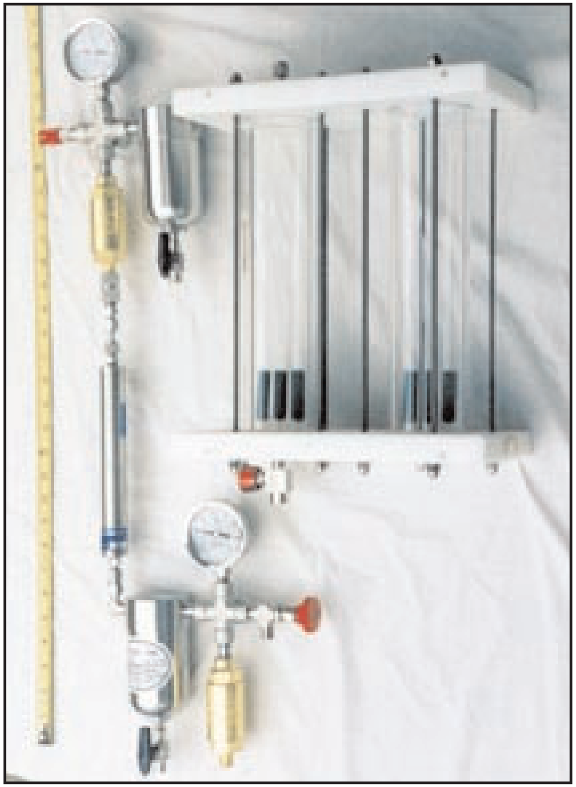
A Double-Bubbler (C, p.85) with water columns and sparger-frit aquarium-type bubblers can provide several useful functions. It can serve as a visual

TOC

◀ ▶

flow indicator, KOH scrubber, flame arrestor, liquid back-flow preventer (for intermittent operation), upstream or downstream leak detector, and imbalance detector (requires 2 units for comparison of O_2 and H_2 production).

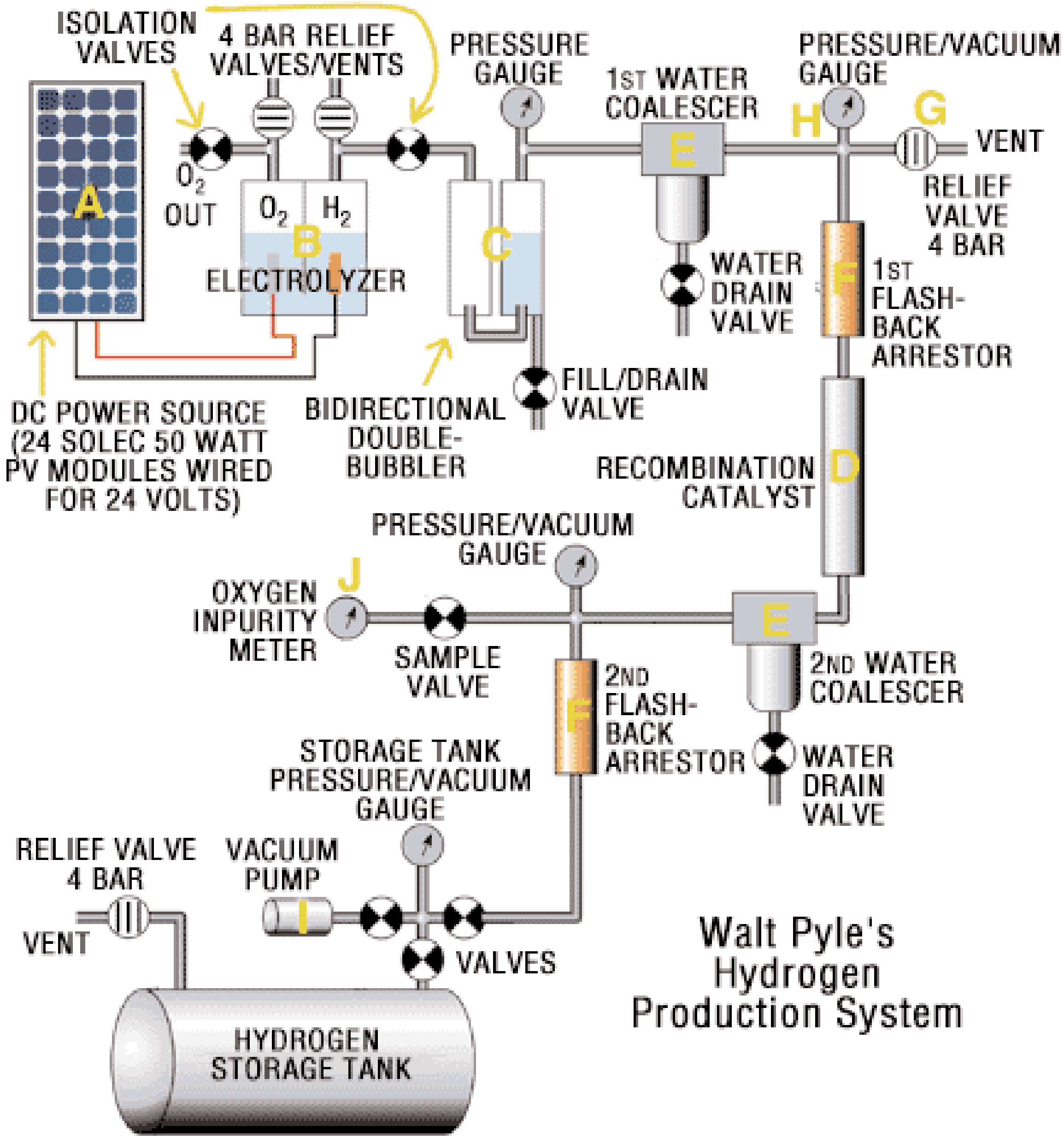
The water in the bubbler columns must be changed during regular maintenance servicing, as it becomes alkaline over time. Some operators have reported using cider vinegar instead of water for longer life between column liquid changes. A color change apparently occurs when the acidity of the vinegar is neutralized by the KOH/water aerosols. Soon, we're going to try it here to see for ourselves.



The Double-Bubbler™ and purifier system

Water Coalescers and Water Drain Valves

Our coalescers (E, p.85) have stainless steel bodies, and bowls with replaceable filter elements inside. The **coalescer filter removes rust, nickel,**



Walt Pyle's Hydrogen Production System

TOC
◀ ▶

The relief checkvalve, pressure/vacuum gauge, and tops of a flash-back arrestor and coalescer.

plastic, and dirt particles from the hydrogen gas stream. Coalescers also **remove water vapor aerosols**, known as fog.

The first coalescer removes bubbler aerosol. The second removes recombination-water aerosol, produced by deoxidation of the hydrogen as it passes over the catalyst beads. Our coalescer is a Finite unit manufactured by Parker Hannifin Corp. It captures water aerosols in the 0.001 to 10 micron size, using a glass micro-fiber element. We chose to use a type C filter media in the coalescers. It is compatible with hydrogen gas and can be used on the oxygen side as well.

These coalescers are position-dependent, and must be mounted so that their water capturing bowls and drain valves face down. The coalescers require horizontal piping connections at the entrance and exit. With horizontal piping, the bowls will gravity fill with coalesced water.

TOC

Each coalescer is equipped with a small ball valve on the bottom of the bowl to allow regular draining of water captured from the hydrogen. **The coalescers must NOT be allowed to fill up with water**. We drain the water from the coalescers about once a week.

A flash-back arrestor

Flash-back Arrestors

Flash-back arrestors (FBA) (F, p.85) are used to isolate the purifier from other components upstream or downstream in the hydrogen system piping. An **FBA will stop a flame from propagating through a pipe**.

Hydrogen is flammable and easily ignited when oxygen is present. The FBA isolates flammable air and hydrogen, or oxygen and hydrogen mixtures, from any source of ignition. An open flame, spark, or hot metal surface can be a source of ignition.

A **catalyst can** also **be a source of ignition**, even at room temperature. By bracketing the catalyst with an FBA on either side, the upstream or downstream mixture will not be ignited. This is true even if there is a flammable mixture in the line due to a malfunction or mistake.

TOC

FBAs are made with a plug of fine silica sand restrained by screens in a wide section of piping. The sand quenches any flame-front and stops combustion. We prefer the FBAs that have an integral check valve to prevent backflow. Western Enterprises, Inc. makes an FBA appropriate for hydrogen and acetylene gas service.

Check Valve Pressure Relief

A check valve (G, p.85) for pressure relief is set to 4 bar (58 psig) to prevent over-pressuring the system by error. If this pressure is exceeded, the relief check valve “cracks” and hydrogen gas is released out of the vent line. When the pressure is reduced to normal operating value (0.5 to 3.5 bar gauge), the valve closes once again. **Relief valves are subject to drift over time, so check to be sure that the set pressure and the actual pressure are the same.** This should be done at regular maintenance shutdowns.

Compound Pressure Gauges

We use pressure gauges (H, p.85) with all stainless parts to prevent corrosion failure. They are compound gauges measuring both vacuum and pressure. We use the vacuum gauge function to evacuate the system after maintenance, or before startup of the hydrogen plant. The pressure gauge monitors operation of the plant when making hydrogen gas.

De-oxo Catalytic Recombiner

Our catalyst (D) is packed in a stainless steel tube by the supplier and performs the **key purification function: removing oxygen** from the hydrogen gas stream. The catalyst tube must be placed so that the flow enters through the top and exits at the bottom. This will prevent lofting the particles in the catalyst bed and fluidizing them. Keeping the catalyst pipe vertically oriented helps to keep the flow uniform. Thus, the **water formed during de-oxo purification** flows towards the bottom in the same direction as the hydrogen gas. It can be removed from the purified hydrogen by the second coalescer before it reaches the second FBA.

Connecting the Purifier to the Electrolyzer

The hydrogen duct coming from the electrolyzer is first connected to the gas inlet port of the Double-Bubbler for KOH/water scrubbing. The scrubbed hydrogen gas is then fed to the purifier for oxygen removal. We used 1/4” stainless tubing with Swagelok fittings to connect the electrolyzer, bubbler, and purifier.

Purging the Purifier

Before starting the hydrogen plant, **flush any possible flammable gas mixture out of the piping with an inert purge gas** such as nitrogen or carbon dioxide.

An alternate method to remove flammable gas mixtures from the piping and other components is to use a mechanical vacuum pump (see p.85). It must be capable of producing a vacuum of at least 20 mbar (approximately 20 Torr). **A vacuum cleaner will not work for this**. A two-stage laboratory vane-type vacuum pump with a thermocouple pressure gauge will work well.

Compound pressure gauges are very useful, because you can see when the vacuum has reached less than 20 millibar (>29 inches Hg vacuum). It is also easy to check if the piping holds vacuum after the pump is removed. Vacuum measurement units have become more standardized in recent years. Unfortunately, many gauges are still on the market that register vacuum in inches or millimeters of Hg (mercury) below atmospheric pressure. This can be confusing to the uninitiated.

Start-up of Electrolyzer and Purifier

Once the purifier is ready, we start the electrolyzer by closing the main electrical breaker to the DC power supply. Then, we wait twenty minutes or so for the float valves on the Hydrogen Wind electrolyzer to fill. Next, we close the vent valve on the electrolyzer. Pressure in the electrolyzer will begin to rise. Slowly, we open the isolation valve between the electrolyzer and the Double-Bubbler. Gas will enter the purged purifier. After the hydrogen flow through the Double-Bubbler has stabilized, we open the isolation valve all the way, and leave the valve open.

Measuring Hydrogen Purity

When production of gas is underway, we check the purity of the gas before storage. Several oxygen meters are available. We use a Panametrics XMO2 oxygen analyzer (J, p.85) that has a range of 0 to 5% oxygen. This meter has high accuracy and is reliable. A less expensive oxygen meter is available from Figaro USA. Our hydrogen has less than 0.01% oxygen after the purifier. We have used this catalytic purification system continuously for almost three years with no loss in performance.

Future Direction

We are now planning to store and use the electrolyzer's purified oxygen production for both fuel cells and a hydrogen-oxygen torch. The purifier has been operational for almost a year. Since we lack a suitable meter to measure the hydrogen contaminant in the oxygen, we still vent it to the atmosphere. Next month, our long-

The Panametrics XMO2 oxygen analyzer measures the amount of O_2 in the hydrogen.

awaited hydrogen meter from DCH, Inc. is due to be delivered. The DCH meter is designed to measure from the ppm level to 100% hydrogen. In a future article, we will share our experience with oxygen purification and storage.

Acknowledgements

The author gratefully acknowledges the assistance of the following individuals in fabricating, testing, and documenting this system: Mark Hayes, H-Ion Solar, Inc.; Reynaldo Cortez, Shadowbox Construction Co.; Don Mackinder, H-Ion Solar, Inc.; Larry T. Pyle, Pyle Manufacturing Consulting; and Pat and Angello Scipi, A & K Machine.

Access:

Author: Walt Pyle, H-Ion Solar, 6095 Monterey Ave., Richmond, CA 94805 • 510-237-7877 Fax: 510-232-5251 • hionsolar@aol.com Web: www.hionsolar.com

Safety Information: Air Products and Chemicals, Inc., “Safetygram 4” on Gaseous Hydrogen • 610-481-4911

Alkaline Electrolyzer: Hydrogen Wind Inc., RR2 Box 262, Lineville, IA 641-876-5665

Catalyst Suppliers: Resource Systems Inc., Six Merry Lane, East Hanover, NJ 07936 • 973-884-0650 • Fax: 973-515-3166 GPT, Inc. • 732-446-2400 • Fax: 732-446-2402

Access (continued)

Coalescer:
A.F. Equipment Co., Inc., 1273 Forgewood Ave., Sunnyvale, CA 94089-2216 • 408-734-2525
Parker Hannifin Corp., 17325 Euclid Ave., Cleveland, OH 44112 • 800-506-4261 • 216-531-3000

Complete Purifier System (Model PT-4) and Double-Bubbler (Model DB-3): H-Ion Solar, Inc., see Walt Pyle above.

Flash-back Arrestor (Western Enterprises Model FCV-3A): Atlas Welding Co., 1224 6th Street, Berkeley, CA 94710 510-524-5117 • Fax: 510-524-9098

Hydrogen Membrane Dryer: Perma Pure Products, Inc. • 732-244-8140

Palladium-alloy Membrane:
Johnson Matthey, Inc. • 44-1763-253306 (Great Britain) 610-971-3100 (USA)
Teledyne-Wah Chang, Inc. • 541-967-6904

Polymeric Membrane: Permea, Inc. • 800-635-8842

Pressure Gauge: Fluid Gauge Co., P.O. Box 881833 San Francisco, CA 94188 • 415-285-0648

Stainless Pipe Fittings: Oakland Valve and Fitting Co., 2441 Sprig Ct. - Unit A, Concord, CA 94520• 510-676-4100 Fax: 510-798-9833

Hydrogen Storage

by Walt Pyle

Originally published in Home Power #59 • June / July 1997

Hydrogen storage is needed for homes, businesses, and vehicles, to realize the dream of the Solar Hydrogen Age. Since hydrogen gas is useful as a fuel for cooking, heating, electricity production, and vehicle propulsion, we need a way to store the solar hydrogen made during the day for use at night, and seasonally as well.

For more insight on how this wonderful fuel can be used and produced see the chapters about cooking with hydrogen (p.118 and 129), space heating with hydrogen (p.143), making electricity with hydrogen (p.169), and hydrogen production from PV and wind electricity (p.20, 32, 38, 44).

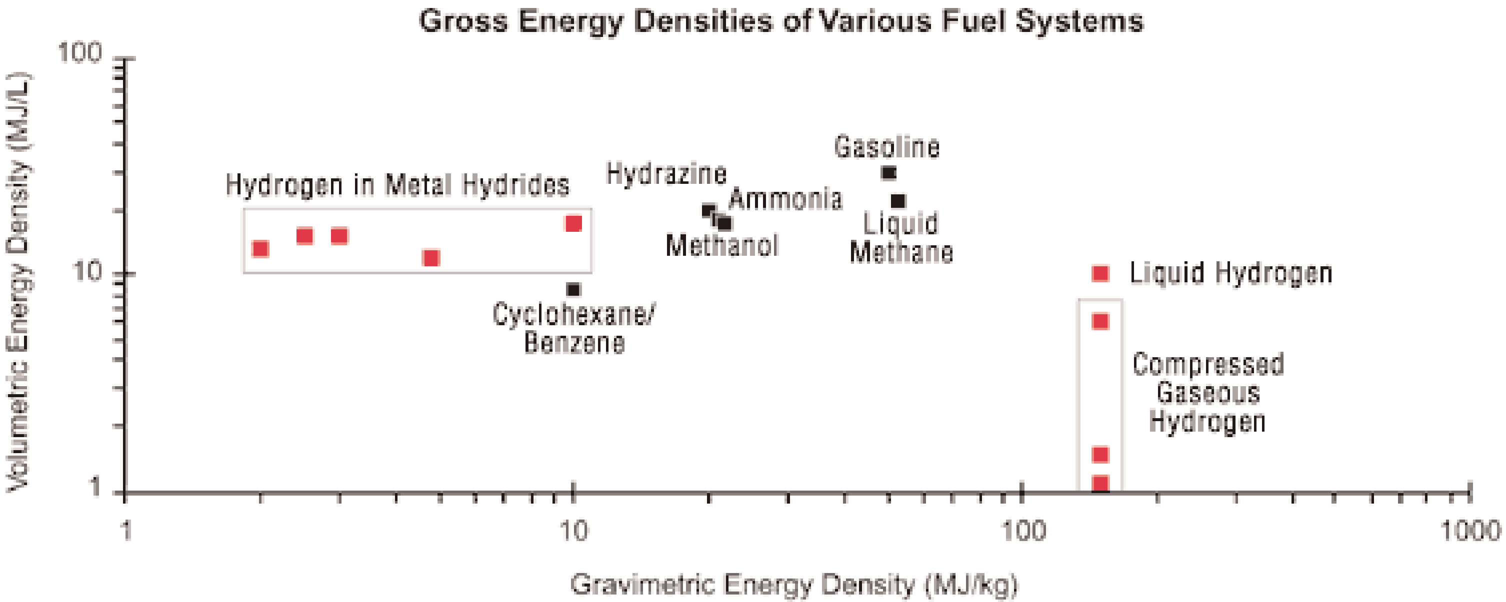
Most home energy use occurs in the evening when there is no solar hydrogen production occurring from a home hydrogen plant. Over-night hydrogen storage can solve this problem. Summer-time solar hydrogen production can meet or exceed home consumption requirements. Winter-time hydrogen demand (for heating) is maximum at the time when solar hydrogen production is at a minimum. Seasonal home storage can correct this out-of-phase relationship.

TOC

LPG gas tanks used as medium pressure storage for hydrogen and oxygen.

Vehicles require on-board storage of hydrogen fuel, and fuel providers away from home (service stations) require larger bulk hydrogen storage capacity. Storage options for hydrogen to be used at home are considered in this article.

TOC
◀ ▶



What are some of the storage options for hydrogen?

Many different schemes have been investigated and applied in research programs and demonstrations since the first “oil shock” in 1973. Some of the options are listed below:

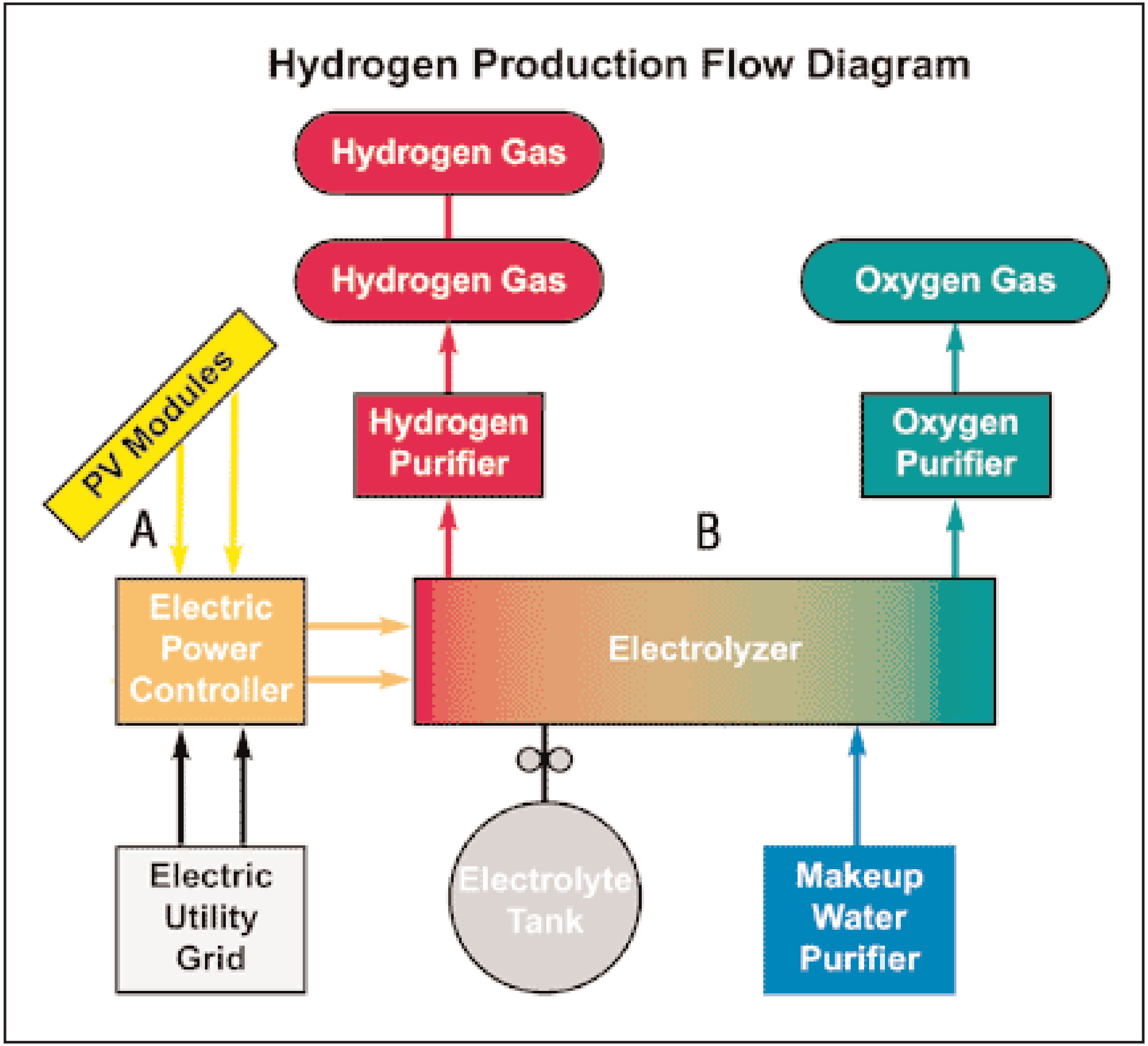
- compressed hydrogen gas (CHG) in cylinders or tanks
- tethered balloon, “bag,” or water displacement tank (low pressure CHG)
- hydrogen adsorbed into metal to form metal hydride (MH)

- liquid hydrogen (LH_2) in cryogenic tank
- adsorption on high-surface-area carbon powder in tank
- encapsulation in glass micro-spheres (experimental)
- adsorption on carbon “nano-tubes” (experimental)
- in water (H_2O) (not a “fuel”)
- in ammonia (NH_3)
- in liquid hydro-carbons: gasoline, diesel fuel, alcohol,
- liquid natural gas (LNG), propane or butane (LPG), etc.
- in gaseous hydrocarbons: compressed natural gas (CNG), bio-gas, etc.

The first three hydrogen storage options above, CHG, MH, and LH_2, are the “stateof-the-art” methods most frequently applied in vehicular and stationary applications. The energy density of different hydrogen storage options are shown below, and compared to that of gasoline.

The last two hydrogen storage options, using liquid and gaseous hydro-carbons, are the fossil-fuels that dominate our global fuel production and consumption systems today. For example, a large amount of hydrogen is added to petroleum feedstock to make gasoline. These liquid hydrocarbon fuels are widely used in transportation because of their extremely high energy density.

Hydrogen Storage

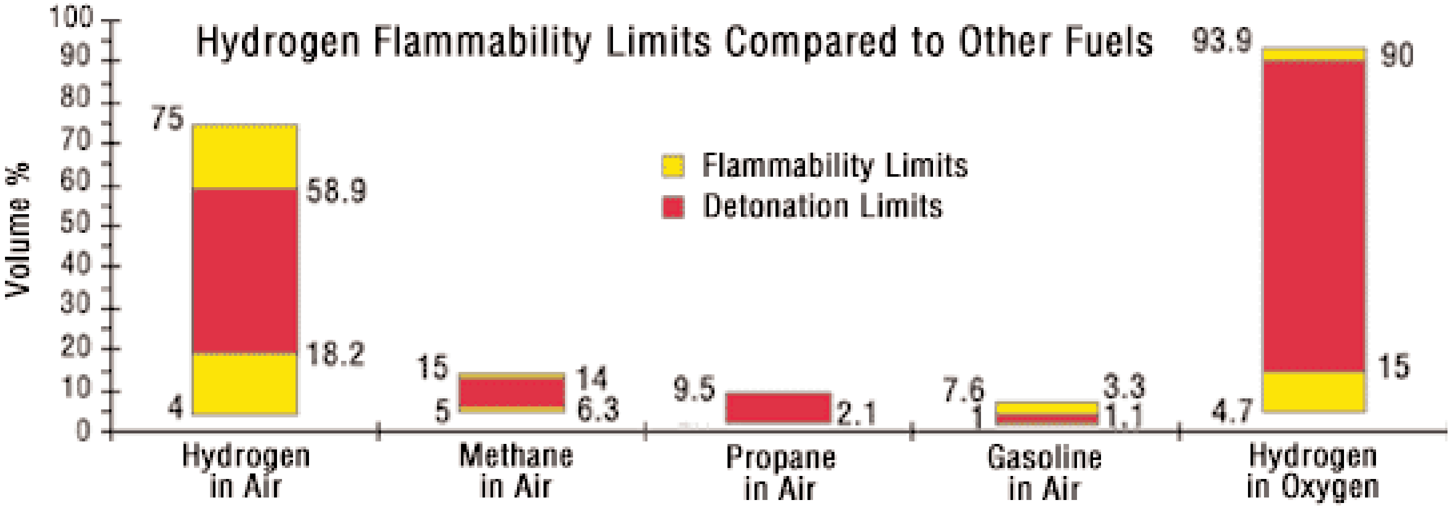


In this article we are focusing on the CHG and MH storage options, since they are the easiest to implement for home power applications at this time. LH_2 production requires a large energy expenditure for refrigeration to liquefy gaseous hydrogen. LH_2 is primarily used for transportation applications, so we choose not to elaborate on this method now. We also "gloss over" the experimental hydrogen storage options in this article, since their values are still being proven.

Safety First!

If hydrogen is to be stored, it must first be made safe to store. Hydrogen and air, or hydrogen and oxygen mixtures are not safe to store if the O_2 contamination is significant. Hydrogen has much wider flammable and explosive limits compared to other fuels, especially in hydrogen-rich mixtures with air or oxygen. Hydrogen flammable limits are shown on page 16 and compared to some common fossil fuels.

Hydrogen should never be stored unless it is well below the lower flammable limit (LFL). Normally, industry standards for storage safety call for well below 0.25 LFL, (or less than 1% oxygen in the hydrogen.) To meet this standard, some way of accurately measuring the oxygen contaminant in the produced solar hydrogen must be available. Some hydrogen sensors are listed in the access section at the end of this article



Compressed Hydrogen Gas (CNG)

CHG is one of the simplest methods for storing hydrogen fuel for later use. The hydrogen storage density becomes greater as the pressure is increased. Hydrogen production from an electrolyzer can provide pressures suitable for storage at low and medium pressures. Low-pressure CHG is the basis for balloon or “bag” storage, often seen used for weather balloons or for “bag” storage of fuel gas. The same principle is applied to hydrogen storage that has been used for natural gas storage at low pressure: bus roof storage bags and underground water displacement tanks. Low-pressure tanks are widely used in China and India for storage of bio-gas fuels. Pressures in these low-pressure CHG containers are only slightly above atmospheric pressure, and they are characterized by very large volume and low container weight.

Medium Pressure CHG Storage

This type of storage has been done using tanks originally designed for air or propane (LPG) service. Typically these tanks are rated for about 17 bar (250 psig) maximum pressure in the intended service, and de-rated to 4.1 to 8.6 bar (60 to 125 psig) maximum when used for storing hydrogen.

The tank alloy should be low-carbon steel or another material resistant to, or unaffected by, hydrogen embrittlement (weakening) of the tank alloy. High-carbon steel tanks are not appropriate for storing hydrogen under pressure. To avoid hydrogen tank embrittlement, avoid steels that are: a) cold-rolled or cold-forged, or b) have weld hard spots in excess of about Vickers Hardness Number 260.

Non-metal tanks such as composite-fiber tanks avoid hydrogen embrittlement concerns and de-rating.

Medium-pressure CHG storage tanks are characterized as having smaller size and greater weight, for a given storage capacity, relative to low-pressure CHG tanks.

Safety First!

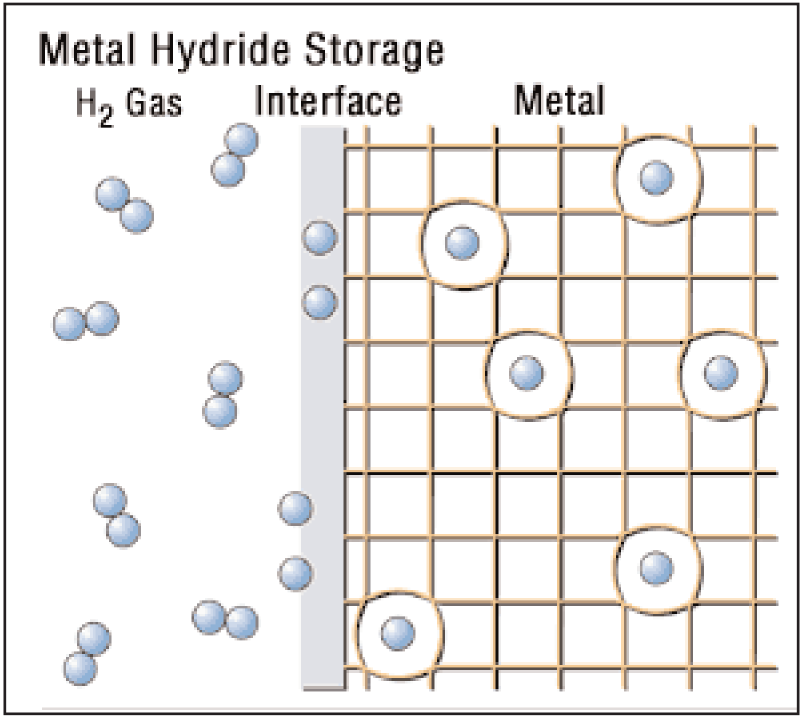
Tanks intended for use with significant hydrogen pressure should be hydrostatically tested to at least twice the intended operating pressure, and equipped with a suitable pressure release device. All storage tanks for hydrogen should be installed outdoors, never inside buildings or enclosed spaces. A flash-back arrestor should be used on each of the tank's input and output lines to prevent flame propagation, in the event a flammable mixture forms due to any mistake or system break-down.

High Pressure CHG Storage

This is the densest compressed hydrogen gas storage option. A compressor is normally used to increase the hydrogen pressure. Typical storage pressures of 140 to 400 bar (2000 to 5800 psig) maximum are used in welding cylinders, tube trailers, and composite-fiber cylinders. It is possible to eliminate the hydrogen compressor by operating the hydrogen production process at the desired high pressure, for example, by using a high-pressure electrolyzer.

Most merchant CHG that is used for welding or other industrial purposes is handled in steel cylinders that contain 5.7 to 8.5 m 3 (200 to 300 scf). These small cylinders are about 1.4 m high and 0.2 m diameter (56 inches high and 8 inches diameter). When we have visited hydrogen demonstration projects we observed lots of these small cylinders in use. Usually, they were all empty! When we recently filled-up one of our small cylinders with 99.95 % welding purity CHG at our local supplier, it cost $22.50 for the gas, or, about 10 cents per scf. A cylinder of electronic grade high purity hydrogen costs about three times as much.

Tube trailers can supply larger applications. The cylinders in tube trailers are much larger. Tube trailers are available in 10, 36, and 45 tube versions as well as a 10 tube ISO container version.



Metal Hydride (MH) Storage

MH is an option for storing hydrogen that is very dense and safe. The downside is that the hydrogen produced for MH storage must be very high purity.

That is, the produced hydrogen must have a very low oxygen contaminant content. Typically 10 ppm O_2 maximum in H_2 must be achieved, so as not to damage the MH storage alloy. Carbon monoxide, hydro-carbon, and water contaminants must also be very low. Contaminants can alter the MH surface so that hydrogen will not be adsorbed. MH storage containers are relatively heavy compared to LH_2 , but MH container weight is of greater concern for transportation application than it is for home storage.

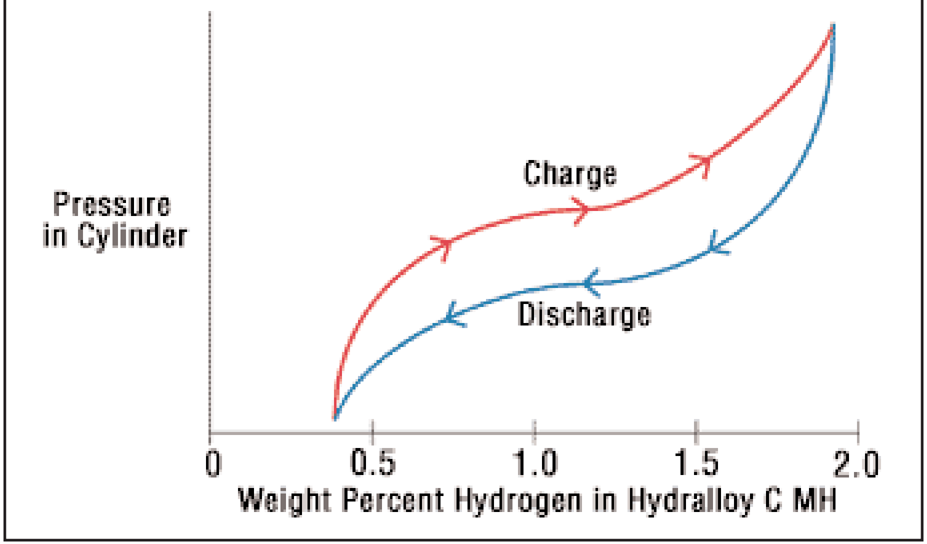
The MH alloys are characterized in several “families” according to the ratio of the alloying elements: AB, A2B, AB2, AB5, etc.. We chose to work with an AB2 alloy, called Hydralloy C made by GFE in Germany. Hydralloy C has A = titanium and zirconium, and B = vanadium, iron, nickel, chromium, and manganese. The main elemental ingredients of Hydralloy C are iron and titanium. Hydralloy C holds about 2% hydrogen by weight when fully charged, and about 1.5% is recoverable during normal charge-discharge cycling.

The hydrogen is stored in these MH alloys after they are “activated” using a break-in treatment process on newly produced alloy. The activation procedure is only used once normally, and extremes of temperature, vacuum, and hydrogen pressure are needed for the procedure. Activation removes the oxide surface films from the alloy, giving the hydrogen molecules access to the metal alloy surface. When hydrogen molecules (H_2) arrive at a clean MH surface they dissociate to produce two hydrogen atoms (2H). The hydrogen

TOC

atoms are so small they enter the crystal structure of the metal alloy and fill the voids between the metal atoms. The pressure and weight percentage for charge/discharge reactions are shown below. The curves shown are for one temperature; the pressure curves will increase for higher temperatures and decrease for lower temperatures.

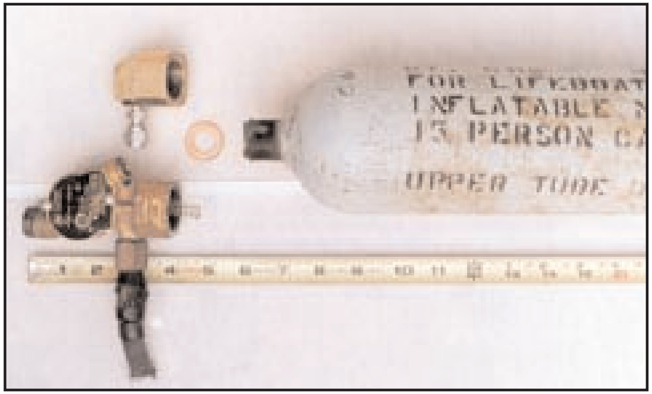
Charging & Discharging Metal Hydride Cylinder



Hydrogen Storage Homebrew

Activation of a tank filled with MH was accomplished after a few false-starts. Our first attempt was made using a small high-pressure cylinder (originally intended for CO_2 storage for life-boat inflation) that we obtained at an industrial surplus store. The cylinder had a volume of 2.3 liters (0.035

scf), weighed 3.6 kg (8 lbs) and carried a DOT rating of 3AA 145 bar (2100 psig). A rupture-disk rated at 139 bar (2000 psig) is installed in the brass cap.



CO2 cylinder to be converted to H2 storage in metal hydride.

The copper washer used to seal the cylinder cap was wet-polished with fine emery paper and then coated on both sides with a thin film of Permatex Ultra Copper Hi-Temp RTV Silicone Gasket P/N 101B, just before re-assembly. We loaded the cylinder with 6.8 kg (15 lbs) of Hydralloy C, about two-thirds full, to conservatively allow for more than 18% expansion of the alloy, expected after activation.

Filling a cylinder with alloy

The cylinder components (cap, particle filter, isolation valve, thermocouple, pressure relief valve, rupture-disk, and pressure gauge) worked fine, but our first activation procedure did not

TOC

◀ ▶

work. In the photo at right, the cylinder is shown with a pressure relief valve, filter, shut-off and isolation valve, a supply line for hydrogen, and a vacuum line to evacuate the cylinder during “rinsing” steps.

Filter, valves & fittings on MH cylinder

The first MH activation attempt involved heating the cylinder by wrapping electrical heating tape around the cylinder as shown in the photo below. The highest temperature achievable without melting the heating tape insulation was 182° C (360°. F) during the “rinse” steps with medium pressure hydrogen filling followed by vacuum pumping. The pressure applied was 13 to 34.5 bar (190 to 500 psig) during the last step of the procedure. No activation occurred. We believe this was because

Heating tape did not work!

TOC
◀ ▶

we did not have the cylinder hot enough during the rinse cycles, or did not apply adequate pressure during the last step (we were limited to 500 psig max. by our relief valve at that juncture.)

Our next attempt was made using a higher temperature electric tube-furnace obtained at our favorite industrial junk-yard. The heater was cleaned, then wired to ac power, with each of three zone-heaters connected to a variac for temperature control. The temperature of the MH container was measured with a thermocouple, and pressure was monitored with a pressure transducer. Hydrogen flow was measured and controlled during activation using a mass-flowmeter. All of the data was collected on a PC data acquisition system.

Luigi Bonadio preparing tube furnace

We successfully used this MH activation recipe for Hydralloy C:

1 Evacuate container of MH to 10 -2 mbar (about 10 mTorr) using mechanical vacuum pump.

2 Turn off vacuum and charge MH container with 5 bar (72.5 psig) pure hydrogen (99.999% or better) at room temperature.

3 Make a leak test with gas leak detector, if system is tight and there are no leaks, proceed.

4 Turn off hydrogen supply and vacuum out MH container to complete first “rinse” cycle.

5 Repeat hydrogen charge to 5 bar.

6 Remove H_2 by vacuum pump to 10 -2 mbar to complete the second “rinse.”

7 Heat container in tube-furnace to 375°C (707°F) while continuing to evacuate to remove hydrogen and contaminants like water vapor (about 4 hours).

8 Turn off vacuum and charge MH container with 5 bar pure hydrogen at 375°C (hold for 8 hours).\

9 Evacuate to complete third “rinse.”

10 Repeat 5 bar hydrogen charge at 375°C (hold about 4 hours).

11 Evacuate to complete fourth “rinse.”

12 Under 5 bar hydrogen pressure cool down the MH container to room temperature.

13 Leak test the cylinder to verify that the sealant is still good after the high temperature rinse steps. If no leaks are present, continue.

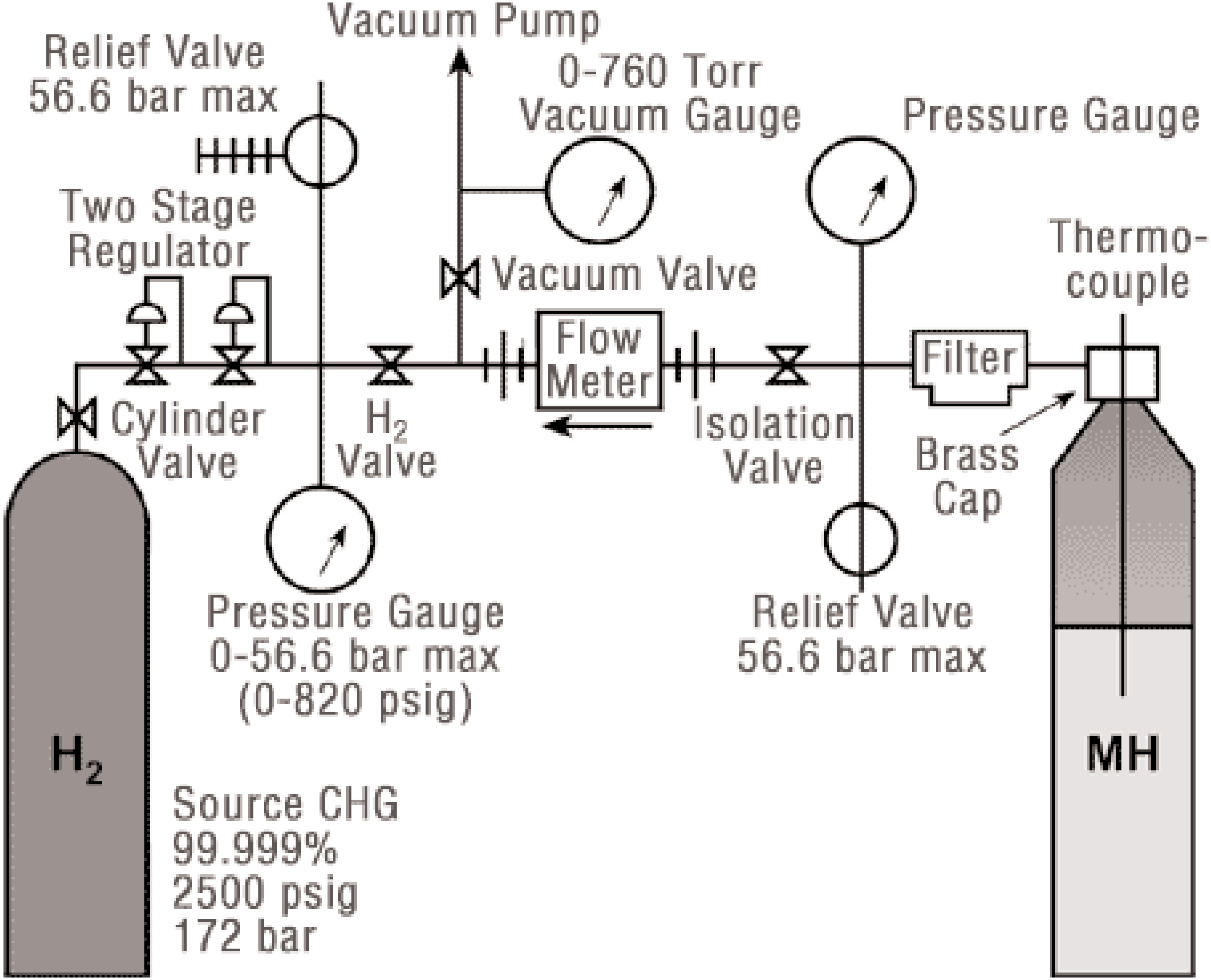
14 Charge the MH container to between 10 and 20 bar (150 to 300 psig) with pure hydrogen, to hydride the Hydralloy C. Once hydriding begins the cylinder will heat up and faint “cracking” sounds can be heard coming from the cylinder as the new chunks of Hydalloy C inside crack and break into smaller pieces under the stresses of hydrogen penetration.

15 After hydriding is complete and the cylinder cools to room temperature, close hydrogen supply valve and close cylinder’s isolation valve, then remove cylinder for use.

Electric tube furnace ready for activation of MH cylinders

During activation under 10 to 20 bar pressure, the cylinder becomes very hot due to the heat-of-formation of the metal hydride phase

Metal Hydride Activation Process



TOC
◀ ▶

($2M + H_2 = 2MH$ + heat). Our cylinder container reached a temperature of over 70°.C, so we turned on an air fan to cool it. After about two hours the hydriding reaction was complete and the container gradually cooled down to room temperature. Each time the cylinder is filled with hydrogen, the cylinder releases heat. After activation, the cylinder can be re-charged at much lower pressure. For Hydralloy C we were able to recharge the container, after activation, with hydrogen at only 8 bar (100 psig) pressure, without any external heating, cooling, or vacuuming. Using a higher hydrogen pressure during charging resulted in a faster fill and greater heat-release rate. Note; one batch of MH that we made required 50 bar (725 psig) pressure to hydride the first time, probably because of thicker surface oxide films.

Removal of Hydrogen from Hydralloy C

This was done by opening the MH container's valve and feeding gas to a hydrogen cooking burner. As the gas was removed from the MH container, the container became cold enough to form ice on the outer surface (from the moisture in the room air freezing). At lower hydrogen removal rates, ice did not form because the container gained heat from the ambient air fast enough to keep up with the reverse reaction ($2MH$ + heat = $2M + H_2$). MH has been used in refrigeration systems because of this unique property and because of hydrogen's "ozone friendly" nature compared to other refrigerants like CFCs. A discussion of MH refrigeration is beyond the scope of this article.

Our cylinder container held about 6.8 kg of Hydralloy C so we expected to obtain about 1.5% weight of hydrogen, or about 100 grams of hydrogen on discharge. This might not seem like very much hydrogen, but since hydrogen is very light, the volume of 100 grams hydrogen at atmospheric pressure is large, about 1.1 m 3 (39 scf). Not bad for a cylinder with a volume of 0.0023 m3 (0.035 scf). By comparison, we would need to boost the pressure in the same cylinder with CHG to 1.1/.0023 = 478 bar to get as much hydrogen into it as with 14 bar in a MH cylinder! Since the cylinder is rated at only 145 bar, this is impossible.

On the first hydrogen fill, the storage volume may not be as large as that obtained after several charge/discharge cycles. The MH breaks down into smaller and smaller particles during the first few cycles and the storage volume increases. We obtained about 0.64 m 3 (640 liters or 23 scf) of hydrogen from the cylinder after the first filling following activation.

The pressure inside a filled Hydralloy C MH cylinder varies from about 5.5 to 8.3 bar (80 to 120 psig) depending on ambient temperature 5 to 27 deg. C (40 to 80 deg. F). When the isolation valve is opened to feed gas to a cooking burner, the pressure drops. If the valve is then closed, after a time the pressure will recover, as the hydrogen leaves the alloy and fills the space in the cylinder. When the cylinder is emptied (weight % H 2 less than about 0.5) the pressure will not recover after valve shutoff, and it is time to recharge the cylinder with hydrogen.

Future Direction

As we go to press, a second MH container is being activated with Hydralloy C, a third cylinder of Hydralloy F 50/9 (AB 4.8 alloy) is being activated, and a cluster of small MH cylinders is being installed inside a large stainless steel container (formerly used as a swimming pool filter case). Water and anti-freeze solution will be circulated around the MH cylinders, to remove heat during hydrogen charging, and to supply heat during hydrogen discharging. A base support has been added so the pool-filter-case with it’s MH cylinders can be installed at home or in a small pick-up truck. We’ll tell you about it later on.

Acknowledgments:

Mike Williams, Shieldalloy Metallurgical Corporation for many enlightening discussions on MH and Hydralloy

C Luigi Bonadio, University of Melbourne (Australia) for assistance in activation of Hydralloy C and preparation of experimental hardware and computer data acquisition system at H-Ion Solar Company

Michael Gottschall, GFE Mbh for MH engineering applications information

Dr. Meinhard Aits GFE Mbh for MH technical information

Acknowledgments (continued)

Dale McIntyre, Metallurgical Engineer, Aramco, Saudi Arabia for information about metallurgy of hydrogen handling systems in refineries, sour gas fields, and gas sweetening units

Jim Healy WH6LZ for assembly of laboratory apparatus, experimental data collection, and safety checks

David Booth for assistance with the CO_2 cylinder conversions

Reynaldo Cortez for some of the photographs

Access:

Author: Walt Pyle WA6DUR, H-Ion Solar Company, 6095 Monterey Avenue Richmond, CA 94805 Tel: (510) 237-7877 FAX: (510) 232-5251 e-mail: Hionsolar@aol.com

Metal Hydride Review article:

"Hydrogen Metal Systems", by Gary Sandrock, Y. Yurum, Editor, NATO ASI Series E: Applied Sciences - Vol.295, Kluwer Academic Publishers, Dordrecht, 1995, pp.135-166

Hydralloy C MH-alloy and tank sources

GFE Mbh, Hofener Strasse 45 D-90431 Nurnberg, Germany Tel: 49 (country code) 93(city code) 15 332 FAX: 49-31-49-80 or 49-9315-491

Shieldalloy Metallurgical Corp., 12 West Boulevard Newfield, New Jersey 08344 Tel: (609) 692-4200 FAX: (609) 692-4017

TOC

Hydrogen Purifiers

Resource Systems Inc., East Hanover, New Jersey Tel: (201) 884-0650 FAX: (201) 515-3166 RCP-10- 2000-4ss catalytic hydrogen purifier

Johnson-Matthey Corp., Orchard Rd, Hertfordshire, SG8 5HE, England
Tel: (01763) 25-3000 FAX: (01763) 25-3313
Thin Pd-Ag membrane H2 purifiers

Bend Research Inc. 64550 Research Road, Bend, Oregon, 97701-8599
Tel: (503) 382 4100 FAX: (503) 382 2713
Pd membrane purifiers

REB Research, Ferndale, Michigan Tel: (810) 545-0155
FAX: (810) 545-5430 Hydrogen purifiers and Membrane Reactors

GPT Inc., Manalapan, New Jersey Tel: (908) 446-2400 FAX: (908) 446-2402 Hydrogen De-oxo purifier D-50- 1000

Hydrogen and Oxygen Purity Sensors

DCH Technology Inc., Sherman Oaks, California Tel:1-{818) 385-0849
FAX: (818) 385-0849 e-mail: dchinc@aol.com (ppm to 100% hydrogen)
Robust Hydrogen Sensor (ppm to 100% hydrogen)

Figaro USA Inc., Wilmette, Illinois Tel: 1-(708) 256-3546 FAX: (708) 256-3884 KE50 oxygen sensor (to detect oxygen contamination in hydrogen)

Panametrics inc., Waltham, Massachusetts Tel: (800) 8333-9438 FAX: (617)-894-8582 Thermoparamagnetic Oxygen Transmitter 0–5% O_2

Hydrogen flash-back arrestors

Western Enterprises, West Lake, Ohio. Model FA3-CV flash-back arrestor with integral check valve (used for acetylene) Tel: (216) 871-2160 Hydrogen pressure relief valves, shut-off valves, tubing, gas filters.

Oakland Valve and Fitting Co., Concord, California Tel: (510) 676-4100 Includes Swagelock, Whitey, Cajon, Nupro product lines

Hydrostatic Testing of Cylinders

Compressed Gas Association, 1725 Jefferson Davis Highway, Suite 1004, Arlington, Virginia 22202-4102

Articles on storage of hydrogen in carbon "nanotubes" and on carbon powder

"Advanced Materials for Hydrogen Storage: Carbon Nanotubules", T.A. Bekkedahl and M.J. Heben, National Renewable Energy Laboratory, Golden, Colorado

"Hydrogen Storage Systems using Activated Carbon", J.S. Noh, R.K. Agarwal, J.A. Schwarz, Int.J.Hydrogen Energy, Vol.12, No.10, pp.693-700, 1987.

Cookin' On Hydrogen: Stove Burner Conversion

by David Booth and Walt Pyle

Originally published in Home Power #33 February / March 1993

Converting conventional stove top burners to run on hydrogen is a simple process. Knowing the proper handling procedures of hydrogen will make your installation safe and efficient.

Theory Before Practice

Hydrogen burns differently than either propane or natural gas. In particular, hydrogen's rate of diffusion and flame velocity are roughly ten times or greater than that of propane or natural gas. Diffusion rate measures how long it takes a gas introduced in one side of a room to be detected on the other side. Flame speed is how fast a flame travels to burn available fuel-air mixture.

Flashback of the flame into the primary mixture of fuel gas and air must be prevented in all burners. This is typically achieved with natural gas and propane by adjusting the fuel velocity so that it is higher than the normal flame velocity. The flame velocity of hydrogen is too high for this technique to be practical. Another flashback control strategy employs burner ports with a minimum quenching diameter which theoretically will not allow the flame to pass back through the port. In practice, however, it is very difficult to make the holes small enough to quench a hydrogen flame. Fortunately, flashback can be minimized by preventing hydrogen from mixing with air before the burner port. Some flashback may still occur creating a loud popping sound but this noise is usually harmless.

Figure 1 (next page) shows the principal parts of a typical range top burner used with conventional gaseous fuels. Usually the fuel streams in through a gas orifice with a delivery pressure between 3-15 inches of water column. Primary air is then drawn in with the gas stream through an air-gas mixer. Secondary air openings to mix in more air may or may not be present. Finally, as the mixture exits through the burner ports, combustion occurs, if a spark ignition source or pilot light is present.

Horse of a Different Color

This burner design will not suffice for hydrogen in an unaltered state. Burners optimized for hydrogen combustion require that undiluted hydrogen be delivered directly to the burner ports without primary or secondary air mixing. So, if we are trying to work with an existing burner in a typical gas appliance, we will have to find a suitable method to seal off any openings that were installed for this purpose. There's no method that will work in all instances. The actual openings we are referring to may be an integral part of

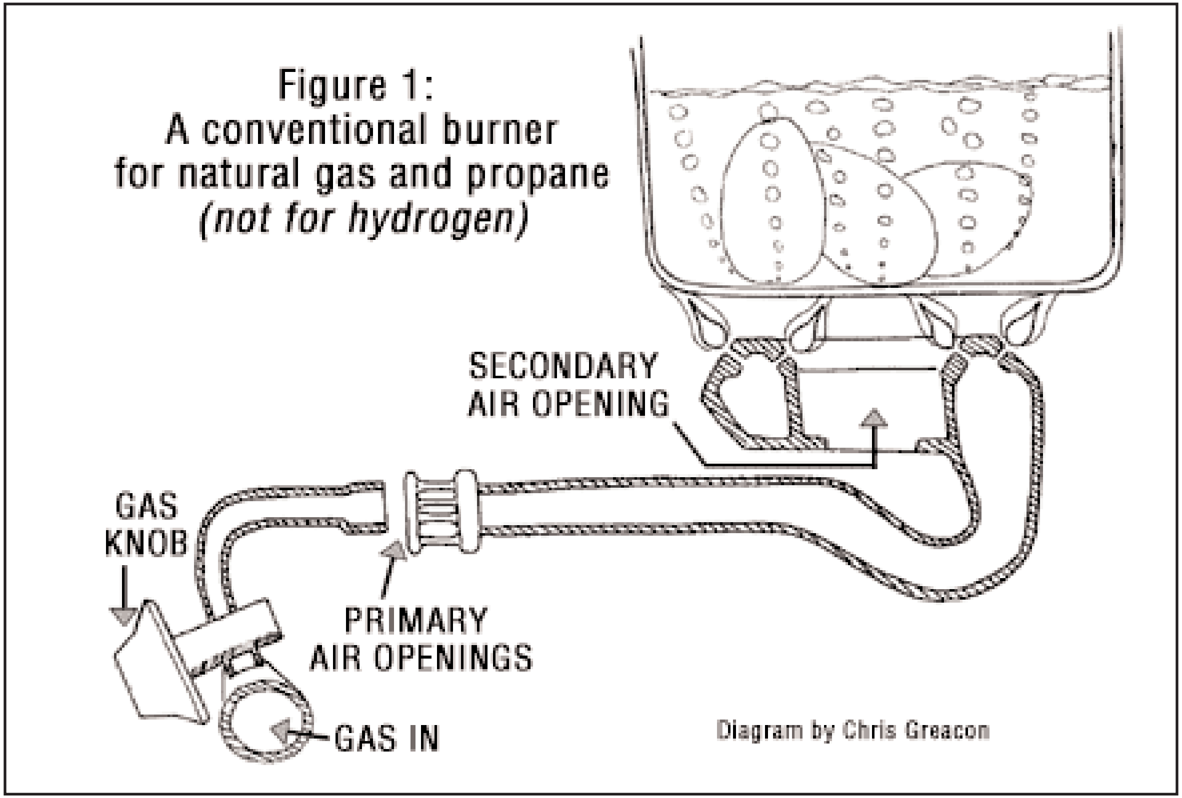


Figure 1:
A conventional burner
for natural gas and propane
(not for hydrogen)

Diagram by Chris Greacon

TOC

a cast iron body. Or the primary air openings may be a modest distance from the burner head in an aluminum delivery tube with an adjustable closure. We used silicon sealant with stainless steel tape and ring clamps in one recent alteration, but this simple Coleman stove conversion hasn't been subjected to long term use as yet.

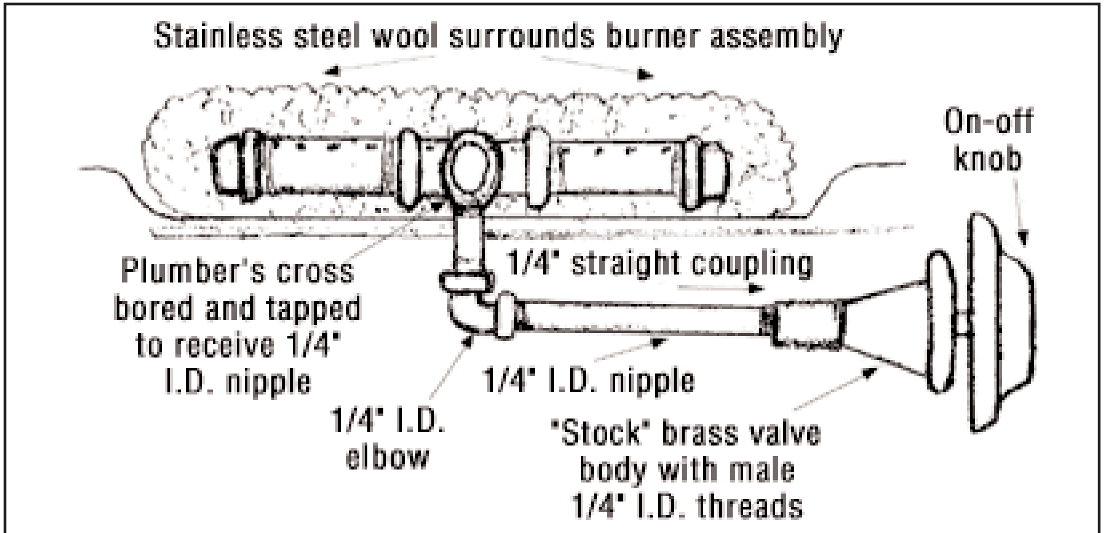


Figure 2: Pure hydrogen is delivered to burner without primary or secondary air mixing.

Diagram by David Booth

From Scratch

One might opt to build a simple hydrogen burner and direct fuel delivery apparatus from the ground up, rather than deal with the problem of sealing off a nagging assortment of useless holes. Burners and their attached parts get hot, and transfer heat readily through conduction. Sorry, duct tape and chewing gum won't cut it. Our first attempt at a simple hydrogen conversion utilized a rudimentary two burner range of cast iron construction. See Figure 2, above.

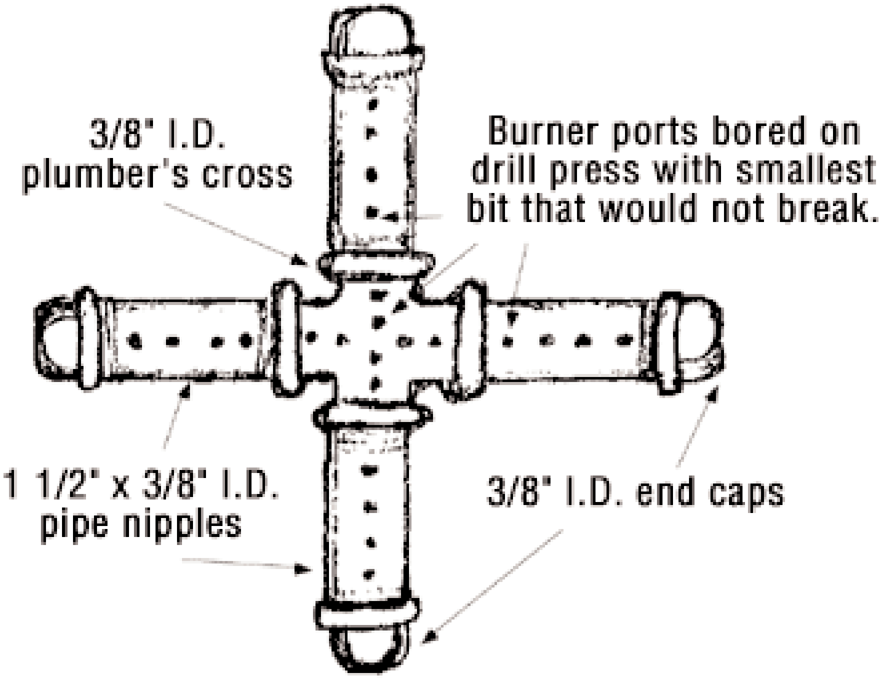


Figure 3: Top view of radial burner made from scratch using black iron pipe fittings.

Diagram by David Booth

After we tossed the existing burner assembly, and removed the screwed-on brass orifice, a threaded adaptor was exposed. To this we attached a 1/4" NPT straight coupling followed by a short length of black iron pipe of the same diameter. Don't use galvanized pipe, becauseof the fumes that will be released at high temperatures.Then we installed a 90° elbow followed by a shortvertical nipple of more pipe. Next, a 3/8" NPT fitting shaped like a cross with four female threaded openings was drilled and tapped to create a fifth hole. See Figure 3. This threaded onto the short vertical nipple, and four slightly longer nipples of equal length extended out radially from the remaining holes. Finally, these terminated in threaded end caps. A drill press is almost essential for drilling a series of very fine holes which lineup along the top of the radial burner arms, and through the top of the cross. Ideally, these burner ports would-have a 0.057 cm (0.0225") diameter or less, which is the approximate minimum quenching diameter.

The Catalytic Advantage

It has been observed in early experiments that the flame combustion of hydrogen/air mixtures can lead to unacceptable levels of nitrogen oxide (NO_x) pollutant emissions. The primary end product of hydrogen combustion is simply water vapor. However, if the temperature of combustion exceeds a threshold level of about 1315°C (2400°F), a significant amount of oxygen and nitrogen from the air may react and form this unwanted byproduct. This also occurs with natural gas (primarily methane), propane, and other hydrocarbon fuel combustion.

Fortunately, you can use a catalyst to lower the combustion temperature, thus preventing the formation of nitrogen oxides. The catalytic material is not used up or altered in any fashion in the process.

There are two catalytic conversion techniques which succeed in producing negligible levels of NO_x emissions.The first approach is based on Billings and his associates' work with flame assisted catalytic burners. Their conversions utilized the catalytic properties of stainless steel at elevated temperatures. Later, in another article, we'll describe the conversion of a catalytic space heater which optimizes "flameless" combustion with a small-amount of platinum.

Flame Assisted Catalysis

The technique developed by the Billing's research team to reduce NO_x formation relies on controlling two interacting phenomena. First, as has already been described, hydrogen/air mixing is inhibited by blocking off any primary air openings. Second, a stainless steel wire mesh is arranged tightly around the circular burner head orradial burner arms, as shown in Figure 2.

Where does one find stainless steel wool or wire mesh? Look for stainless steel pot scrubbers in a large, thoroughly stocked supermarket in the housewares section.

Getting our NO_x Off

This stainless steel wool blanket around the burneractually serves two complementary functions. It inhibits the mixing of air and hydrogen thus producing a zone immediately surrounding the burner head where the concentration of hydrogen is very high and the concentration of air is very low. The wire mesh should be thick enough so that the flame does not radiate above it or out too far laterally.

Stainless steel also works as an excellent catalyst for hydrogen combustion. If there isn't a sufficient amount of stainless steel mesh, the catalytic capability and ability to prevent NO_x production could be lost. Hydrogen and oxygen are thus combined on the surface of the catalyst at a lower temperature than would occur without the catalyst. The result of the lowered combustion temperature is that nitrogen oxides are virtually eliminated. The steel wool proceeds to glow bright red even at these temperatures, indicating that the otherwise invisible hydrogen flame is present.

According to Roger Billings in *The Hydrogen World View*, the flame-assisted catalytic technique can lower NO_x emission from hydrogen combustion in range burners, ovens, and space heaters to negligible levels. The resulting data showed NO_x emission levels between 1 and 5 parts per million (ppm) for a catalytic assisted burner. This can be compared with 40 ppm for conventional range burners operated on natural gas and up to 250 ppm for a hydrogen burner without a catalyst. These burner emission levels are all quite low, however, compared to internal combustion engine exhaust gas NO_x production.

More to Come

We need to build a sound understanding, before we can confidently proceed to implement hydrogen for scores of potential uses. If you'd like more information, dig into the references at the end of the article.

In the next issue, we will delve into a technique for transforming the chemical energy stored in hydrogen to available heat energy without the presence of a flame. This form of combustion is possible when hydrogen is oxidized in the presence of certain specific catalysts such as platinum. This is considered "pure" catalytic combustion. Water vapor is the only byproduct along with heat, so no venting of the appliance may be necessary (if means to prevent oxygen depletion for the room air are assured). At this time, most city and county building codes require an exhaust flu for stoves running all gaseous fuels, and we recommend that the room where the stove is being used be vented to the outdoors.

We're in the process of putting together a system that will convert renewable solar electricity into the storable chemical energy of hydrogen through the process of electrolysis. The process is still underway but we will offer detailed accounts of our endeavors in forthcoming issues.

Spreading the Invisible Flame

There may well be a wealth of undiscovered and untapped hands-on information available from other hydrogen enthusiasts out there scattered through the countryside. If you are among the other backyard tinkerers and hydrogen pioneers who are putting theory into practice, let us hear from you. The time has come to spread the word about hydrogen's unique advantages. It is clearly the hands-down winner among the possible candidates of alternative fuels for the future in our environmentally beleaguered world.

A Note on Safety

Remember that storing pure hydrogen can be regarded as a relatively safe procedure, but storing hydrogen/air or hydrogen/oxygen mixtures is foolhardy and strictly inadvisable.

Much of the research that we referred to in this article was performed by Roger Billings, N. R. Baker, and their associates of the now defunct Billings Energy Corporation. This pioneering work was done mostly in the 1970s. An early research endeavor involved conversion of all the gas appliances on a Winnebago recreational vehicle from propane to hydrogen operation. To demonstrate hydrogen's practicality even further, five natural gas appliances were converted to hydrogen. This multi-phased project in Provo, Utah was called the Hydrogen Homestead. Included among the appliances converted for this home were an oven, a range, a barbeque, a fireplace log burner, and the booster heater for the home's heat pump system.

Access

Authors:

David Booth, Alternative Energy Engineering, POB 391, Miranda, CA 95553 • 707-923-4336

Authors (continued):

Walt Pyle, WA6DUR, Richmond, CA • 510-237-7877

Further Reading

1. *Oxides of Nitrogen Control Techniques for Appliance Conversion to Hydrogen Fuel*, technical paper #74003, by N.R. Baker is available from the International Academy of Science, 26900 Pink Hill Road, Independence, MO 64057 • 816 229-3800.

2. *Hydrogen Homestead*, technical paper #78005, by Roger Billings is available from the International Academy of Science.

3. *Fuel from Water* by Michael Peavey is available from Alternative Energy Engineering for $16 and Real Goods.

4. *The Hydrogen World View* by Roger Billings is available from the International Academy of Science.

TOC

Barbecuing with Hydrogen Gas

by Walt Pyle, John Dabritz, Reynaldo Cortez, and Jim Healy

Originally published in Home Power #43 • October / November 1994

Barbecuing with hydrogen is cleaner than using charcoal or propane because there's no carbon in hydrogen. When hydrogen burns, it emits only water vapor and traces of nitrogen oxide. No toxic pollutants, smoke, or particulates are released by a hydrogen flame. When hydrogen is produced by renewable energy, the water-to-fuel-to-water cycle can be sustained virtually forever!

For generations, barbecue fires have been made from charcoal. Though we also have natural gas and electricity for cooking, these resources are largely based on fossil fuels and are not sustainable. PV produced hydrogen is sustainable. (See "Solar Hydrogen Production by Electrolysis," p.44 to see how PV electrolysis is accomplished. Cooking with hydrogen also appears the previous chapter, p.118.) Air pollution from barbecues is becoming objectionable in densely populated areas. Outdoor cooking is very popular on hot summer days. Unfortunately, that's also when air quality is usually at its worst. Legislation regulating barbecuing has even been enacted in some areas.

TOC

Propane Barbecues

The propane gas barbecue before modification

Propane barbecues are more convenient and produce fewer emissions than charcoal models. Propane also eliminates waiting while the coals get hot. The propane burner is ignited by turning on the gas and pressing the piezo-electric igniter button. A spark ignites the fuel-air mixture escaping from the burner. The flame heats lava rocks, distributing the heat to the grill. Liquids that drip onto the lava will vaporize and burn, shielding the burner from contamination. After cooking is finished, the gas is turned off and the heat stops. The lava cools quickly to ambient temperature.

Gaseous fuel is safer than charcoal in some respects. For instance, there's no need to supervise the fire after cooking. You're less likely to start a fire when a gust of wind comes up and rekindles "dead" coals! There's also much less ash residue. Though propane flames emit carbon oxides and hydrocarbons, amounts are less than from charcoal. Better fuel-air mixing results in less smoke. Cooking time is also shorter with propane.

The propane flow to each burner is controlled by a valve and delivered to an orifice. The orifice limits the gas flow and produces a high velocity jet,

TOC

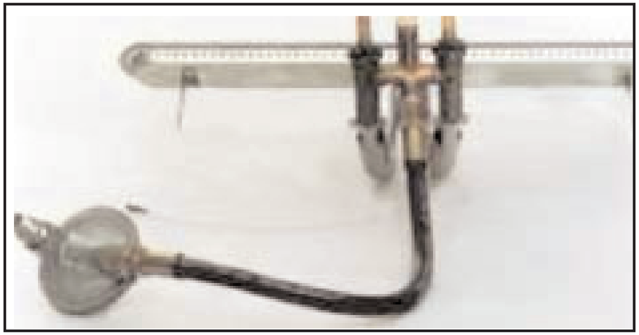
which aids fuel-air mixing. The high velocity gas enters the pre-mixer, drawing air through ports on each side of the burner delivery tube.

Conversion of a Propane Barbecue to Hydrogen

We started with a two-burner Kenmore propane barbecue. It has 1451 square centimeters (225 square inches) of cooking area and is rated at 24,000 Btu (5.9 kW) per hour. Sears had it on sale for under $100. We converted our barbecue by changing the burners and gas delivery tubes to prevent pre-mixing of the hydrogen fuel and air. Other parts of the barbecue were usable without modification. The covers, grill plates, gas supply line, control valves, pressure regulator, and

By removing the cooking grill and lava rock support, you can see the stainless steel propane burner.

The propane gas supply valves, burner, and pre-mix tubes, and pressure regulator.



TOC

piezo-electric igniter all worked as purchased. We will use the propane tank in a future hydrogen storage experiment.

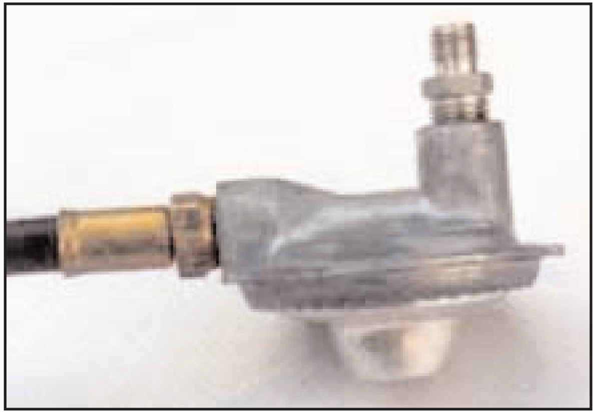
The propane burners installed in our barbecue use fuel-air pre-mixers.

Step 1. Feeding Hydrogen to the Pressure Regulator

Remove the pressure regulator from the propane tank. Attach 0.64 cm (0.25 inch) Swage lock stainless steel tubing to a 1/4" NPT fitting. This will replace the original pipe fitting on the "INLET" side of the regulator. We used stainless tubing, but copper or brass tubing and fittings can be used as well. They may also be easier to obtain at your local hardware store.

Set the hydrogen gas supply pressure to about 1 bar (14.5 PSIG) at the pressure regulator "INLET". Most propane-type regulators are rated for

The gas pressure regulator with Swage lock tubing INLET pipe fitting.



A close-up of hydrogen burner showing gas diffusion ring. By coating the surface of the burner pores with a catalyst, nitrogen oxide emissions can be reduced.

17 bar (250 PSIG) maximum inlet pressure. Do not exceed the rated value. Use safety relief-valves in the piping and storage tank so excessive pressure cannot cause an unsafe condition. A welding-type compressed hydrogen cylinder with two-stage regulator can be used to supply the pressure regulator. For safety, include a shutoff valve to isolate the hydrogen supply from the pressure regulator during idle periods.

Before we continued our hydrogen conversion, we wanted to try the barbecue on hydrogen in its “propane” configuration. We supplied the pressure regulator inlet with 1 bar (14.5 PSIG) pressure from the hydrogen tank and checked for leaks. Donning safety glasses, we turned on the control valve and pushed the igniter button. The fuel-air mixture in the burner and supply line promptly lit with a loud “BANG” that resembled a firecracker! We weren’t surprised. The pre-mixed gas and air was flammable. The velocity of a hydrogen flame is much higher than that of propane. The flame moved backwards against the hydrogen flow. It traveled from the igniter at the burner pre-mix outlets to the orifice at the

TOC
◀ ▶

mixer. The flame burned freely on the open jet of hydrogen coming out of the orifice, heating the pre-mix tube instead of the burner. The hydrogen diffusion burner and gas distribution plate are designed to prevent the pre-mixing of hydrogen with air. In a gas diffusion burner, fuel is burned without premixing the fuel (hydrogen) with air.

Pure hydrogen fuel passes out through the porous surface of the burner. The hydrogen and oxygen from the air then mix within the outer pores of the burner. This prevents flash-backs and keeps the flame from propagating from the outer burner surface back into the fuel supply.

Step 2. Making The Burner

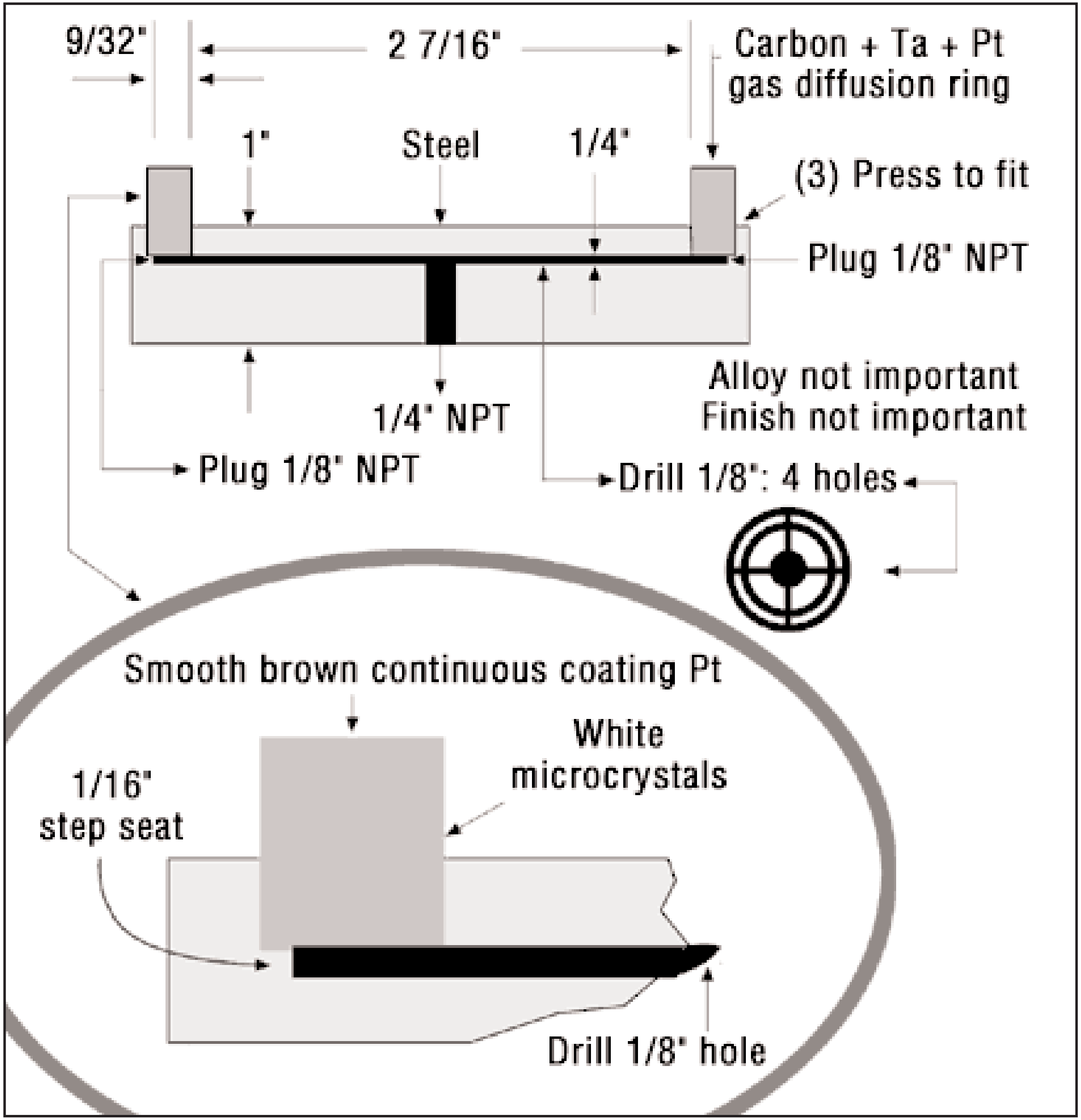
Machining the hydrogen gas distribution base from low carbon steel requires the following steps:

1) For the gas diffusion ring, cut a circular groove with a shoulder step on the outside. The step prevents the ring from being pressed all the way to the bottom of the circular groove.

2) Drill two long holes completely through the steel base at 90° to each other. The holes will connect the gas feed fitting at the center of the burner to four different locations around the circular gas distribution groove.

3) Tap the outermost ends of the four holes for 1/8” NPT pipe plugs.

TOC


9/32"
2 7/16"
Carbon + Ta + Pt
gas diffusion ring
1"
Steel
1/4"
(3) Press to fit
Plug 1/8" NPT
1/4" NPT
Alloy not important
Finish not important
Plug 1/8" NPT
Drill 1/8": 4 holes
Smooth brown continuous coating Pt
White
microcrystals
1/16"
step seat
Drill 1/8" hole

The burner installed in barbecue

4) Tap the center gas feed point of the base to accept a $^1/_4$" NPT-to-stainless tubing supply line fitting.

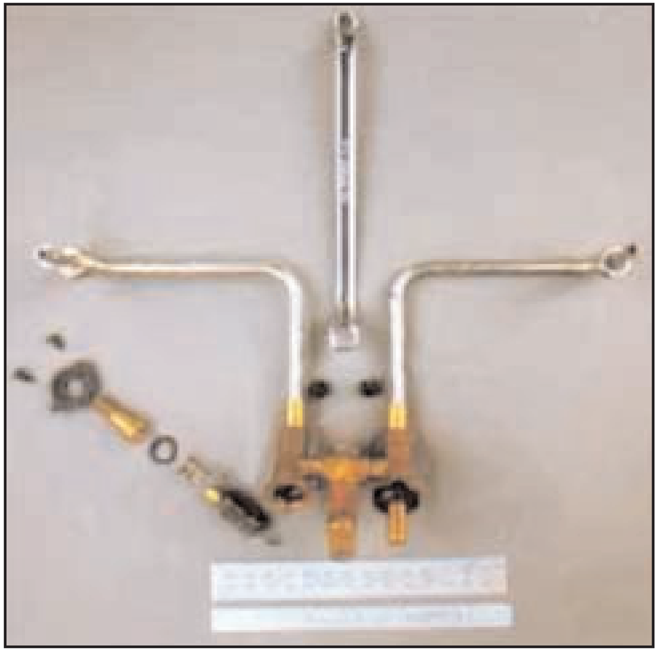
The burner gas diffusion ring is made from tantalum foam tubing. The rectangular ring segment can be cut with a table saw or chop saw. Another source of the tantalum burner-ring material is automotive air-bag deployment shell diffusers. Besides tantalum, other high temperature foam materials are also available from Ultramet (see access).

The burner ring is plated with platinum catalyst. Attach the ring to the negative (cathode) lead of a low voltage D.C. power supply. Attach the positive (anode) power supply lead to a platinum wire. Immerse the ring and wire in an electrolyte solution. The solution is made by dissolving 1 gram of platinum in about 20 ml of aqua-regia and diluting to 100 ml with distilled water. Apply 1-2 Amps of current for several hours until the surface of the tantalum ring is coated with a thin layer of platinum.

Press the burner ring into the gas distribution base using a mechanical press. A completed burner is shown in the photo. The lava rocks have been removed from one side for clarity.

TOC

Step 3. The Hydrogen Delivery Lines



Remove the jets and valve components before silver-soldering stainless tubing

Extend the hydrogen gas delivery lines from the flow valve to the burner with two stainless steel "L" shaped 22.5 cm (9", 0.25" diameter) lengths of tubing. Remove the jets from the valve body using a 10 mm (3/8") box end wrench. Insert the stainless tubing lengths in the former jet holes. Before soldering, disassemble the brass flow valves and remove heat sensitive components and lubricant. Position the stainless tubing sections securely and silver solder them in place. Be sure to put the sheet metal support bracket over the tubes before soldering them into the valve bodies. Also check that the bent sheet metal tabs face away from the valve bodies.

Clean the valve bodies after soldering. Reassemble the heat sensitive stem, spring, and plastic detent retainer. Use silicone stopcock grease as seal and lubricant.

Step 4. Install the Igniter

The barbecue's underside with burner, hydrogen delivery tubes & valves.

Install the piezo-electric igniter's insulator and high voltage lead near the new hydrogen gas diffusion burner. It will be used to light the burner. Bring up a ground lead alongside to position the spark gap near the burner gas diffusion ring. A loud "POP" will occur at the moment of ignition. The hydrogen-air mixture ignites at the spark and will propagate to the burner surface. Thereafter, combustion will occur primarily in the pores of the burner ring.

Safety First!

Hydrogen gas testing should be done outside or in a well ventilated area. Only pure gas should be used or stored. Remember, though hydrogen diffuses rapidly away from a source when released, it's flammable over wider ranges of air-fuel ratios than propane. It must be handled with respect. Hydrogen safety precautions are discussed on pp. 149, 153 and 184.

Step 5. Testing

Test setup showing barbecue, NO_x meter at 50% hydrogen flow (86 ppm)

Use a soap solution to leak test the tubing connections, pipe fittings, valves, and regulator. Test with about 1 bar (14. 5 PSIG) hydrogen gas pressure.

We also tested the completed burner for heat release and nitrogen oxide emissions. A NO_x meter was used to sample the burner's hot exhaust gas plume at different positions. We used a Bacharach NONOXOR II with a range of 0-2000 parts per million (ppm) NO_x. These meters are used for field testing engine exhaust for emission compliance.

At the "LOW" gas valve setting, NO_x levels varied from 60-80 ppm in the flame 5 cm (2") above the burner ring. At 12 to 30 cm (5-12") above the burner center, NO_x varied from 2-6 ppm.

For "HIGH" hydrogen flows, NO_x levels varied from 80-160 ppm 2.5 cm (1") directly above the burner ring. At 30 cm (12"), the NO_x dropped to 36-47 ppm. The NO_x increased with increasing flow at all positions. The NOx level also increased as the probe was moved closer to the burner.

Cooking Steaks on Hydrogen Gas Barbecue

At about 50% flow, the cooking temperature was just about right. Fortunately, the heat release can be set to the proper level for cooking on the lava with no further changes to the hydrogen flow valve and valve ports. We reinstalled the rock and food grills and made a NO_x measurement at the cooking grill surface above the burner and rocks. We recorded 65-90 ppm at 50% flow and 180-260 ppm at “HIGH” flow.

Background NO_x released by the hydrogen burner exposes the cook to no more than 2 ppm. The eight hour time-weighted average set by the U.S. Occupational Safety and Health Administration (OSHA) is 25 ppm NO_x. For reference purposes, our natural gas stove burner ran at mid-range with 15-25 ppm NO_x at 2.5 cm. (1”) above the natural gas burner flame.

Cooking Tests were conducted: Hydrogen Steaks!!

We tried steaks for our first hydrogen barbecue as seen in the photo above.

Endurance testing is needed to determine the lifetime of the burner. Some burner ring “break-in” has occurred. After several hours of operation, the

TOC
◀ ▶

sharp edges of the gas diffusion ring have become rounded by excessive heating. Whether this will stabilize remains to be seen. Lifting the rock grill higher above the burner ring will probably reduce the reflected heat reaching the burner ring from the glowing lava.

Possible Future Improvements and Measurements

1) Coating the steel base to prevent rust caused by combustion water condensation at startup and "LOW" hydrogen flows.

2) Venting the lid to prevent the buildup of an explosive mixture. This could occur when the gas is "on", the cover is closed, and ignition has not yet occurred. An interlock could be used to prevent hydrogen from flowing to the burner when the barbecue cover is closed and the flame has not yet been lit.

3) Measuring the flow rate of the hydrogen gas delivered to the burner at different valve settings.

4) Measuring the temperature of the burner surface at different hydrogen flow valve settings.

Acknowledgements

Ultramet, for the foam tantalum and silicon carbide tubing samples.

A&K Machine Shop, Richmond, California for machining the burner gas distribution plate.

TOC

Access

Authors:

Walt Pyle WA6DUR 510-237-7877,

John Dabritz 510-242-5366,

Reynaldo Cortz 510-237-9748,

and Jim Healy WH6LZ 510-236-6745

Diffusion Burners for Hydrogen:

Fraunhofer-Gesellschaft Institute for Solar Energy Systems, Tel: (Freiberg, Germany) 49-761-4014-0 Ext. 164 or 210.
FAX: 49-761-4014-100

Diffusion Ring Tubing:

Ultramet, 12173 Montague Street, Pacoima, CA • 818-899-0236
FAX 818-890-1946

Chemical supplies (platinum powder and wire, aqua-regia):

Aldrich Chemical Co., 1001 W St Paul Ave, Milwaukee, WI 53233 • 800-558- 9160

Heatin' with Hydrogen

by Walt Pyle, Jim Healy, Reynaldo Cortez, & David Booth

Originally published in Home Power #34 • April / May 1993

We want to share our experiments running a catalytic space-heater on hydrogen fuel. Three space-heaters are now installed in various rooms of one of the author's Richmond, California home. They are currently fueled with natural gas. These heaters present an almost ideal opportunity for conversion to hydrogen combustion. We plan to operate these space heaters routinely in the near future on hydrogen produced at home.

Gas Appliance Conversion

In the chapter "Cookin' On Hydrogen" (p.118), we examined an approach for modifying conventional kitchen stove burners (intended for natural gas or propane use) to allow cooking on hydrogen fuel. This method involved using stainless steel wool as a catalyst, and delivering hydrogen to the burner head without pre-mixing the fuel with air. The originators of this technique refer to this approach as "flame assisted catalytic combustion of hydrogen."

In this article we'd like to focus on pure catalytic combustion of hydrogen and air. Catalytic combustion of hydrogen and air can occur in the presence of certain noble metal catalysts (such as platinum or palladium), without any flame whatsoever. Water vapor and heat are byproducts of the reaction.

TOC

The Platinum CAT™

Catalytic space-heaters are available as mass-produced, low-cost consumer appliances. Some are intended for propane and some are for natural gas fuel. We chose to work with a Platinum CAT™ catalytic space-heater since it was the only model with forced external venting and an American Gas Association approval. Our intended application was for a home, not a recreational vehicle.

The manufacturer of the Platinum CAT™ flameless, catalytic, radiant space-heater is Thermal Systems, Inc. of Tumwater, Washington. The propane versions were conceived with the recreational vehicle market in mind, so they rely on 12 VDC power. The natural gas models are very similar in overall design, but they require 120 vac for operation of the solenoid gas valve and blower fan. Both types require a vent to the outdoors for the exhaust gases.

Our Platinum CAT™ was a Model 1500 120 vac 60 Hz version with a gas orifice sized for pipeline natural gas. (Model 1500 can also run on propane with the correct orifice installed.) The first CAT was installed in the living room during 1991 and operated for one year on natural gas to gain service experience. We were so pleased with its performance that we ordered and installed two more CATs during 1992.

Multiple Benefits

The radiant heat available from the Platinum CAT™ is long wavelength infra-red radiation similar to the sun's own rays. Radiant heat, unlike convection or conduction heat, is transmitted through space, and only releases its energy when the rays strike objects and/or people. Warmth from this space-heater is felt immediately, unlike forced air convection systems which first must heat the surrounding air.

The efficiency of catalytic hydrogen-air combustion with platinum catalysis is extremely high. The range of efficiencies commonly reported in technical literature is 85 - 100%. Efficiency is high because the combustion takes place at a substantially lower temperature than under ordinary conditions. This means in the presence of the platinum catalyst, no pilot light, spark, or glow plug is needed to initiate flameless combustion. This important safety feature helps prevent the accidental buildup of unburned gas and air mixtures. Also, catalytic combustion occurs far below the threshold temperature at which oxygen and nitrogen can react to form polluting nitrogen oxides

(NO_x). As a result, these emissions are 0.1 parts per million (ppm) or less compared to conventional burners at 200 to 300 ppm.

In the future, we will take full advantage of the higher heating value of hydrogen. This can be accomplished if the byproduct - water in the vapor state - changes back to a liquid and gives up its heat before it leaves the heated space. This is called the latent heat of condensation.

Conversion of The Platinum CAT™ to Hydrogen

These space heaters can be modified for the direct use of pure hydrogen by controlling the feed flow rate of hydrogen gas (and thus the heat release rate). The hydrogen flow rate to the Platinum CAT™ can be adjusted by raising or lowering the delivery pressure, or by resizing the gas inlet orifice. It may not be necessary to adjust anything if you are content with less output from the space heater.

Piping and Wiring the CAT

An excellent instruction and installation manual comes with the Platinum CAT™. The installation must conform to local codes. In the absence of local codes, the installation must conform with American National Standard (National Fuel Gas Code) known as NFPA 54 and ANSI Z223.1 1984. We used threaded 3/4" black iron pipe for the fuel delivery line with a high quality thread sealer (Permatex Industrial Hydraulic Sealer). A fuel gas shut-off valve was installed at the appliance entrance flex hose.

A 2" plastic flue pipe was used since the flue gases are low temperature with the fan running. The heater will not open the fuel gas solenoid valve unless the fan is running. No provision was made for condensed water removal, since we are operating the unit in a mild climate where this is not a problem.

A soap solution was used for leak testing the piping after installation. A product useful for this purpose is called Rectorseek Leak Detector (Rectorseal Corporation). A thermostat is supplied with the unit to control the temperature in the room. It works by turning the space heater "on" or "off" as required. We mounted our thermostat at the upper right of each unit so the wires could be hidden behind the heater frame. With this configuration we found that one must set the thermostat to a higher temperature than that desired for the room. The thermostat is heated by local conduction somewhat and tends to shut off prematurely. Placing the thermostat further away from the space-heater would benefit some installations.

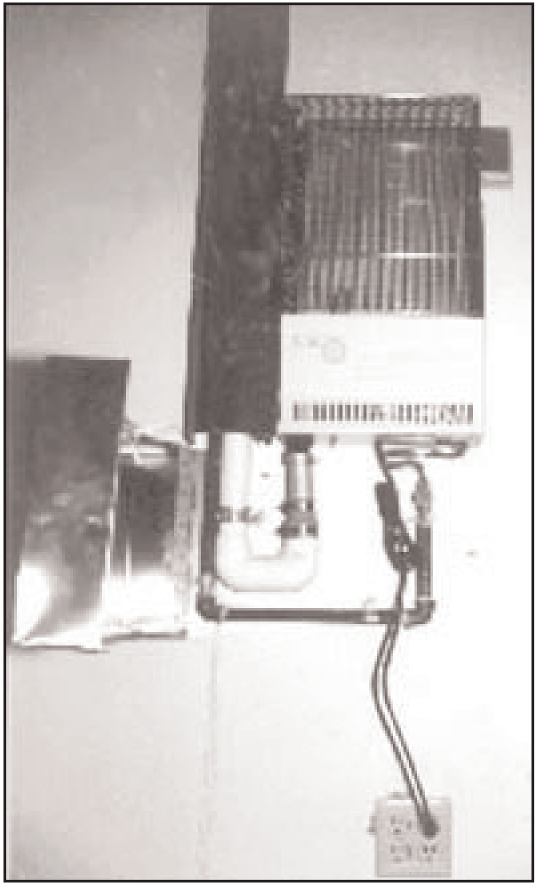
The control unit for our natural gas approved Platinum CAT™ had a 120 vac power card, so we just plugged it in and we were "on the air"!

TOC

Is Venting Needed?

Platinum CAT™ heaters produce radiant heat as the result of flameless catalytic combustion, whether or not hydrogen gas is the fuel of choice. With propane and natural gas, the space-heater exhaust gases will contain water vapor, carbon dioxide, and minimal quantities of carbon monoxide, NOx, and hydrocarbon pollutants. Common sense, AGA safe practices, and local building code regulations require that space-heater exhaust gases be vented away from the living space.

Only with hydrogen fuel is water vapor the primary combustion end product. So, why must the space-heater on hydrogen be vented? Well, you might argue, homes heated in the winter are in need of further humidification to raise the "comfort factor", and much valuable heat is lost (your energy dollars) up those exhaust flues. It is



Platinum CAT™Space Heater in basement bedroom showing vent piping and fuel supply line.

Photo by Reynaldo Cortez

TOC

tempting then, to think about venting the space-heater into the room. We advise against this practice.

Dangerous and harmful situations could arise if a space-heater on hydrogen (or conventional fuels) is not vented to the outdoors:

- Excessive moisture could condense in the home causing damage to building materials and the growth of unwanted bioorganisms.
- Loss of oxygen in the breathing atmosphere of a tightly sealed or “superinsulated” home could lead to asphyxiation or loss of consciousness for occupants.
- Confinement of a potentially explosive mixture of hydrogen and air is possible.

A simple well designed vent can prevent these problems from occurring with any hydrogen appliance. The vent system (shown in photo on the previous page) was made for our second Platinum CAT™ space-heater, which we installed in 1992 in a basement bedroom.

Our Experience to Date

During the summer of 1991 we made the first test of the Platinum CAT™ using hydrogen fuel. The hydrogen came from a high pressure compressed gas cylinder followed by a two stage pressure regulator. This allowed us to drop the pressure from as high as 2300 psig (pounds per square inch gauge) down to a pressure of about 4” of water column (w.c.), suitable for a gas appliance. We found that the hot wire starter for natural gas operation was unnecessary for initiation of hydrogen-air catalytic combustion. The hydrogen gas reacted with air on contact with the platinum coated silica quatz pad, giving off about as much heat as when running on natural gas.

A few weeks later, we contacted Thermal Systems, the manufacturer of the Platinum CAT™, and discussed operation on hydrogen with Arnie Lind, their resident R&D Lab Engineer. Arnie was interested in our approach. A few weeks later when we talked again, Arnie told us about some experiments he had run in the lab using hydrogen in a Platinum CAT™. Arnie became even more interested in the hydrogen fuel space heater after talking to Sandy Stuart from Electrolyser Corporation in Canada (to whom we had provided a copy of the Platinum CAT™ literature). Arnie confirmed that he had reliably obtained catalytic combustion of hydrogen and air without the ignitor, within 45 seconds or less after he turned the Platinum CAT™ on. Using a 5” w.c. hydrogen supply pressure to the Platinum CAT™, Arnie measured fuel consumption of about 16 cubic feet per hour. On natural gas, the fuel consumption was about 5 cubic feet per hour using 4” w.c. pressure at rated output of 5200 BTU/hour. An even combustion pattern was seen on the silica quartz pad face, glowing a dull orange when viewed in a dark room. Arnie found that he could get the same heat release as natural gas if he enlarged the natural gas orifice (normally 0.043”) to 0.052” (drill size #55).

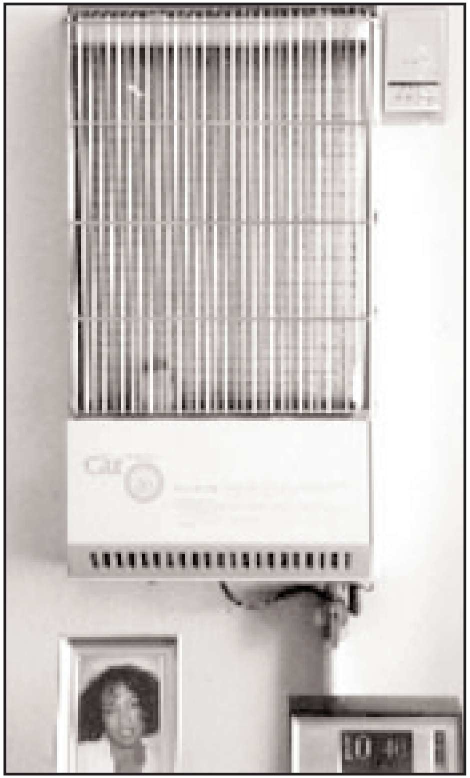
One of Arnie Lind’s primary concerns was in testing to assure that the surface of the catalyst silica quartz pad was not damaged by overheating (temperatures greater than 1100°F were known to cause problems). By using a non-contact infrared thermometer he found that the surface temperature of the rock wool was only 600° to 800°F when operating on hydrogen at the rated heat input, and not a problem. Another of Arnie’s concerns was about the flue gas composition. He planned to obtain samples of the gas for analysis. Maybe there will be an AGA approved hydrogen Platinum CAT™ in our future! We hope so.

Demonstrating Flameless Combustion

We shared the news of this novel appliance with David Katz of Alternative Energy Engineering. He proceeded to order one for his home, but initially it became our handy demonstrator unit for a recent alternative energy fair and a one day hydrogen workshop. Even without plumbing or wiring this device, we amazed more than a few curious souls and skeptics with a simple demonstration of flameless combustion. After removing the protective grill on the heater, a silica quartz pad with minute amounts of platinum is left exposed. All that was needed to instantaneously produce heat and a

TOC
◀ ▶

reddish-orange glow was the direction of a slow, steady stream of hydrogen from our compressed gas cylinder across the surface of this material. Of course, this was only done to visually confirm the novel quality of flameless combustion. We don't suggest that this approach is in any way a substitute for a properly piped and wired installation. In one of our demonstrations, the hot silica quartz pad surface started a flame in the stream of hydrogen, which jumped out to the end of our delivery line! The catalytic combustion temperature was above the ignition temperature, and a hydrogen flame was kindled. Flameless combustion or oxidation is really not that unique a phenomenon. The body's oxidation of carbohydrates, the yellowing of newspapers, and the rusting of iron are well known examples.



Multi fuel space heater at work warming the living room. The heater normally runs on natural gas, but runs equally well using hydrogen.

Photo by Reynaldo Cortez

Safety Warning

Please be forewarned that although our experience may indicate that such a conversion is relatively simple, the use of this appliance with hydrogen fuel is not yet approved by the manufacturer. Approval from the American Gas Association must be obtained before the Platinum CAT™ on hydrogen will be ready for commerce. The use of any gaseous fuel in a space heater, other than the one recommended specifically by the manufacturer will void the warranty, and may not comply with American Gas Association (AGA) safe practices.

If you want to try any hydrogen space-heater experiments on your own, be aware:

- Installation should only be done by a qualified service person.
- Any changes to the heater or its controls, or attempts to clean the catalytic pad can result in damage, defective operation, and may be dangerous.
- Any experiments with hydrogen fuel should be done outside.
- Hydrogen gas is odorless; you cannot smell a leak.
- Remember that hydrogen gas and air mixtures are potentially combustible and explosive over wide mixture ratios (4 to 75% hydrogen in air). Only pure gases should be stored, never mixtures of hydrogen and air.

TOC

Access

Authors:

David Booth, Alternative Energy Engineering, PO Box 391, Miranda, CA 95553 • 707-923-4336

Walt Pyle, WA6DUR, Richmond, CA • 510-237-7877

Jim Healy, KD6LYV, Richmond, CA • 510-236-6745

Reynaldo Cortez, Richmond, CA • 510-237-9748

Platinum CAT™ Heater:

Thermal Systems Inc., Mottman Industrial Park, 2757 29th St. SW, Tumwater, WA 98502 • 206-352-0539

Safety Regulations:

NFPA 54 and ANSI Z223.1 1984 from:American National Standards Institute Inc., 1430 Broadway, New York, NY 10018 or National Fire Protection Assoc., Batterymarch Park, Quincy, MA 02269

Understanding Fuel Cells

by David Booth

Originally published in Home Power #35 • June / July 1993

Fuel cells are likely to replace internal combustion engines in the next century. Internal combustion (IC) engines and fuel cells are both energy converters which transform chemical energy into a more usable form of energy. Fuel cells are electrochemical devices which efficiently convert chemical energy into DC electricity and some heat (thermal energy). IC engines transform chemical energy into mechanical energy and a substantial amount of heat.

Energy Converters

Coupling a fuel cell to an electric motor produces mechanical energy. Similarly, an IC engine produces electrical energy if we couple it to an alternator or dynamo. Fuel cells offer an incredible efficiency advantage over IC engines, especially gasoline engines in stop-and-go service. Atmospheric pollution could be greatly reduced with the use of fuel cells. These clear advantages may ultimately cause the bell to toll for the internal, infernal combustion engine.

TOC
◀ ▶

All Fuel Cells are not the Same

Typically, fuel cells are categorized according to the kind of electrolyte which is utilized within these devices. The electrolyte may consist of a liquid solution or a solid membrane material. In any case, the electrolyte serves the vital function of ionic transfer of electrical charge. Some of the technologies are relatively advanced while others are still in their infancy. There are basically five fuel cell versions:

Phosphoric acid fuel cells (PAFC)

Alkaline fuel cells (AFC)

Molten carbonate fuel cells (MCFC)

Solid oxide fuel cells (SOFC)

Proton exchange membrane fuel cells (PEMFC)

The proton exchange membrane fuel cell is a promising candidate for stand-alone home power generation.

PAFCs: The Most Mature Approach

Phosphoric acid fuel cells (PAFCs) probably represent the most mature fuel cell technology. Westinghouse, International Fuel Cells, and at least a trio of Japanese manufacturers have been refining the design of mid-sized

TOC ◀ ▶

PAFC cogeneration plants. They are intended to fill the niche for stand-alone power generation for utility substations, factories, restaurants, hotels, and hospitals.

The fuel choice for PAFCs is not restricted to pure hydrogen. Typically, these near-term plants will use natural gas, methanol, or light distillates derived from fossil fuel sources. These cells operate at moderate temperatures (less than 200°C) with auxiliary reformers. Reformers convert the hydrocarbons to a mixture of hydrogen and carbon dioxide gases for the cells. The requirement for the initial reformation step sacrifices some efficiency, but the advantage of PAFCs is that they are tolerant of CO_2 and other reformate impurities. The overall efficiency improves above the 40-50% range if the installations are used as cogeneration plants, and the waste heat is used to make hot water and/or steam.

AFCs: Extraterrestrial & Terrestrial Applications

Another fuel cell technology which has been with us since the 1960s is the alkaline fuel cell (AFC) system. AFCs were first developed for spaceflight applications as part of the Gemini program to produce reliable onboard power and fresh water for the astronauts. International Fuel Cells and Siemens are currently major players in this field.

AFCs operate at relatively low temperatures, and don't require noble metal catalysts, strong advantages in their favor. Highly purified hydrogen, such as electrolytic hydrogen, is required as the fuel source. Unfortunately, AFCs also require pure oxygen as the oxidant, not air. AFCs are intolerant of even meager amounts of CO_2 which effectively poisons them. If air is to be used as the oxidant, expensive CO_2 scrubbers would have to be used to prevent a degradation of AFC performance.

The use of AFCs in transportation applications is doubtful; it is generally assumed that oxygen will not be stored on-board light vehicles. In home systems with solar hydrogen production, oxygen will also be produced in most cases, so this may not be a problem.

MCFCs: The New Hot Shots on the Block

Little will be said here about molten-carbonate fuel cells (MCFCs) and solid-oxide fuel cells (SOFCs). These second generation fuel cell strategies require very high temperatures for operation, (600°-1200°C). This allows for the internal reformation of fuels such as natural gas, methanol, petroleum, and coal. These devices tolerate CO_2 without requiring any further treatment and are possible substitutes for large to mid-sized thermal power plants, substations, or as cogenerators for factories. MCFCs and SOFCs are less likely to be utilized for remote home power generation by you or me, even in the distant future.

PEMFCs: Promise for Home Power Generation

One remaining fuel cell design approach has been saved for last. It is the solid polymer fuel cell, perhaps more commonly referred to as the proton exchange membrane fuel cell (PEMFC). This technology deserves the most careful scrutiny by advocates of decentralized renewable energy and alternative transportation.

Proton exchange membrane fuel cells (PEMFCs) appear to be the “new kids on the block”. In reality they represent a technology that was virtually “forgotten” for about a decade. This was an area of fuel cell research that languished in relative obscurity, and which received minimal R&D funding until only recently. General Electric pioneered the early work. The interest really revived in the last few years when Ballard Power Systems of Vancouver B.C., Canada went public with their results. Other private organizations which have gotten into the act in recent years include: H-Power, Ergenics, Energy Partners, Lynntech, Siemens, and Billings (International Academy of Science). United States educational and public institutions which have on-going laboratory research in this field include the Schatz Fuel Cell Project at California State University at Humboldt, the Center for Electrochemical and Hydrogen Research at Texas A&M, and Los Alamos National Laboratory. New players are entering and exiting this field so frequently that this lineup may already be out of date.

Elegant Simplicity

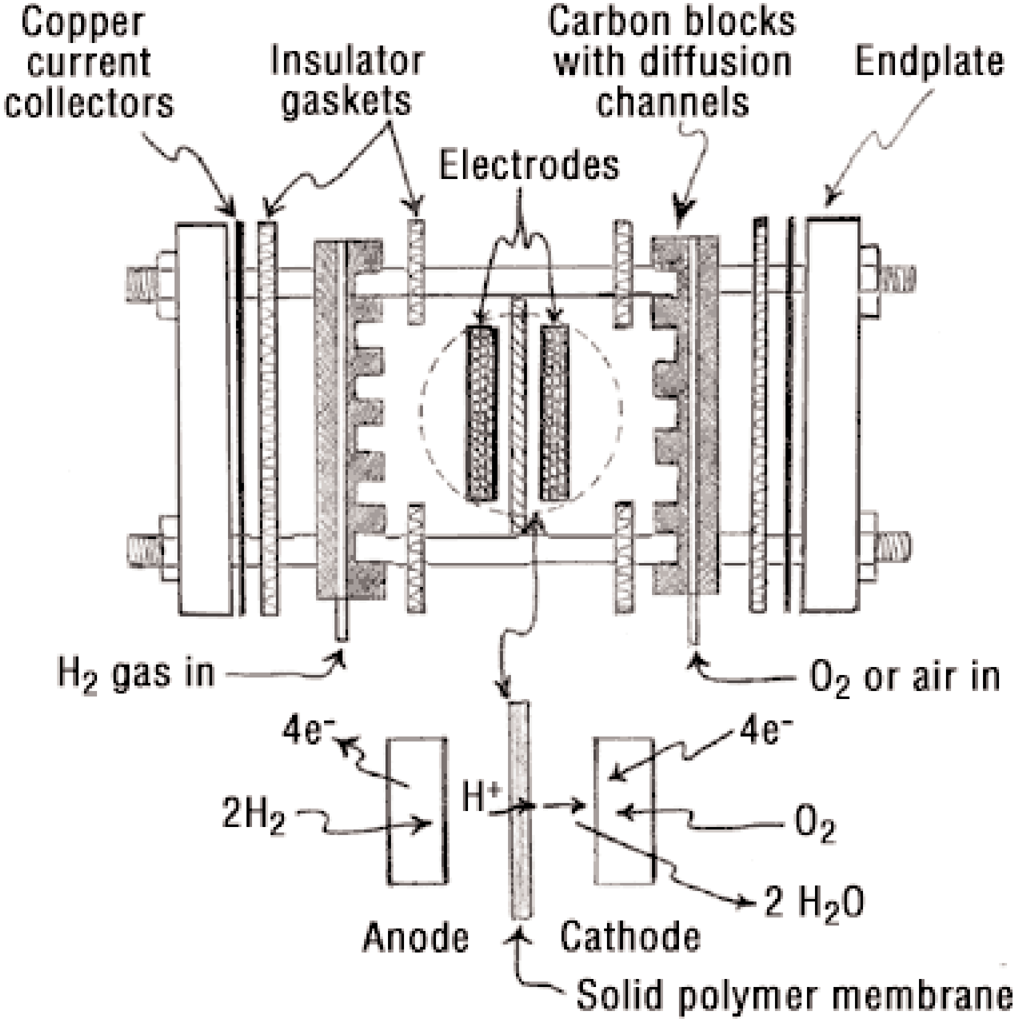
One can hardly examine PEMFCs without being impressed with their elegantly simple design concept. Yet, closer study reveals their complexities and potential pitfalls in operation. Although PEMFCs are currently available commercially from a few vendors on special order, don't rush for your checkbooks unless you have deep pockets and a strong heart. PEMFCs are currently in the prototype development stage, although laboratory research continues as well.

So, most of us must exercise a little patience for the vast promise of these devices to be fulfilled. Unless, that is, you're an impatient do-it-yourselfer, and choose to follow in the footsteps of others like Walt Pyle, Reynaldo Cortez, Alan Spivak, and Jim Healy who have built an operational single cell PEMFC. A detailed description of their procedures can be found in the next chapter "Making Electricity with Hydrogen" (p.169).

A Look Inside PEMFCs

The similarity between fuel cells and electrolyzers may be apparent from the illustration below. As Rob Wills points out in "Hydrogen Fuel Cells - the Power Source of the 90s" (p.223), fuel cells are essentially electrolyzers operating in reverse. Both of these electrochemical cells share certain internal elements along with batteries. They all have negatively charged electrodes,

TOC



Expanded schematic view of single cell solid polymer electrolyte fuel cell

TOC

positively charged electrodes, and an electrolyte that conducts charged ions between the electrodes.

Hydrogen is introduced into a PEMFC through a porous conductive electrode, which is frequently composed of graphite (carbon). The porous conductors may consist of special carbon paper. They may be graphite blocks milled with many gas delivery channels. The porous conductors may even be formed by pressing a carbon powder with a binder into a die with sufficient heat and pressure. The particular type of porous conductor construction is determined by the size and complexity of the cell or cell stack.

Gas Separator and Ion Conductor

The solid polymer electrolyte membrane makes the PEMFC unique. Most current prototypes of PEMFCs use either a Nafion membrane from DuPont or one that is simply referred to as the “Dow membrane”. Each is a perfluoronated sulfonic acid polymer, but the Dow membrane is said to have more sulfonate side chains. There are even other versions by Asahi Chemical and Chloride Engineers, Inc. The simple beauty of this design is that the membrane acts both as a conductor of hydrogen protons, and as a separator to keep the reacting gases from mixing and combusting. This feature allows for compact, lightweight cells, because the membranes themselves are very thin (0.007—0.015”).

A sheet of Nafion 117 doesn't look much different than a thick sheet of polyethylene or Saran Wrap. Onto this Nafion substrate is deposited a dispersed coating of platinum, a noble metal catalyst. This facilitates the chemical reactions, so they proceed at lower temperatures. Approaches which have been used with success for depositing the platinum include: thin film vacuum processes, brushing or precipitating a dilute solution of chloroplatinic acid, and hot pressing powders (carbon, platinum, and teflon). Significant reductions in the amount of expensive platinum have apparently been achieved, from 20 mg/cm^2 to 0.4 mg/cm^2 , without sacrificing performance.

Seen from a Molecule's Point-of-View

Okay, now we're ready to travel the inner journey traversed by individual hydrogen and oxygen molecules on the path to their new union (see figure). If we introduce pure hydrogen through the porous conductive hydrogen electrode, it arrives as a diatomic gas, H_2 . Each molecule is dissociated into two hydrogen atoms and stripped of two electrons as it interacts with the catalytic surface of the membrane. Devoid of their electrons, they exist as two H^+, hydrogen protons. The membrane itself will not conduct electrons. However, the electrons will flow readily via the conductive hydrogen electrode through the external circuit to the opposite oxygen electrode. Along this path, the current may flow through an external load accomplishing work. Meanwhile, the protons are moving their way through the solid polymer electrolyte on their way to meet oxygen ions. Simultaneously, diatomic oxygen molecules, O_2, are diffusing through the oxygen electrode where they contact the platinized surface on the opposite side of the membrane. Here we would find that oxygen molecules separate into oxygen atoms which are held momentarily in a "receptive" state on the active platinum. Once electrons coming from the load meet the two protons arriving at this site, they combine with the oxygen atom in a spontaneous union. Voila! This results in the formation of one molecule of water, H_2O.

Only one half as much oxygen is needed in this process as is needed of hydrogen. A chemist might write a synopsis of the entire process as shown below. The reaction at the hydrogen electrode of a PEMFC:

$2H_2$ ––> 4H ––> 4 electrons + $4H^+$

The reaction at the oxygen electrode of a PEMFC:

O_2 ––> 2O

then,

4 electrons + 4H + + 2O ––> $2H_2O$

The overall reaction within a PEMFC is simply

$2H_2 + O_2$ ––> $2H_2O$.

What's the Rub?

Well, this works very well in theory, but there is a little more to the story. In actual practice there are some additional complications involved in PEMFC operation. First, the hydrogen which is introduced into the cell must be saturated with H_2O vapor or else the membrane will dry out on the hydrogen side hindering performance markedly. Second, on the opposite side of the membrane a delicate balance must be struck with humidification also. Water is continually forming on the oxygen side which aids hydration of the membrane. But if droplets of water condense on the active surfaces, the reaction rate can slow to a halt as the cell literally drowns in its end product. Some waste heat is also building up simultaneously, even though the process is usually between 55-80% efficient. It is primarily the need for moisture and thermal management of both sides which has plagued a number of the PEMFC designs. Leakage of gases around gaskets or o-rings is another difficulty. As series cell stacks are built up of adjacent cells in a bipolar configuration to produce useful output voltages, these problems may magnify several fold.

So What is the Prognosis?

There is every reason to believe that the operational difficulties encountered in PEMFCs will be solved in the near future. The progress needed to make these fuel cells viable should not require any major “technological breakthroughs”. PEMFCs hold great promise for automotive and other transportation applications, because they should prove to be both light and compact as well as extremely efficient compared to internal combustion engines.

When transportation energy analysts compare various drive train systems for future automobile designs, they frequently speak of criteria such as energy density and power density. Energy density is commonly expressed in units such as kWhr/kg, whereas power density pertains to the ability of a system to deliver performance quickly, and is expressed as kW/kg. Since fuel cells themselves do not produce torque, they would need to be coupled with highly efficient electrical motors. The coupling of hydrogen stored onboard an automobile as a liquid, hydride, or compressed gas with PEMFCs would seem to have superior energy density as an integral system than any battery electric vehicle configuration on the horizon. However, in order for these fuel cell vehicles to come close to matching the power of today’s internal combustion engine vehicles, perhaps the best configuration would be a hybrid one. These hybrids would likely use a “base load” fuel cell for cruising with a quick discharging battery for the higher instantaneous demands of acceleration. This is exactly the conclusion arrived at by three independent research analysts, and published in two scientific papers which have recently been published (see references).

The Pregnant Promise of Fuel Cells

We can only hope that fuel cell research coupled with engineering refinements continues at an accelerated pace. The inefficiency of the internal combustion engine cannot be tolerated much longer. Atmospheric pollution, global warming resulting from greenhouse gas emissions, and the steadily declining reserves of petroleum are all part of the legacy left us by dependence on fossil fueled IC engines. Many scientists and energy analysts believe that a solar based hydrogen energy system is the answer to these problems. The timely maturity of hydrogen fuel cell technologies will be of critical significance, if the world is going to successfully wean itself from fossil fuels. An appropriate analogy might be made between the development of integrated circuits and fuel cells. The first integrated circuits were a landmark advance that ushered in the electronic and information age. As fuel cells replace IC engines, I believe a Solar Hydrogen Age will blossom from the dust of the passing fossil fuel era.

Access

Author:

David Booth, Alternative Energy Engineering • 707-923-4336

Further reading

Hydrogen Fuel-Cell Vehicles, Mark DeLuchi, Institute of Transportation Studies, University of California, Davis, CA 95616

TOC
◀ ▶

Further reading (continued)

The International Journal of Hydrogen Energy, Permagon Press. Contact P.O. Box 248266, Coral Gables, FL 33124

Hydrogen-Fueled Vehicles Technology Assessment Report for California Energy Commission, Dr. David Swan and Debbi L. Smith, Technology Transition Corporation and Center for Electrochemical Systems and Hydrogen Research, Texas A&M University, 238 Wisenbaker ERC, College Station, TX 77843

Making Electricity with Hydrogen

by Walt Pyle, Alan Spivak, Reynaldo Cortez, and Jim Healy

Originally published in Home Power #35 • June / July 1993

A gas fed battery that never needs recharging! This article describes a process for building a fuel cell using tools and techniques any skilled hobbyist with a well-equipped shop can duplicate. The fuel cell that we built can produce direct current electricity from stored hydrogen and oxygen. We obtained the hydrogen for this fuel cell commercially but plan to produce hydrogen and oxygen from a renewable energy system based on solar photovoltaics and water electrolyzers.

Cookbook Approach to Building a Fuel Cell

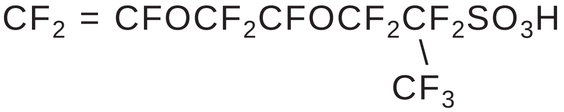
In this article we reveal the process we used to make a proton exchange membrane (PEM) fuel cell. First, we describe what the PEM material is, and where to get it. Then we cover the steps necessary for preparing the membrane to use it in a fuel cell. Next, we describe the catalyst and binders used on both sides of the PEM and the method of “hot-pressing” them all together to form the single fuel cell catalyst-PEM-catalyst “sandwich”. Finally, the holder for the catalyzed PEM fuel cell with its gas supply piping, insulators, and wiring studs is shown.

TOC

Some PEM fuel cell performance data were obtained using an electrical resistor to provide a variable load. Two digital multimeters and a shunt resistor were used to measure the voltage and current, so we could calculate the power produced. Although the fuel cell described produces a relatively low voltage, several fuel cells of this kind can be wired in series to produce higher voltages and do useful work.

The PEM Material

The PEM (proton exchange membrane) material is a perfluorosulfonic acid polymer film. Several manufacturers make PEMs in one form or another. We used one made by du Pont called Nafion 117. Nafion 117 is a transparent polymer film about 175 microns (0.007") thick. Dow Chemical Co., Asahi Chemical Co., and Chloride Engineers Ltd. make something similar. A patent describing how one PEM manufacturer's film is processed is listed in the references section at the end of this article. The basic structural unit formula for Nafion 117 is shown below:



$$CF_2 = CFOCF_2CFOCF_2\underset{\substack{\backslash \\ CF_3}}{CF_2}SO_3H$$

Nafion 117 contains fluorine, carbon, oxygen, sulfur, and hydrogen arranged in repeating polymer molecules. The hydrogen atom on the SO_3 part of the molecule can detach from one SO_3 site. The free H^+ proton can

TOC

hop from SO_3 site to SO_3 site through the material, to emerge on the other side of the membrane. This is the reason it is called a proton exchange membrane. It can be thought of as solid sulfuric acid, an electrolyte.

The PEM is relatively expensive at this point in time. We paid about $100 for a 30.5 centimeter by 30.5 centimeter (12 inch by 12 inch) piece of Nafion 117 from a chemical supply house. Some manufacturers want your first born child in exchange for a sample. However, duPont really is in the PEM business, and they will sell it to you with no strings attached from their pilot plant production. The price comes down to about $65 for the same size piece when you buy four times as much PEM direct from duPont. The piece we bought was large enough to make about six of our round fuel cells ($10 - $16/cell).

Punching PEM from sheet with arch punch

photo by Reynaldo Cortez

Punching the PEM Disk from a Sheet of Nafion 117

We set the sheet of Nafion 117 on a piece of clean acrylic plastic using clean cotton gloves to avoid contaminating the sheet with fingerprints. Then we punched out some round PEM disks using a 4.76 centimeter ($1^7/8$") arch punch and a mechanics hammer filled with lead powder. After one or two tries, we found that several strikes with the hammer at different angles was best for cutting the disk free from the sheet. Striking the punch too hard shattered the acrylic sheet.

Handle the PEM with tweezers or forceps to prevent contamination. We used a pair of stainless steel tweezers which were ground flat and polished on the grasping faces to eliminate burrs and prevent puncturing or denting the soft PEM. Grasp the PEM disks only on the outer peripheral edge, never on the inner active area.

Preparing the PEM for Catalyst Application

We prepared the film for catalyst application by dipping it in six different heated solutions in glass beakers. The solutions were all held at 80°C (176°F) by immersing the beakers in a heated pan of water on top of two gas stove burners as shown above right. Each beaker held the PEM film for one hour in sequence. Use safety glasses and gloves while working with the solutions. The sequence of beakers used to dip the PEM was set up as follows:

Beaker 1 = 100 milliliters of distilled water [hydrate the membrane and dissolve surface contaminants].

Beaker 2 = 100 milliliters of 3% hydrogen peroxide solution (USP) [remove organic contaminants from PEM surface].

Solutions in beakers on top of stove

photo by Reynaldo Cortez

Beaker 3 = 100 milliliters of sulfuric acid (new battery electrolyte) [remove metal ion contaminants from PEM surface, and sulfonate the PEM surface].

Beaker 4 = 100 milliliters distilled water [rinse sulfuric acid from surface and hydrate PEM].

Beaker 5 = 100 milliliters distilled water [repeat rinse].

Beaker 6 = 100 milliliters distilled water [repeat rinse].

While the PEM disk is in a beaker, there may be a tendency for the film to curl and lift on the steam bubbles, rising to the surface. It should be kept submerged so the top side doesn't get exposed to air. Use a clean inert polyethylene plastic or glass probe to keep it down in the dipping solution.

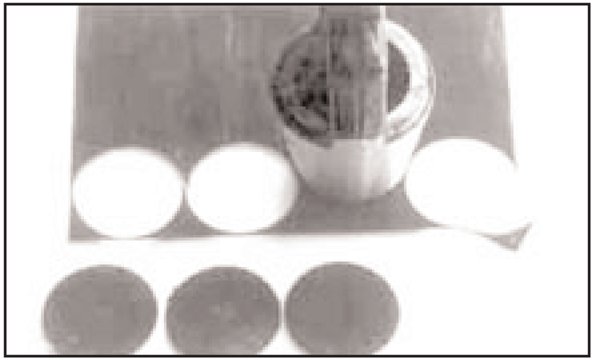
We used a Taylor candy thermometer for controlling the beaker bath temperature, and adjusted the gas stove burner controls as needed. From time to time, more water had to be added to the bath surrounding the beakers, due to evaporation.

After the PEM disk was dipped in each of the six hot solution beakers for an hour, it was then wiped with a piece of lint-free lens cleaning tissue, and air-dried in a clean place.

The Catalyst Layer Material

The catalyst layer is the most expensive part of this fuel cell. It is made from a mixture of platinum, carbon powder, and PEM powder, bonded to a conductive carbon fiber cloth. We obtained ours from E-Tek Inc. The cost for an order of their ELAT catalyst cloth sheet includes a setup charge. So get together with others for a larger order if you want to keep costs down. We paid $360 for a piece of ELAT 15.2 centimeters by 15.2 centimeters [6” by 6”] including the $150 setup charge. This piece provides enough for about twelve disks. Each fuel cell requires two disks of ELAT and one larger disk of PEM to make the sandwich, so you can make six cells from this size piece of ELAT ($60/cell). The cost may have come down by now due to increased production at E-Tek. In the future it may be possible to reduce the cost by putting the catalyst coating directly on the PEM with a platinum-carbon ink, as practiced by Los Alamos National Laboratory.

TOC



Cutting ELAT catalyst disks

photo by Reynaldo Cortez

Preparing the ELAT Catalyst/Binder Layers

Two catalyst layer disks were punched from an E-Tek ELAT sheet. The sheet was placed on clean acrylic plastic and the disks were punched with a 3.8 centimeter (1.5”) arch punch and the mechanics hammer.

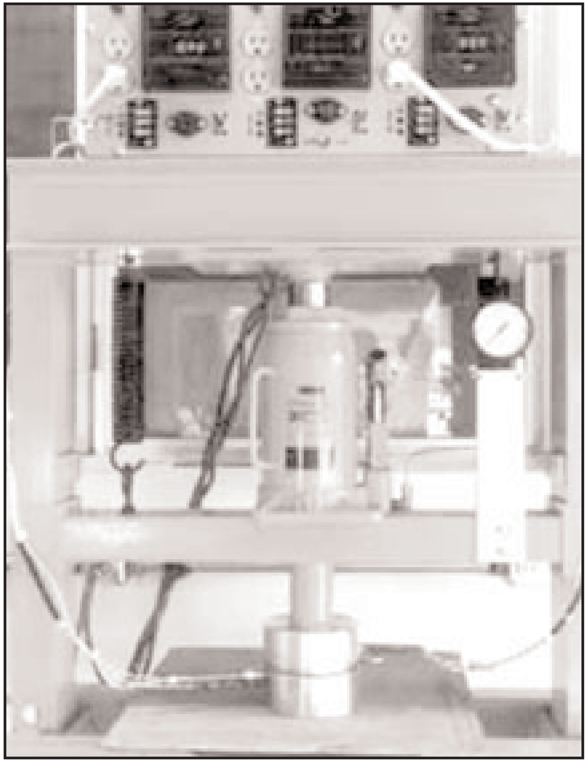
Be careful to keep track of which side is the active side of the catalyst impregnated carbon cloth. The active side has more of the carbon-platinum binder powder and is smoother.

Hot-Pressing the Sandwich Together

A hot press was made using a hydraulic 20 ton shop press, and two homemade aluminum heating plates. Each heating plate was drilled to accept an electric cartridge heater and a thermocouple. A temperature controller was connected to the heater and thermocouple on each heating plate.

The bottle jack on the hydraulic press was drilled and tapped to accept a $^1/_4$” NPT pipe to connect to a pressure gauge.

Procedure for Hot Pressing



Hot press and heating plates

photo by Reynaldo Cortez

First, two ELAT catalyst disks were coated with liquid Nafion 117. The coating only went on the active side that was to be bonded to the PEM. We used a cosmetic brush to put on a single coat (thick enough to give a wet appearance) then let it air dry at room temperature in a clean place for one hour. The liquid Nafion 117 has a strong alcohol odor, so do this coating process in a well-ventilated area.

Next, we coated the heating plates with graphite from a number two pencil and smoothed it out with a Q-tip to make a release and contamination shield layer. The three layers (catalyst-PEM-catalyst) of the sandwich were then set on top of the lower heating plate. After carefully aligning the layers, so that the smaller catalyst disks were centered above and below the larger PEM disk, the upper heating plate was

TOC

placed on top of the sandwich. At this time the heaters were off and the plates were at room temperature.

Next, the two temperature controllers were activated and the sandwich was taken up to 90°C (194°F) for one hour to evaporate the solvents from the liquid Nafion 117 catalyst coating. The temperature was then raised to 130°C (266°F) over the next 30 minutes. This is the PEM glass transition temperature.

Once the heating plates and the sandwich reached 130°C, pressure was applied using the hydraulic jack, up to 2.16 MPa (300 psig). Shortly thereafter, the pressure fell off as the PEM was squeezed by the heated plates and the sandwich became thinner.

After two minutes at temperature and pressure, the temperature controllers were turned off and the plates and sandwich cooled to room temperature.

The heater plates were opened, and the finished fuel cell sandwich was removed using the special tweezers. We noted that the PEM disk was no longer round, but instead somewhat elliptical. This may be due to alignment of the film molecules in one preferential direction. The fuel cell sandwich did not stick to the aluminum heater plates, so the graphite release coating appeared to be effective.

Fuel Cell Test Fixture

Our fuel cell test fixture was made from a commercially available membrane filter holder. We spot-welded electrode studs to the two halves of the fixture case, one for the hydrogen side and one for the oxygen (air) side. A groove for an o-ring was machined into each half of the case, to provide a seal to prevent the gases from leaking around the edges of the gas distribution plates.

Kapton tape was applied to the inside diameter of one case to insulate it from the other. Kapton tape was also applied to the outer diameter of the mating case to insulate the retaining ring and prevent the two cases from shorting together. An ohm-meter was used to assure that the two cases were well-insulated from one another.

The PEM sandwich was trimmed with a pair of scissors until it was round again, and placed between the filter holder's two stainless steel gas distribution plates to make a five layered sandwich. The five-layered sandwich was then dropped into the Kapton lined case and the other case (with the Kapton on the outside) was applied on top and attached by the threaded retainer ring.

Fuel cell membrane test fixture

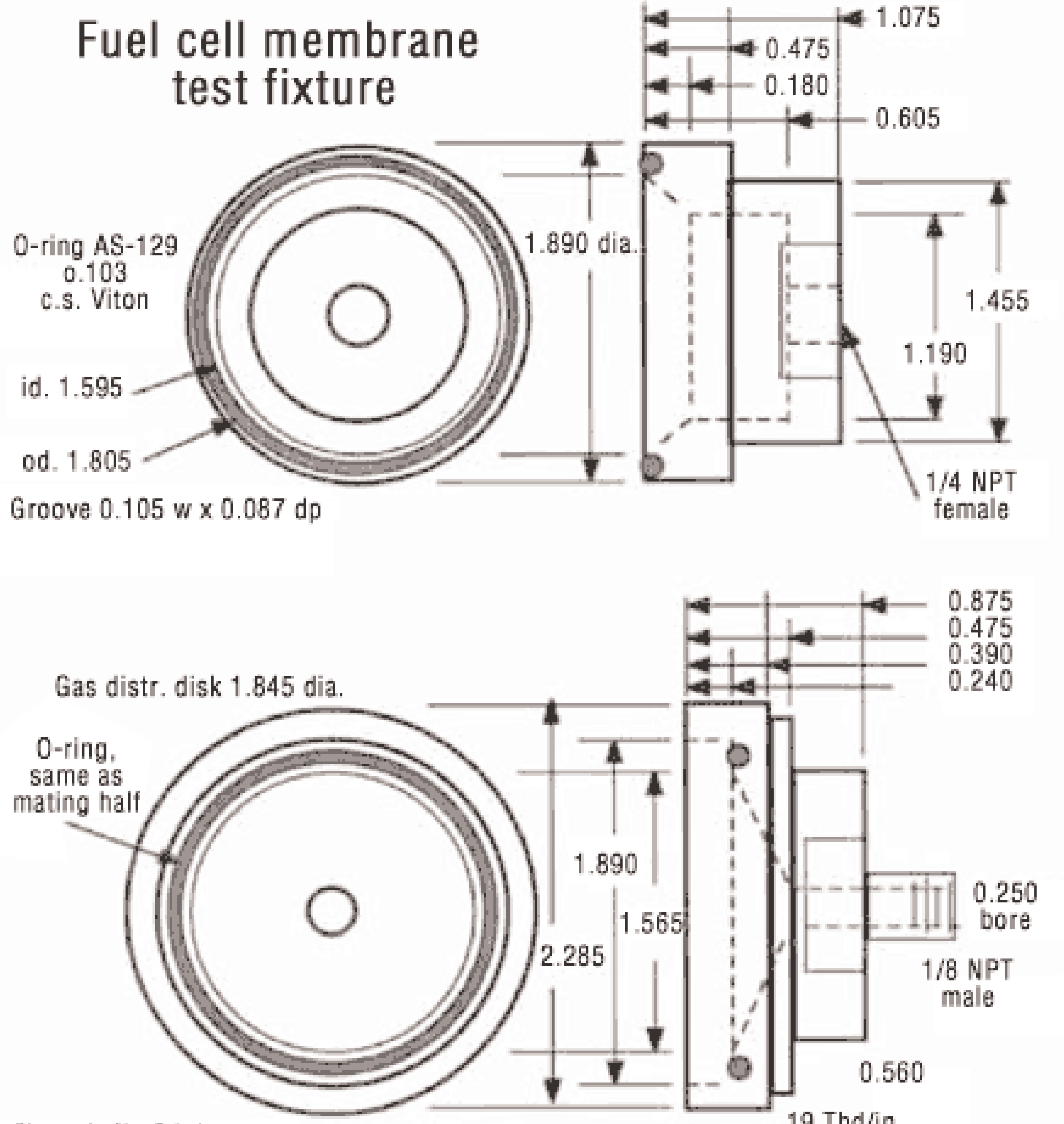
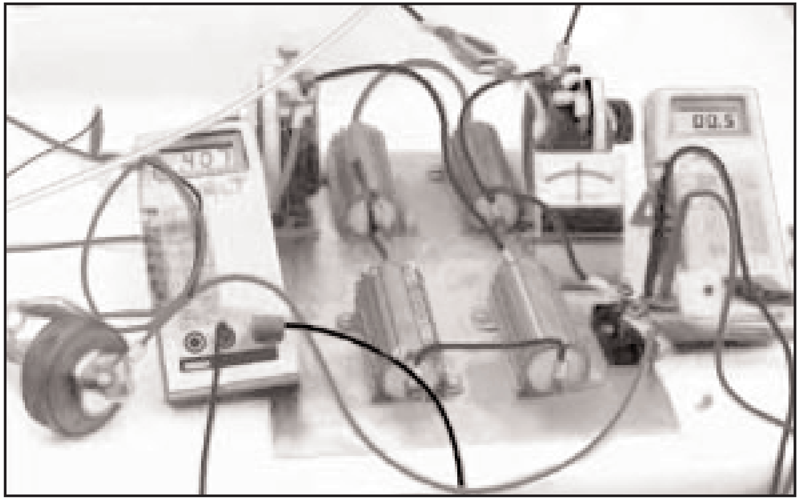


Diagram by Alan Spivak

TOC
◀ ▶

Fuel Cell Load Test System

An electrical testing load system was prepared as shown below using two variable resistance potentiometers rated at 0 to 1.0 ohm at 25 watts, a current measuring shunt, and two digital multimeters.



Electrical test system. The four fixed resistors were not used.

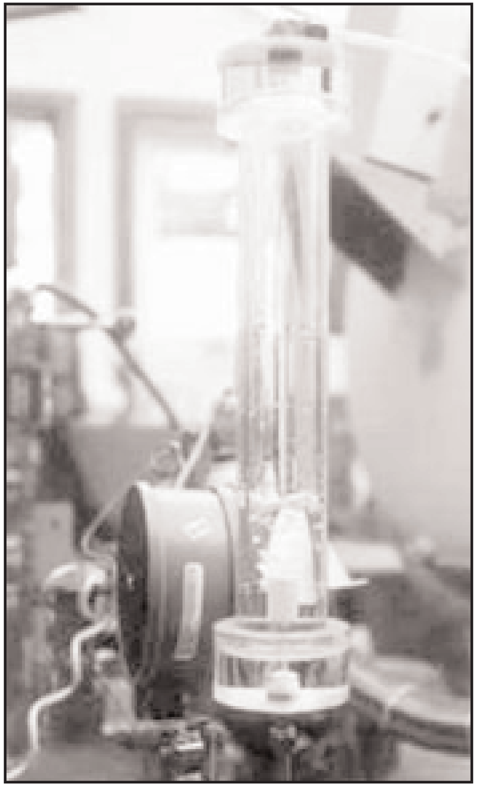
Photo by Reynaldo Cortez

Hydrogen Humidification Bubbler

A hydrogen humidification bubbler was made to prevent the fuel cell PEM from dehydrating under load. Moisture management in the PEM is an engineering challenge, due to ohmic heating when high currents flow, and osmotic drag of moisture towards the oxygen side of the sandwich. The osmotic drag is caused by the migration of protons through the PEM.

We made the bubbler out of a 30.5 centimeter (12”) length of 5.08 centimeter (2”) outside diameter, 1/4” wall, acrylic tubing, and two 5.08 centimeter (2“) lengths of 7.6 centimeter (3”) diameter acrylic round bar stock. The round bar stock pieces were then machined to accept the length of tubing and glued together, using acrylic cement.

Holes were tapped in the center of each piece of bar stock to accept 1/4" NPT pipe, and a Kordon Mist Air aquarium bubbler was glued into a smaller hole on the bottom inside of the bubbler.



H_2 humidification bubbler.

Photo by Walt Pyle

First Test Results

Our first test was made on our fuel cell at the Schatz Fuel Cell Laboratory at Humboldt State University during January 1993. Leak testing was done by setting the fuel cell test fixture in a container of water. We applied atmospheric air pressure and hydrogen pressure (approximately 100 KPa (14.5 psig)) and found significant leakage of hydrogen around the edges of the sandwich. The open circuit voltage of the fuel cell was almost zero, because the hydrogen was leaking into the air side. With the help of the Humboldt State wizards, however, a piece of tubing was inserted into the air fitting. Blowing air into the tubing flushed out the leaking hydrogen through the annulus and provid-

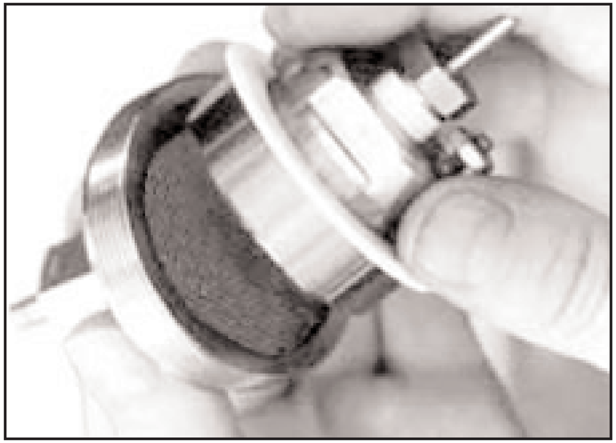
TOC

ed oxygen. This gave an open circuit voltage of 0.68 Volts, showing us that we had a functional but very leaky cell.

If At First You Don't Succeed....

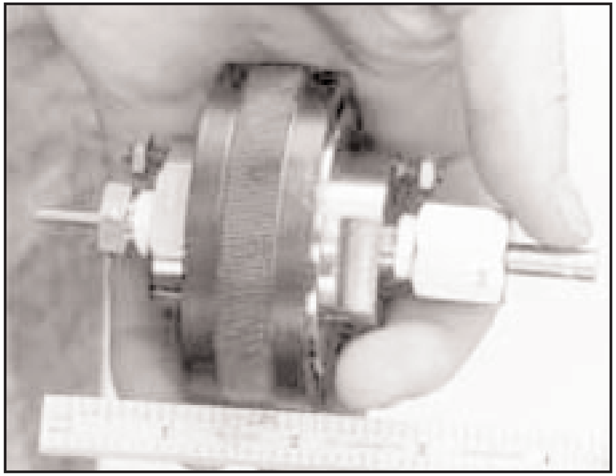
Following our visit to the Schatz Lab, we went back to the drawing board and added the o-ring seals to the case. In March 1993, the cases were machined to accept the o-rings and we were ready to try again. Another dip in the water container with 200 KPa (30 psig) hydrogen pressure showed that the leaks in the fuel cell test fixture had been stopped.

Another series of tests were run on our shop resistance load tester. This time, the open circuit voltage reached 0.95 Volts. Using the Humboldt tubing and annulus flushing technique on the air side, we were able to prevent the



Fuel cell disassembled, showing a gas distribution plate on the left.

Fuel cell assembled.



Photos by Reynaldo Cortez

nitrogen gas from concentrating inside the cell (as the oxygen was consumed from the air). We obtained a short circuit current of over 1.5 Amperes for short periods of time (minutes). And then, by varying the load resistance we obtained data at different operating voltages and currents for the cell. Sustained power output was limited, we think, by poor moisture control on the cathode (too dry) or anode (too wet). A graph of the current-voltage response of the cell is shown above.

Future Direction

This saga has only just begun, and we are learning some valuable lessons as we go. Water management on both sides of the cell is a major challenge. On the hydrogen side, the PEM must be kept damp so it won’t crack, and short or leak. On the oxygen side, water is produced which must be removed so the ELAT catalyst won’t “drown” and get starved for oxygen.

We plan to try some experiments with oxygen instead of air on the anode side. Wick-like materials will be tried for passively absorbing and transporting water to the PEM and transporting water from the ELAT anode catalyst.

Ultimately, we’d like to have a 12 Volt or 24 Volt fuel cell that could be used in the home to power a 2 kW inverter for supplying 120 Volts, 50/60 Hz alternating current. Batteries would be eliminated, and solar energy would be stored as hydrogen and oxygen in tanks until it was needed. Others are dreaming of PEMFC cars, and locomotives. As we go to press, Ballard Battery Co. in Vancouver B.C. is driving a fuel cell powered bus around the parking lot!

Please let us hear from you if you have any suggestions for improvements or new experience to share. We don't want to squirrel this technology away; we'd rather set it free!

Hydrogen Safety Considerations

For a more thorough discussion of the safety consciousness one should develop when working with hydrogen, see the chapter "Heatin' with Hydrogen" (p.142). The bottom line is:

- Work with hydrogen out of doors or in a well-ventilated area.
- Store only pure hydrogen or oxygen, never mixtures of gases.
- Remember the explosive mixture limits are wide and different from other fuels: even very rich hydrogen-air or hydrogen-oxygen mixtures can burn violently.

Access

Authors:

Walt Pyle, WA6DUR, Richmond, CA • 510- 237-7877

Alan Spivak, KC6JZN, Berkeley, CA • 510-525-4082

Reynaldo Cortez, Richmond, CA • 510-237-9748

Jim Healy, WH6LZ, Richmond, CA • 510-236-6745

Reference

U.S. Patent No. 4,661,411, *Method For Depositing A Fluorocarbonsulfonic Acid Polymer From A Solution,* April 28, 1987; Inventors: C.W. Martin, B.R. Ezzell, J.D. Weaver; Assigned to Dow Chemical Co., Midland, MI

Acknowledgements for Articles and Discussions

Supramaniam Srinivasan, A.C. Ferreira, Imran J. Kakwan, David Swan; Texas A&M University, College Station, TX

Roger Billings, Maria Sanchez; International Academy of Science, Independence, MO

Peter Fowler, E-Tek Inc., Framingham, MA

Peter Lehman, Tom Herron, Ron Reid; CA State University at Humboldt,

Schatz Fuel Cell Laboratory, Arcata, CA

David Booth, Alternative Energy Engineering, Redway, CA

PEM Materials

Nafion 117 PEM (du Pont) 0.007 inch thickness:

Aldrich Chemical Co., Catalog No 29,256-7

PEM Materials (continued)

Nafion 117 solution (Nafion perfluorinated ion-exchange powder 5% mixture of lower aliphatic alcohols and 10% water d 0.874):

Aldrich Chemical Co., Catalog No. 27,470-4 • 800-558-9160

Nafion 117 PEM (orders greater than 0.61 m by 0.61 m [24 inches by 24 inches] or larger):

I.E. du Pont de Nemours & Co., Customer Service Dept. • 302-695-5249

Catalyst/Binder Materials

ELAT Solid Polymer Electrolyte Electrode 20% Pt/C with 0.4 mg/cm 2 Pt loading: E-Tek, Inc., 1 Mountain Rd, Framingham Industrial Park, Framingham, MA 01701 • 508-879-0733

Test Fixture

Stainless Steel In-line Filter Holder: Catalog No. L-02929-20 (47 mm), Cole-Parmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL 60648 • 800-323-4340

Hot Press Components

20 Ton Hydraulic Press: Post Tool Co. 800 E. 8th Street Oakland, CA • 510-272-0331

Temperature Controllers, Thermocouples, Cartridge Heaters: Omega Engineering Inc., 1 Omega Dr., Stamford CT 0690 • 203-359-1660

Alternatives to Fossil Fueled Engine/Generators

by Clifford W. Mossberg

Originally published in Home Power #21 • February / March 1991

For most of us who live in secluded areas and who employ alternative energy technologies to provide us with a contemporary standard of living, looking for more efficient alternatives is second nature. Most of us have wondered about an alternative to the use of fossil-fueled engine/generators to back up our more desirable energy sources.

Photovoltaics and wind energy are intermittent or diffuse technologies which require storage to be effective and are limited in output. Hydro power is site specific and will not be available in many places. Alternative energy generation also costs a lot of money initially and the temptation to go with the cheapest and sometimes only affordable power source is strong. Usually that is a fuel driven engine/generator. There are lots of reasons to use a "light plant," but sooner or later the moment of truth comes: These things are noxious, noisy, take more maintenance than a new born baby, and eat more than a teenager. "Isn't there something else!?"

Yes there is. The advantage to a "light plant" is that by paying the price we are able to create energy in large quantities and at our discretion using easily obtainable and conveniently transported fuel. We are not at the whim of wind, sun and water. So any replacement technology must have, at a minimum, this element of discretionary use.

TOC

Steam Power

Historically one of the earliest alternatives to fossil fuels is a wood fired boiler producing steam which powers an engine driving a generator. I've noticed interest in this recently among letters from Home Power readers. I would like to share some perspectives on steam power and its alternatives.

First the good news: Steam **can** be produced from wood; allowing us to use Ma Nature to produce and store our energy for us in our own back forty. This, unfortunately is about the only advantage. The bad news is that steam power has all the disadvantages of an engine/generator and several more all its own. Ma Nature may provide the fuel but we, the user, must "condition" it. The wood must be chopped and carried, cured, split, and fed, just as for any wood stove. Ashes must be handled and hauled. The entire installation requires constant babysitting while it is running - no walking away from this thing to do the wash! But the real kicker is the inherent danger in steam.

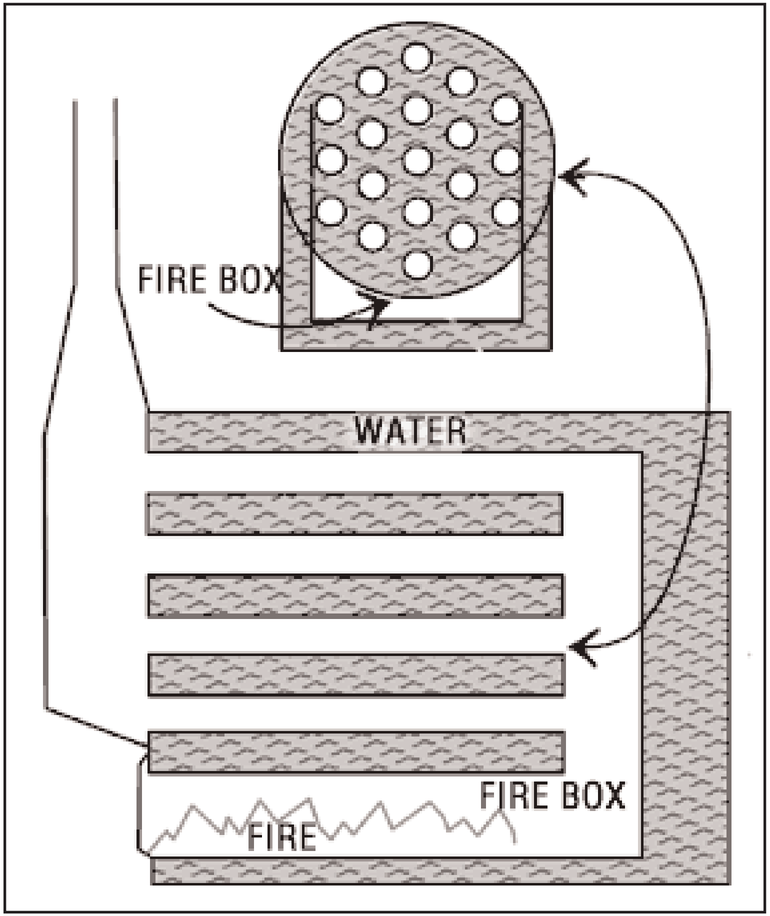
Steam occupies about 1200 times the volume of water at atmospheric pressure (known as "gage" pressure) - that's **one thousand two hundred times!** Producing steam requires heating water to above boiling temperature under pressure. Water boils at 212° F. at sea level. By pressurizing the boiler it is possible to raise the boiling temperature of water much higher. At a pressure of 52 psi gage the boiling temperature is 300°, at 120 psi gage it is 350°. Elevating steam temperature like this HAS to be done to use the the

TOC

generated steam for any useful work otherwise the steam would condense in the supply lines or inside the cylinder of the steam engine itself. Typical working limits for a small simple "home style" boiler are in the range of those given above.

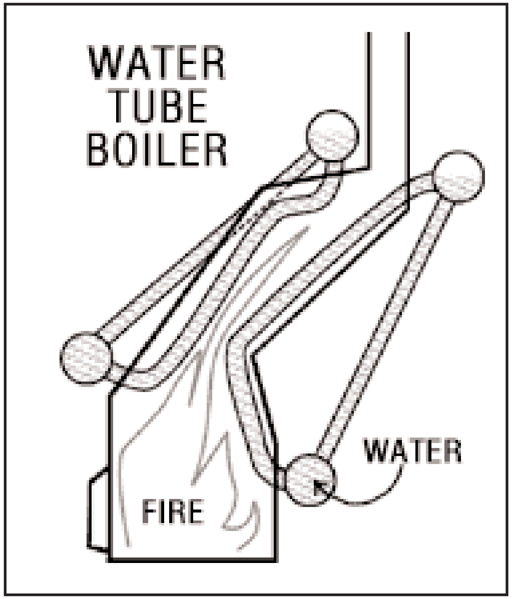
Fire Tube Boiler

There are two basic kinds of boilers: The first is the **fire tube boiler** where the water is heated in a large pressurized tank. To increase the surface area so that heat may be transferred to the water more efficiently there are tubes passing thru the boiler carrying hot flue gases. Essentially these tubes are multiple smoke



Fire Tube Boiler

stacks which run from the fire box through the water before exhausting up a chimney. This type of boiler can hold a significant amount of water.



Water Tube Boiler

The second type of boiler is a **water tube** type. In this unit water is carried through the fire box in pipes. Steam is produced in these pipes and goes to the point of use. This type of boiler has much less water heated and under pressure at a given time. Why worry about the amount of heated and pressurized water? Picture a very small boiler, maybe the size of a fifty-five gallon drum. Rough dimensions of one of these drums is around 24” in diameter by about 36” long; about 9.5 cubic feet of water at 70 pounds per square inch (all pressures are given as "gage" here, which means the atmospheric pressure of about 15 psi is subtracted from the "absolute" pressure reading) and 316° F.

What happens if the boiler springs a leak? Pressure immediately falls. Since there is less pressure on the heated water, it immediately starts to boil. As the water boils it produces steam which raises the pressure on the water

TOC
◀ ▶

and inhibits boiling. This condition normally exists in a boiler and produces a controlled reaction. The "leak" is the boiler steam outlet pipe.

But what happens if there is an uncontrolled leak in the boiler such as equipment failure might produce? As pressure drops and water starts to boil there is no restriction to stabilize the pressure and **all** the water can immediately flash into steam. In our example if you start out with $9^{1}/_{2}$ cubic feet of superheated water and reduce the pressure to zero you almost instantaneously have 1200 times $9^{1}/_{2}$ cubic feet, equal in volume to a single story house measuring about 35 by 40 feet. You suddenly have 11,400 cubic feet of steam in a $9^{1}/_{2}$ cubic foot pot and a real - but short lived - problem; a massive boiler explosion.

At the core of this explosion is superheated steam at 316°. If the shrapnel and concussion is daunting enough, this 316° steam will instantly cook any flesh it comes in contact with and can literally strip flesh off the bone. Does the average small homesteader want to play dice with this process? (The hypothetical boiler in our example has a total internal working force of about 125 tons applied to it!)

A water tube boiler is more benign. It may only result in an explosive steam volume of one or two "rooms" in the "house" in the example. Therefore a water tube boiler is the preferred design for anyone getting

TOC
◀ ▶

serious about steam. Failure of a water tube boiler probably won't take out City Hall, but it would not be comforting to those in the vicinity.

So why not just opt for a water tube boiler and get on with it? Economics. A fire tube boiler can be fabricated from a cylindrical tank with straight tubes running through it from end to end. A water tube boiler is fabricated as a fire box with many small tubes with complicated bends in them welded inside. There is a lot more precise design, welding, and fabrication involved with a water tube boiler.

Then there is the fact that **all** boilers manufactured or used in the United States must be built to rigid specifications and tested in accordance with regulation and prescribed procedure; not just initially but throughout their installed life. Any boiler is potentially dangerous and expensive.

If you are willing to spend money to acquire a working boiler and operate it what do you have? Let's look at efficiency:

The traditional gasoline engine can be used as a baseline that we are familiar with. It is considered to be about 28% efficient. A diesel engine is considered to be about 32% efficient. This efficiency is a measure of the engine's ability to turn heat energy in fuel into useful work and the figures I've given represent an average of a range of values. A better way of thinking of efficiency is that 72% of the heat developed by gasoline burned in a gasoline engine is wasted; or about seven out of every ten gallons of gas you burn goes to heat the air, either through the radiator, radiation from the engine, or out the tailpipe. How does steam compare?

A typical single acting single cylinder steam engine (the kind most of us might easily acquire) runs from about 7% to 12% efficiency. A high performance double acting multi-cylinder unit might run about 15% to 17% efficiency. A well insulated unit with a vacuum condenser might push that up as high as 22% if you were very lucky. Even were you to go to a very sophisticated steam turbine installation - totally out of sight financially for most of us - the efficiency would only be pushed up to about 26%; the lower end of gasoline engine technology. Bear in mind that **you** will bear the direct burden of this inefficiency right on your back. Only 7% of the energy in the firewood you painstakingly lugged out of the woodlot will turn into energy you can use to generate electricity. This doesn't factor in any environmental damage.

I haven't said anything yet about your time. The typical small steam installation will require constant attention to operate. Automatic controls do not adapt well to burning a non-uniform fuel like logwood and are too expensive and complex to find their way into small installations. You will have to hover over this unit to feed fuel, monitor boiler pressure, check feed water, oil equipment, etc. The operator is apt to become the exclusive servant of the machine when it is powered up.

TOC
◀ ▶

Now that I have painted this bleak picture let's ask if there's any alternative to steam as a replacement for the family "light plant"? **Yes!** The surprising answer is that a conventional gasoline or diesel driven engine/generator set can be combined with wood gas technology to do the job. While it has drawbacks of its own, this marriage is much cheaper and safer than steam.

Wood Gasification Basics

Wood gasification is also called producer gas generation and destructive distillation. The essence of the process is the production of flammable gas products from the heating of wood. Carbon monoxide, methyl gas, methane, hydrogen, hydrocarbon gases, and other assorted components, in different proportions, can be obtained by heating or burning wood products in an isolated or oxygen poor environment. This is done by burning wood in a burner which restricts combustion air intake so that the complete burning of the fuel cannot occur. A related process is the heating of wood in a closed vessel using an outside heat source. Each process produces different products.

If wood were given all the oxygen it needs to burn cleanly the by-products of the combustion would be carbon dioxide, water, some small amount of ash, (to account for the inorganic components of wood) and heat. This is the type of burning we strive for in wood stoves.

TOC
◀ ▶

Once burning begins, though, it is possible to restrict the air to the fuel and still have the combustion process continue. Lack of sufficient oxygen caused by restricted combustion air will cause partial combustion. In full combustion of a hydrocarbon (wood is basically a hydrocarbon) oxygen will combine with the carbon in the ratio of two atoms to each carbon atom. It combines with the hydrogen in the ratio of two atoms of hydrogen to one of oxygen. This produces CO_2 (carbon dioxide) and H_2O (water). Restrict the air to combustion and the heat will still allow combustion to continue, but imperfectly. In this restricted combustion, one atom of oxygen will combine with one atom of carbon, while the hydrogen will sometimes combine with oxygen and sometimes not combine with anything. This produces carbon monoxide, (CO) (the same gas as car exhaust and for the same reason) water (H_2O), and hydrogen gas (H). It will also produce a lot of other compounds and elements such as carbon, (C) which is smoke.

Combustion of wood is a bootstrap process. The heat from combustion breaks down the chemical bonds between the complex hydrocarbons found in wood (or any other hydrocarbon fuel) while the combination of the resultant carbon and hydrogen with oxygen - combustion - produces the heat. Thus the process drives itself. If the air is restricted to combustion, the process will still produce enough heat to break down the the wood, but the products of this inhibited combustion will be carbon monoxide and hydrogen, fuel gases which have the potential to continue the combustion reaction and release heat since they are not completely burned yet. (The other products of incomplete combustion, predominately carbon dioxide and water, are products of complete combustion and can be carried no further.) Thus it is a simple technological step to produce a gaseous fuel from solid wood. Where wood is bulky to handle, a fuel like wood gas (producer gas) is convenient and can be burned in various existing devices, not the least of which is the internal combustion engine. A properly designed burner combining wood and air is one relatively safe way of doing this.

Crude Wood Gas Generator

Another path to a similar result is to heat wood in a closed container until it is hot enough for the chemical bonds holding the hydrogen and carbon together to break. This is destructive distillation, a quite different process from that of combustion since no outside oxygen is introduced. You might think that such a device would produce only hydrogen gas and carbon. But that is only because I have kept this explanation oversimplified for clarity. The products of this process will depend on the make up of the wood and the temperature it is heated to. All wood contains some water and this can be anywhere from about 7% to 50% or higher, so this water is available to play a part in the destructive distillation process. Wood also contains many other wild and wonderful chemicals, from alkaloid poisons to minerals. These also become part of the process. They can be assets or great liabilities.

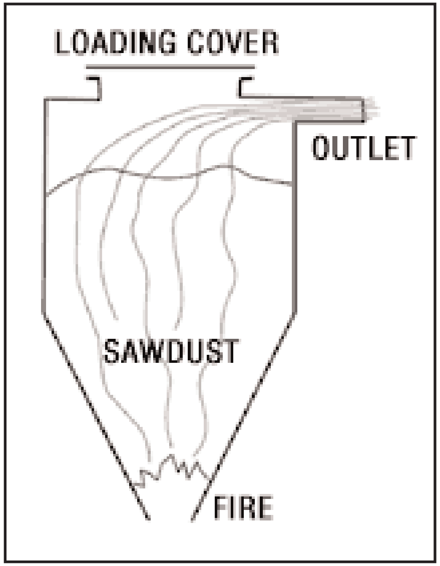
As a general concept, destructive distillation of wood will produce methane gas, methyl gas, hydrogen, carbon dioxide, carbon monoxide, wood alcohol, carbon, water, and a lot of other things in small quantities. Methane gas might make up as much as 75% of such a mixture.

Methane is a simple hydrocarbon gas which occurs in natural gas and can also be obtained from anaerobic bacterial decomposition as "bio-gas" or "swamp gas". It has high heat value and is simple to handle.

Methyl gas is very closely related to methyl alcohol (wood alcohol) and can be burned directly or converted into methyl alcohol (methanol), a high quality liquid fuel suitable for use in internal combustion engines with very small modification.

It's obvious that both of these routes to the production of wood gas, by incomplete combustion or by destructive distillation, will produce an easily handled fuel that can be used as a direct replacement for fossil fuel gases (natural gas or liquified petroleum gases such as propane or butane). It can be handled by the same devices that regulate natural gas and it will work in burners or as a fuel for internal combustion engines with some very important cautions.

Producer Gas Generators



Crude wood gas generator

How do you achieve this? Let's start with the combustion process hardware first: The simplest device I know of is a tank shaped like an inverted cone (a funnel). A hole at the top which can be sealed allows the user to load sawdust into the tank. There is an outlet at the top to draw the wood gas off. At the bottom the point of the "funnel" is opened and this is where the burning takes place. Once loaded (the natural pack of the sawdust will keep it from falling out the bottom) the sawdust is lit from the bottom using a device such as a propane torch. The sawdust smolders away. The combustion is maintained by a source of vacuum applied to the outlet at the top, such as a squirrel cage blower or an internal combustion engine. Smoke is drawn up through the porous sawdust, being partly filtered in the process, and exits the burner at the top where it goes on to be further conditioned and filtered. The vacuum also draws air in to support the fire. This burner is crude and uncontrollable, especially as combustion nears the top of the sawdust pile. This can happen rapidly since there is no control to assure that the sawdust burns evenly.

"Leads" of fire can form in the sawdust reaching toward the top surface. Once the fire breaks through the top of the sawdust, the vacuum applied to the burner will pull large amounts of air in supporting full combustion and leaning out the value of the producer gas as a fuel. This process depends on the poor porosity of the sawdust to control the combustion air, so chunk wood cannot be used since its much greater porosity would allow too much air in, and you would achieve full combustion at very high temperatures rather than the smouldering and the the partial combustion you want. Such a burner is unsatisfactory for prolonged gas generation but it is cheap to build and it will work with a lot of fiddling.

For prolonged trouble-free operation of a wood gas generator, the burner unit must have more complete control of the combustion air and the fuel feed. There are various ways to do this. For example, if the point of our original funnel shaped burner is completely enclosed, then control over the air entering the burner can be achieved. This configuration will successfully burn much larger pieces of wood. One of the most widely known burners was developed by *Mother Earth News* magazine. They produced a complete set of plans for their burner and featured its construction and evaluation in several issues of their magazine. At the end of this article I have listed sources of information and/or hardware for several of the concepts I have written about.

Destructive Distillation Units

If the type of wood gas you would like to produce is to be obtained by destructive distillation then all you need is a canister about the size of a 55 gallon drum that can be loaded with wood and sealed air tight. It must also have an outlet pipe and a source of heat which can be applied to it from the outside. A simple way to do this would be to just build a wood bonfire under the canister. While this has the advantage of being "quick and dirty," it is the equivalent of the simple sawdust burner I described above. It allows little control and requires a lot of time and fussing to make anything work.

The use of a fossil fuel to heat the wood gives good control over the temperature of distillation but defeats the purpose of producing a fuel from wood. An ideal solution to this control problem is to use a combustion type wood gas generator to produce fuel gas, which is then burned to achieve destructive distillation, which produces a higher heat content fuel; a fuel that can then be liquified into methanol.

It is also desirable to mount the canister in such a way that it can be rotated while it is being heated so that the contents inside are evenly "cooked".

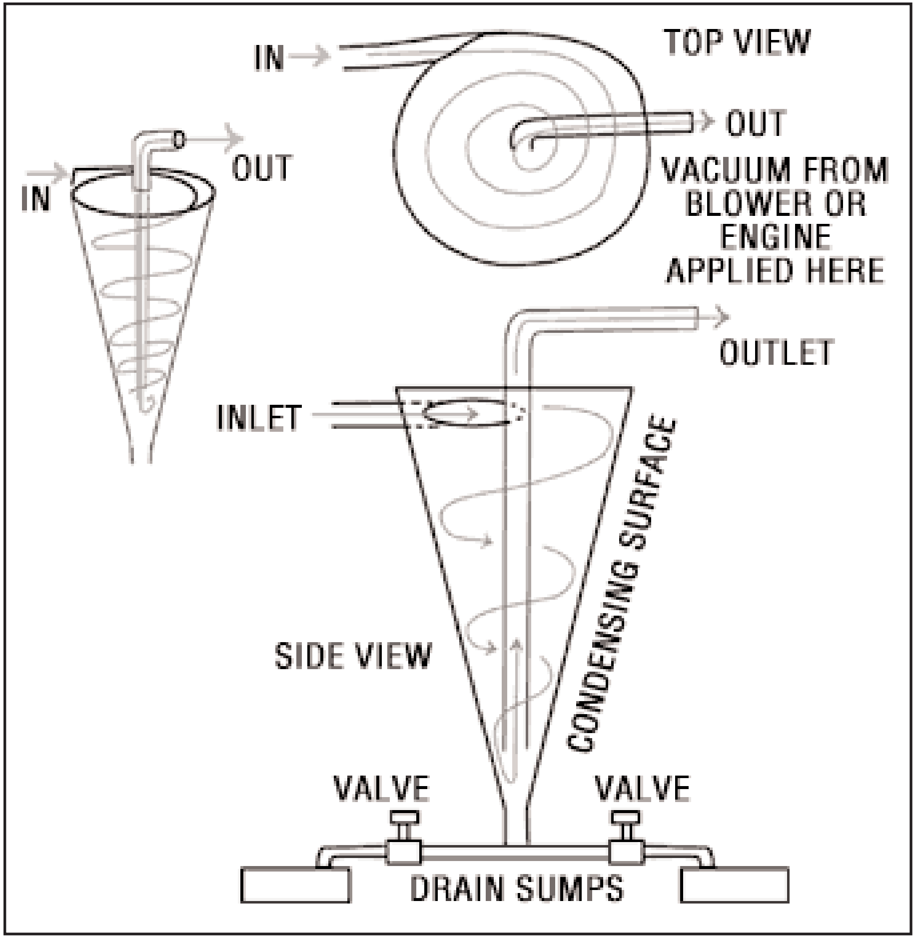
Conditioning And Filtration

However you produce the wood gas, you are certainly not home free when your fuel exits your burner. Far from being the nice clean chemical reactions

I've used for simplicity, the fuel gas you will actually produce will contain ash, gum, heat, water, creosote, acids, and a lot of other weird things which will render any device you try to burn the fuel in dead on arrival. The fuel must be conditioned and filtered before it can be used.

Probably the best first step to achieve gas conditioning is a cyclone separator to get rid of water and particulate matter. This device is, again, an inverted cone, but the bottom is sealed. After the contaminated fuel gas leaves the burner unit, it enters the top on a tangent to the circumference of the side. The exit for the fuel is a pipe which runs up the center of this cone from just above the point at the bottom. Gas coming into the cyclone separator enters with some velocity. Because it has weight, and therefore inertia, it tries to continue in a straight line, even though the sides of the cone are curved. To exit the cone, the gas would have to turn 90° toward the bottom and then 180° up the exit pipe, if it could take the shortest path. However, under the influence of its own inertia, the dirty fuel gas is held against the curved outside wall of the cone, where it takes a circular path toward the bottom and the exit pipe. It circles around and around this wall, all the time moving in tighter and tighter circles toward the point on the bottom, thus speeding up its velocity as the circles get smaller nearer the point. The fuel gas is spinning quite fast near the exit pipe. This rotary gas flow is where the separator gets its name.

Within this stream of rapidly spinning gas, the ash and water vapor, weighing more than the fuel gas, are thrown outward against the walls of the separator by centrifugal force. When the heavier components in the fuel gas come into contact with the relatively cool sides of the separator, the water condenses, wetting the inside of the separator down and flowing downward to a drain at the bottom. Ash and particulate matter are also thrown out against the now wet walls where they get washed out of the gas



Cyclone Separator

TOC

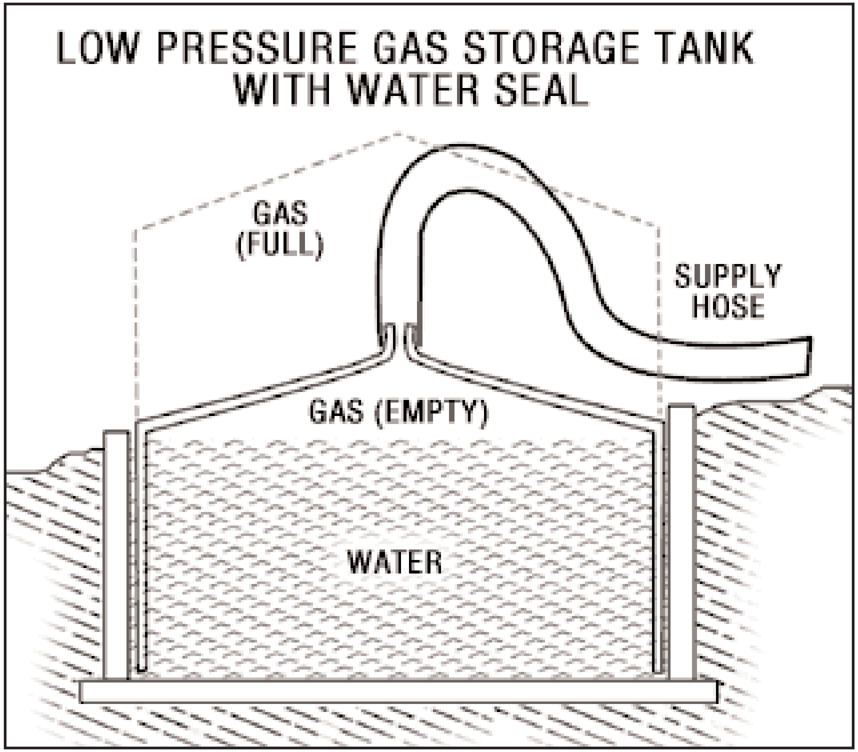
stream by the condensing liquid. All of this gunk winds up running out the bottom of the separator and into a holding tank, which can be drained at intervals.

To help the water condense out of the gas stream, the walls of the cyclone separator may be cooled by water or an air stream to raise the efficiency of the condensation and scrubbing process.

Upon its exit from the cyclone separator, the fuel gas will have to be cooled further. A simple way to do this is to place a vehicle radiator into the gas flow and draw the fuel gas through this. In a perfect world there wouldn't be any water left in the fuel gas after it left the cyclone separator. Unfortunately, there is apt to be quite a bit of uncondensed water vapor still left in the hot fuel gas as it enters the gas cooler. As the gas cools, the water vapor will condense out further. It may be necessary to use multiple stages to completely cool the fuel gas. That is, you may have to use more than one radiator, with the outlet of one connected to the inlet of the next, and so on. Cooling air can be blown through each radiator by an electric cooling fan and each radiator will need a sealed drain canister to carry off condensed liquid.

Once the cool dry fuel gas leaves the cooler, it is ready for the last stage of conditioning. It must be well filtered to keep fine ash and particulate matter from being carried into the engine or burner which the gas will be used in.

TOC
◀ ▶



An alternative to immediate use of fuel gas is storage. The gas can be stored at low pressures - 3 to 5 psi - in a simple tank of the type developed to store biogas from methane/solid waste digester. This is an open tank placed upside down in water. When empty, the tank sinks in the water, but as gas is forced in, the tank rises out of the water. The weight of the tank can be augmented or counterbalanced to control the pressure of the gas inside. Fuel gas is pulled from the gas generator by a simple centrifugal blower, which forces it through the conditioning stages and into the storage tank under pressure. It is desirable (but not necessary) to have a storage tank, even if the gas is to be immediately used as fuel.

Such a reservoir maintains a buffer supply of gas to even out any fluctuations in supply and provides an even, controllable supply of pressure to the end device. It also acts as a cooler and a sink for any impurities which remain in the fuel gas after conditioning. Such a storage tank could pay for itself by saving money on conditioning the fuel gas, since contaminants will cool, condense, and settle out in the storage tank and water seal. Two tanks, used alternately, may reduce the need to condition the gas, requiring only the use of the cyclone separator. In this arrangement, one tank can be filled and cooling off while the user device is run from the second tank.

If your choice is to produce methane and methyl gas rather than producer gas, then the conditioning process will not be so demanding. You will not have a lot of ash and carbon to deal with. The products of destructive distillation will exit the generator canister under their own pressure. If a blower is used to fill a gas storage tank, it should be placed after the gas cooling stages are held at a partial vacuum as condensation occurs, this will improve their efficiency. The final particulate filter can be eliminated, especially if gas storage tanks are utilized.

If your goal is to produce methyl alcohol (methanol) then you will have to catalyze the methyl gas and methane into liquid alcohol. In addition, you will not want to use a cyclone separator, since the condensed liquid contains the methanol you are seeking. Gas coming from the generator canister will pass through a catalyzer unit. The alcohol vapor produced by catalyzation is then routed to the gas cooling stages which condense it to liquid methanol. In this case the drains from the cooler carry off the raw methanol distillate rather than waste condensate. This raw methanol will undoubtably require further distillation to purify it and extract excess water.

Catalyzing the methane and methyl gas can be accomplished crudely but simply. The gas which comes out of the generator canister is routed through a copper pipe with a copper "Chore Girl" pot scrubber inserted in it. A one inch copper pipe about twenty feet long attached directly to the generator outlet and having the "Chore Girl" inserted into it loosely should do the job. The inlet of the pipe should be above the outlet so that any methanol condensing in the catalyzer can drain out. Insulating the catalyzer to keep the temperature up will help greatly. Soft copper pipe formed into a large coil makes a relatively compact catalyzer. The outlet from the catalyzer is attached to the cooling (condenser) stages.

I've suggested a copper catalyst (the Chore Girl) because of its availability and cost, but it is not the most efficient catalyst. It may well be that a platinum catalyst would be much more efficient, but a custom built platinum catalyst would be very expensive. With the common availability of platinum based automotive catalytic converters, use of one of these converters may be a better alternative than what I have described. I have no hands-on knowledge of that though.

Hydrogen Fuel

Another alternative to steam is the use of on-site generated hydrogen as a fuel for an internal combustion engine. Hydrogen makes a very high quality fuel because it burns so cleanly. The only product of idealized hydrogen combustion is water and heat. The use of hydrogen as a motor fuel is very much in the experimental stage right now. Commercial supply of hydrogen just is not commonly available in quantity. Neither is there a convenient technology for storing it in any quantity. Technologies such as metal hydride storage and liquid hydrogen are beyond the scope of this article and beyond the scope of most users. On-site generation of hydrogen is a viable alternative, however.

In the past small scale "home" generation of hydrogen gas was commonly done by electrolysis of water. If a tank is fabricated in a "U" shape with a cathode in one leg and an anode in the other, a current can be passed through the water. The electrical energy will disassociate the atoms of hydrogen and oxygen in the water, with each component gas collecting in a different leg of the tank where they can be drawn off in pure form. Using the right combination of pressure, voltage, and current, this can be done fairly efficiently. The electrical supply can be from an alternative energy source.

TOC
◀ ▶

Recently, however, there has been work done on a gas generator which can produce large quantities of hydrogen simply and efficiently using a device similar to a wire feed (MIG) welder. (See “Hydrogen Fuel Breakthrough With On-demand Gas Generator,” *Automotive Engineering*, August 1985, Volume 93, Number 8, Page 81) An aluminum wire charged with electricity is fed under water to a rotating drum. The arc from the electrical contact causes the aluminum in the wire to combine with the oxygen in the water. The reaction produces hydrogen and oxygen gas and a slurry of aluminum oxide, which settles to the bottom of the tank. This generator is small, portable, and low tech, and can easily be incorporated into a vehicle.

This technology is very promising since either in a vehicle or in a stationary unit, the gas generator can be run by a battery which is charged by alternative energy methods. It is obvious that it can also be charged by the device it supplies, such as an engine/generator unit or a hydrogen fuel cell. This technology also provides a viable alternative to an all-electric vehicle since it takes much less stored battery energy to produce the hydrogen fuel from water than it would to actually power the vehicle entirely with battery storage. This has great potential but I have no hands-on experience with it as yet.

TOC

Safety

It's important to cover some of the safety considerations of fuel gas, alcohol, and hydrogen gas:

Unlike steam power, there is no storage of massive amounts of latent energy in a wood gas generator of either type. Producer gas generators run under a modest vacuum, while destructive distillation proceeds under relatively low pressure. Obviously, all the gases are flammable, and the usual precautions taken with more common gaseous fuels, such as natural gas and liquid petroleum gases, should be observed. In addition there are considerations specific to these home brewed fuels.

Hydrogen, either by itself or as a component of wood gas fuels, has the smallest and lightest molecule of any element. Consequently, it will pass through holes and pores that would be too small for any other gas. Thus, hydrogen is very prone to leak, either from poor connections, or right through the pores of material used for tanks, hoses and caulking. On the other hand, the "Hindenburg Syndrome" not withstanding, there is actually less danger from leaking hydrogen exploding, because it is so light it rises and dissipates readily in the air.

Carbon monoxide is a large component of producer gas and it is deadly. It's not sufficient for anyone overcome by carbon monoxide to just reach fresh air because the monoxide combines with the hemoglobin in blood to render it permanently inert. Blood so affected can no longer carry oxygen to the body and brain. Thus extensive emergency measures must be taken to treat a victim of carbon monoxide poisoning. This means that producer gas generated by a burner is **not at all** suitable for use in stoves, water heaters, gas refrigerators, or any enclosed area where concentrations of the gas might collect if a flame went out. This gas must only be used in **very** well ventilated areas, preferably outside or under a roof with no walls.

Methanol (wood alcohol) is also quite deadly, including the fumes which might be breathed. Methyl alcohol interferes with the function of the nervous system, and will cause blindness and death in small quantities if consumed. The process which produces either a gaseous product from destructive distillation, or which is the first step toward production of wood alcohol, can contain methanol as a hot vapor. Therefore, it is not actually necessary to consume wood alcohol to be poisoned by it. Breathing methanol vapor from a poorly sealed generator system will have the same deadly effects.

Power Producing Hardware

Before I discuss the hardware to produce power from wood gas I would like to warn you that I will not be writing about some of the newest and most promising techniques for the simple reason I am not qualified. Things like

TOC
◀ ▶

fuel cells, Stirling engines, and hydrogen fuel will be ignored. My original work with wood gas grew from trying to use wood as a cheap, renewable, locally available fuel. It evolved through steam technology - which I found too inherently dangerous - to wood gas, and into methanol as a fuel. My purpose for writing this now is to discourage people from fiddling with steam power because of the tremendous damage that the energy stored in latent heat can do in an equipment failure. So I will concentrate on machinery which can be readily used to turn wood into power.

As I've already mentioned, the fuel gases you can generate from wood can be used as any other gaseous fuel; either burned in an external combustion burner, or used as fuel for an internal combustion engine.

Two further considerations are whether the fuel will be used directly as it is produced from the generato,r or whether the gas will be stored and then used.

First, let's briefly discuss the use of fuel gas in an external burner: if you intend to use fuel gas for this purpose, I wish to repeat my warning about the deadly nature of producer gas due to its carbon monoxide content. Producer gas is totally unsuitable for domestic indoor gas use. However, gas produced through destructive distillation is useful for this purpose. Since it is methane, it is similar to natural gas, but unlike natural gas it does not have fractions of the heavier petroleum gases such as propane and butane to fortify the heat content. Fuel gas obtained from destructive distillation is a relatively low heat content fuel and therefore requires larger quantities to do the same job. The significance of this is that a burner will have to be designed to flow larger quantities of gas. In some cases you may find regular stove top and oven burners that will work satisfactory since these are usually highly adjustable so that they can burn either dense LP gas or lighter natural gas. The range of this adjustment may include that necessary for wood gas. Since wood gas is close to biogas in nature, the user will find useful information on burners in the biogas literature, which is more readily available publicly than that on wood gas.

Gas from destructive distillation will burn very clean, so clean in fact you may not realize it is burning. In daylight the flame will be almost invisible under the right conditions. The user is cautioned to consider this as a safety hazard in experimentation.

The Internal Combustion Engine

The most valuable use of wood gas is probably as a fuel for the internal combustion engine, and here both types of wood gas will work well. The technique for using gas directly from a generator is considerably different from what's required to use fuel from a storage tank. This is a special case of the general information.

On the plus side, wood gas burns cleanly in a regular internal combustion engine and as a fuel it has a high "octane" rating or resistance to preignition inside the cylinder. On the minus side, it is lower in heat value than other fuels.

The significance of this is that wood gas can be burned in Briggs and Stratton engines, Wisconsin engines, Ford and Chevy engines and even diesel engines. The high "octane" rating may only have significance to the dedicated wood gas user, so I will come back to that after covering the disadvantages of the lower caloric value of the fuel.

An internal combustion engine is basically an air pump. The physical dimensions of the inside of the engine limit the maximum amount of air that can move through it. There is no such limitation to the amount of fuel that can be added to the air. So the trick to getting more power out of an engine is to get it to pump more air. However the air and fuel must burn to produce any power and this will only happen within a narrow range of air and fuel mixture ratios (by weight). With a gasoline engine the air/fuel ratio is about 14.5 to 1, air to fuel. Reduce the quantity of fuel, and ignition of the mixture in the cylinder will soon stop. If you increase the fuel beyond the ideal air/fuel ratio, all of the air in the cylinder will burn before all of the fuel can burn. This will waste fuel. Thus an internal combustion engine is limited in output by the amount of air it can "swallow" and this also limits the amount of fuel that can be taken in.

TOC

When burning wood gas there is also an ideal ratio of air to fuel, but the limiting factor is still the amount of air the engine can pump. You have a fuel that is lower in heat value than other fuels and cannot produce as much power per pound. The net result is that an engine running on wood gas produces less power at the same speed (pumping the same amount of air). It is a loss of about 20%. The engine will only produce about 80% of the power it would if run on gasoline. As an example, if we were burning wood gas in a 3.5 horse power engine, we could only count on getting 2.8 horse power out of that engine. You would need an engine capable of developing 4.2 horse power on gasoline to give you the same 3.5 horse power output. For practical purposes it’s an easy matter to use a 5 horse power engine instead of a 3.5 horse power engine, but the necessity for this must be kept in mind.

Another "drawback" of wood gas is its lack of lead. I consider this an asset, but some older engines won't. The advantage of fuel gas is that it’s a relatively safe low-tech fuel that can be fed to any old cheap chunk of junk yard iron to develop power. But this older iron was developed with soft valves that depended on tetra-ethel lead to lubricate them. Use with fuel gas will likely cause these valves to burn and the engine will lose compression. The solution here is to try to find an engine designed for low-lead gasoline, or for natural or LP gas fuels. These engines will have hardened valves and seats.

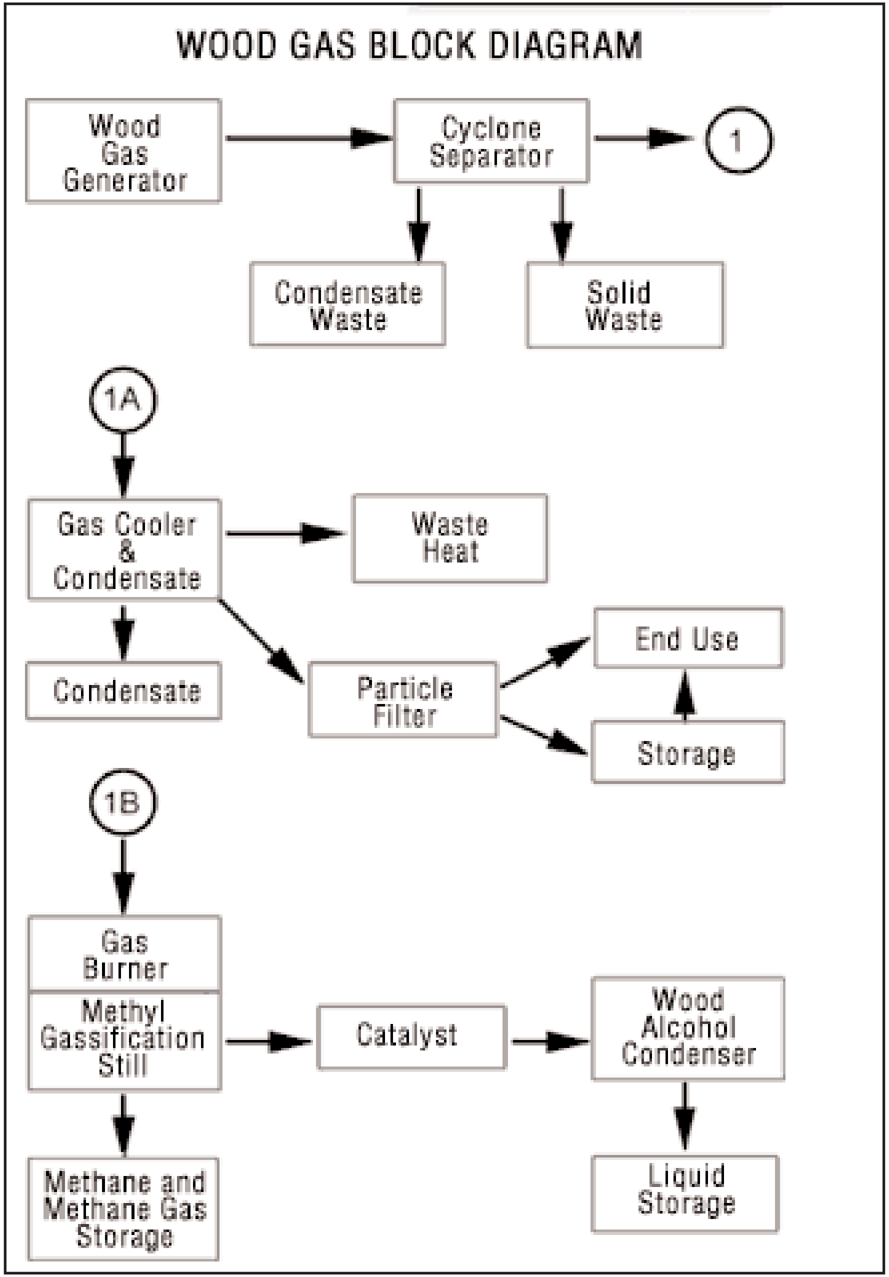
TOC
◀ ▶

Wherever possible, the wood gas user is advised to use already existing controls to adapt an engine to wood gas use. Gas supplied at pressures of up to 5 psi is close to the pressures used to distribute natural gas. Where it's available, natural gas has been in use for many years running industrial and irrigation engines. Controls for supply and mixture of natural gas are readily available, and can be adapted with very little trouble. This presupposes that the fuel gas is held in a tank and supplied to the engine at a constant density and pressure. In the case where producer gas is consumed directly from the gas generator, the pressure and density are controlled by the engine itself through engine vacuum. Typically, in a direct installation, gas flow from the burner to the intake manifold is sustained by the running engine. Engine manifold vacuum pulls the "smoke" through the burner and draws combustion air in; it draws circulating fuel gas through the cyclone separator, through the gas cooling stages, and through the final filter into the engine. Because of this, the engine must be developing vacuum (pumping air) before the gas generator can work. But the engine must have fuel before it can be run to produce a vacuum. The solution to this "chicken or egg" quandary can be solved several ways.

An electric powered blower can be installed in the induction tubing just after the burner outlet. This will provide vacuum to start the burner and will feed fuel gas to the engine so that it can be started and run. The disadvantages are that the blower will be subject to the high heat and unconditioned

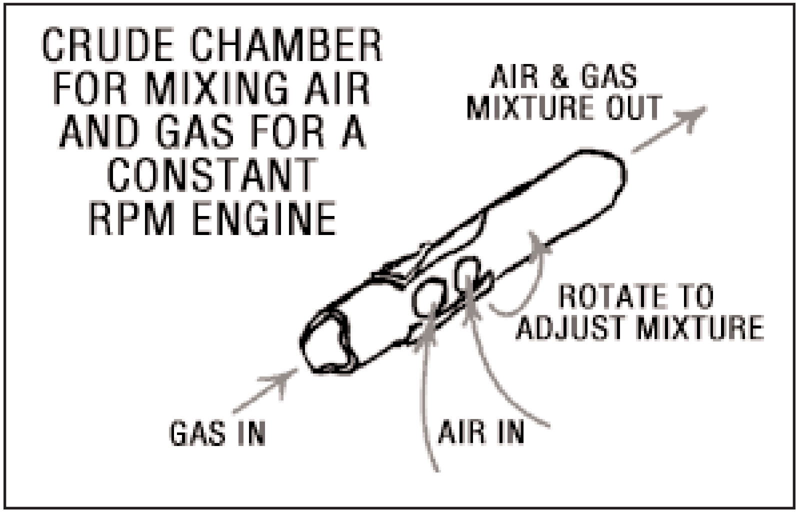
TOC
◀ ▶

gas leaving the generator. This will destroy the blower. Moving the blower downstream to the other side of the gas cooler might seem to be the solution here, but you will find that the low vacuum which a standard squirrel cage blower can generate is not going to be enough to efficiently draw fuel gas through the obstructions of the cyclone separator and the gas cooling stages. Use of a high speed, high efficiency centrifugal blower of the type used on a blacksmith's forge will partly overcome these restrictions. This is the type of blower you will



need if you want to fill a storage tank. Of course, the user can try and get the fuel in the gas generator burning and then just crank the engine over with the starter until the draw from it pulls enough fuel gas in to start it. You will find that this takes quite a while, though. It will require a large battery capacity and will result in the eventual destruction of the electrical starter through overheating.

Another method, used successfully by Mother Earth News in their work, requires starting the engine on gasoline and then switching over to fuel gas on the fly. One way that this can be done is by piping the fuel gas into the top of the carburetor on the running engine. Gasoline is shut off to the carburetor and fuel gas, mixed with air, takes over running the engine. This sounds easy, but getting the transition to occur smoothly between fuels (to occur at all) is very difficult. The Mother Earth method of accomplishing this was to place a "T" in the induction system. The carburetor was mounted on one side of the "T" and fuel gas was piped to the other. A flapper valve was placed at the junction of the "T" so it could select one fuel system or the other. This method works smoothly, but requires a throttle body in the fuel gas system in addition to the one in the carburation system. The single advantage to piping the wood gas into the top of an already existing carburetor is that speed regulation of the engine is done with the existing hardware of the carburetor itself, thus it could be used with an existing machine



(generator, pump, tractor, etc.) without modification. All of these starting methods have specific drawbacks.

The Pony Engine

The method I have finally adopted to get around these disadvantages is to use a small gasoline engine which can be connected and disconnected to the main engine with a clutch. The drawback here is that it is not a compact method and is more useful with a stationary engine where space and weight are unimportant. Using this method the small engine can be started and used to bring the main engine up to speed with the ignition shut off. This has the advantage of prelubing the engine with oil before a load is applied and the main engine can be motored over for as long as it takes to light the burner, draw in fuel gas, and allow the temperature and density of the fuel to stabilize. A flick of the ignition switch will then start the main engine and the "pony" engine is disengaged.

I used a gasoline engine as a "pony" engine because I was experimenting with a 350 cubic inch Chevy V8. If the engine is small enough, it could be motored over using an AC or DC motor and either power line or battery current.

The pony engine method of starting works well with a stationary engine or where space or weight are not a problem. Where these are considerations, the dual fuel approach is worth the effort. A diesel engine can also be run off wood gas with almost no modification. In this case, the engine will be started and run up on diesel fuel. The fuel gas supply will require the usual air mixer and a throttle body before entering the induction of the engine. If constant speed is your goal, you will will also have to add an external governor to control the fuel gas throttle body. Once started and switched over to wood gas, the diesel throttle is set at idle and the small amount of fuel injected is used to ignite the air/fuel gas mixture in the cylinders. Speed is controlled by the fuel gas throttle body.

I mentioned earlier that wood gas had a high resistance to "knock" or a high "octane" rating. This has some interesting ramifications for someone who is not content to put up with a reduction of power while burning wood gas. Modern gasolines will tolerate a compression ratio of around 9 to 1 before the engine starts to knock and self destruct. Wood gas and alcohol will tolerate compression ratios up to 13 to 1 before this happens. So, it

TOC ◀ ▶

would be relatively easy to build an engine based on a high output modern design, using racing parts, which would recapture all of the lost horse power that wood gas costs through higher efficiencies. The efficiency figure of 28% for a gasoline I gave earlier is not immutable. A crude gasoline engine might only get 20% efficiency while some all out racing engines would get as high as 50%. The typical modern engine with overhead cam, fuel injection, and electronic ignition and control systems will get in the neighborhood of 32%. If your philosophy of power production justifies the expenditure, this may be a productive path.

Methyl alcohol is the last fuel I will discuss. Racing engines have been run on alcohol for a long time. The now obsolete Indianapolis 500 engine known as the Meyers Drake "Offy" was a four cylinder engine of about 155 cubic inches which routinely produced 750 horse power on alcohol. An engine burning alcohol fuel has a very high knock resistance and so can use the highest compression ratios to improve efficiency. On the other hand, methanol requires a lot of heat to evaporate it into a vapor, which makes an engine very hard to start. In addition, methanol has much less heat content than gasoline, so it requires much more fuel to do the same work. This means custom jetting carburetors for alcohol - beyond the range which their manufacturers designed them for. On top of that, alcohol is very corrosive and will damage metals, gaskets, fiber parts in carburetors, and hoses not

TOC
◀ ▶

specifically designed to handle it. It is also one of the cleanest burning fuels available. It is quite possible to have a roaring alcohol fire and not even be able to see the flames in the daylight. So, methanol is a mixed bag. It's available in quantity, but you will need a lot of fairly sophisticated mechanical knowledge to make use of it reliably; more than this article can cover.

The most direct applications for wood gas are straight-forward. For example, running a small gas powered generator to charge your battery bank. But consider some other ideas:

A removable flexible hose carrying wood gas to the intake of your farm tractor so that PTO-driven implements like saw mill, chippers, composting hammer mills, and large electric generators could be driven on wood gas without any change in the farm tractor.

A large 350 cubic inch V8 engine running at 1900 to 2000 rpm could be used to directly drive a large three phase motor. The imposed 60 hertz line frequency would make this overdriven motor act like a synchronous generator, feeding electricity back into the grid and earning income as a small power station.

Installation of a large V8 engine and truck transmission in a bulldozer chassis, along with the wood gas generator and filters. By running in low gear this engine will directly replace the slow speed diesel which normally powers such a machine. I have already built this machine and it is practical.

And of course, as Mother Earth News proved, a wood gas generator can be used to power a car or truck. In fact a lot of Europe ran on wood gas during World War II fuel shortages. With modest mechanical skills, this is a technology you can use now, and it's far safer than steam.

Access

Author: Clifford W. Mossberg, POB 75273, Fairbanks, AK 99707

Plans for wood gas burner units:

The Mother Earth News Plans, POB 70, Hendersonville, NC 28793,
Wood Gas Generator, Plan #84030

Parts, hardware, and complete burner units:

Cloidal Cam Engineering Inc., POB 244, Prior Lake, MN 55377
ESMCO, 5555 Boon Ave. N., Minneapolis, MN 55428

Hydrogen Fuel Cells - power source of the '90s

by Dr. Robert Wills

Originally published in Home Power #23 • June / July 1991

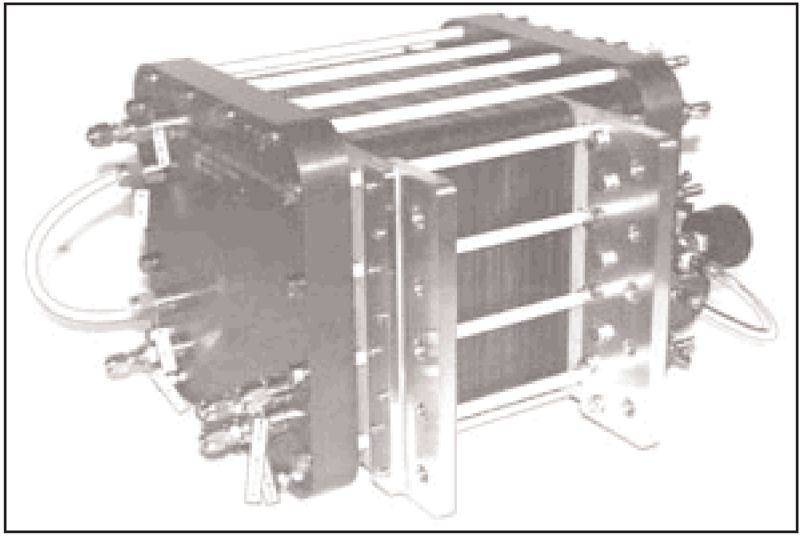
Imagine a car that can travel 300 miles without refueling, that performs as well as the gasoline cars of today, that uses one-half as much energy per mile, eliminates our dependence on fossil fuel and produces only water as a byproduct. Hydrogen fuel cells may make such vehicles a reality before the end of the decade. They could even cost less to run than gasoline cars.

What is a fuel cell

Practical fuel cells were first developed in the 1960s for the U.S. space program. A fuel cell is a device that converts a chemical fuel (generally pure hydrogen) directly into electricity. A fuel cell is like a battery that never runs down. The chemicals that are consumed (hydrogen & oxygen) are continually fed into the cell, rather than being a component that is used up.

Fuel cells may also be thought of as "reverse electrolysers". When two electrodes are put into a salty water solution and a current is passed, water is broken down into hydrogen and oxygen. This process is called electrolysis. Fuel cells perform the reverse action - they combine hydrogen & oxygen to form electricity and water.

Fuel Cell Vehicles



This 1.7 kW prototype PEM fuel stack made by Ballard Power Systems is 20" long and weighs 81 pounds.

Battery electric vehicles can solve some of our transportation problems, but they have three major flaws, all related to energy storage: batteries are expensive, heavy, and even the best offer only limited vehicle range. In the short term, hybrid battery electric vehicles with small internal combustion engine "range extenders" will be used to provide the vehicle range and performance that we are used to. By the year 2000, developments in fuel cell technology promise a cleaner, more efficient alternative to the internal combustion engine, & a new age of pollution-free driving.

The Key: Efficiency

Internal combustion engines are limited by the laws of thermodynamics to a maximum efficiency (the mechanical work output divided by the chemical energy in) of about 30%. Practical engines are closer to 20% efficient, and when stop-start driving is considered, efficiency drops to about 15%. Fuel cells are not limited by the thermodynamic Carnot cycle, and can convert fuel to electricity at up to 80% efficiency. Efficiencies of more than 50% have been demonstrated to date. This means that you can go three times as far in a fuel cell car as in a gasoline car, on the same amount of fuel.

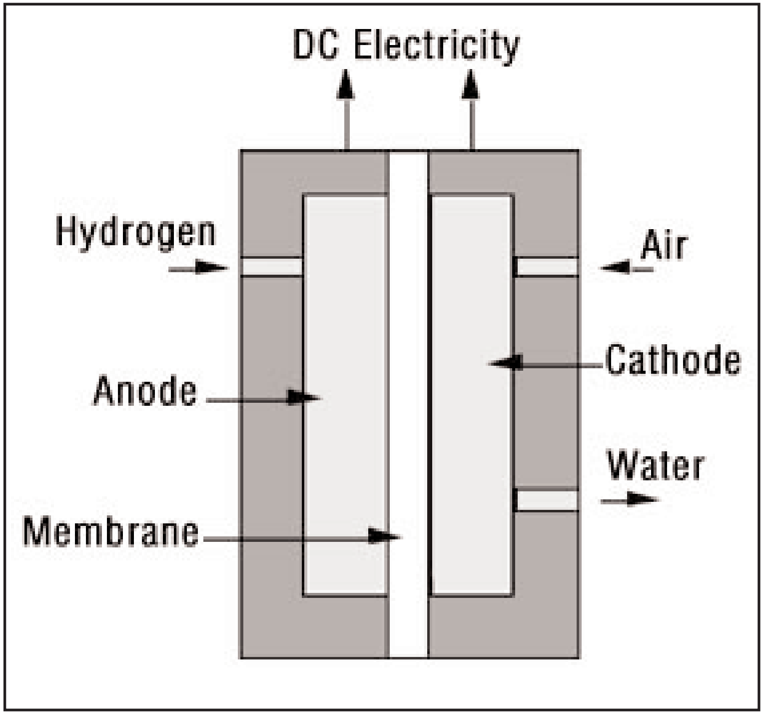


**Diagram of PEM cell:
The Proton Exchange Membrane Fuel Cell has platinum impregnated electrodes either side of a plastic film electrolyte.**

Fuel Options

There are two ways of storing the hydrogen needed to run a fuel cell car. Either pure hydrogen can be stored in gas, liquid, or "metal hydride" form, or hydrogen can be generated onboard from hydrocarbon fuels such as compressed natural gas or methanol.

TOC

The "reforming" of methanol or other hydrocarbons to produce hydrogen and carbon dioxide has the advantage of easy fuel storage but the disadvantages of needing a small, onboard chemical processing plant, and still polluting the atmosphere with carbon dioxide.

Storage of pure hydrogen in cryogenic liquid or high pressure gaseous forms poses safety hazards that are unacceptable for general transportation. Storage in metal hydrides, where hydrogen atoms lodge in the atomic lattice of metals such as magnesium and titanium, offers safety and ease of use, but carries the penalty of high costs and much added weight (only 2-5% of the weight of the storage system is actually hydrogen).

When the system is looked at as a whole, however, this extra weight is compensated by the reduced weight of the drive system (the fuel cell, electric motor and motor controller) when compared to a gasoline engine and transmission, and reduced fuel requirements. Fuel cells capable of 10 kW continuous output and electric motors rated at up to 100 HP should be available at weights of less than 50 lbs apiece.

The safety of hydrogen as a fuel is often questioned. In fact, hydrogen is in many ways far safer than gasoline - it is non-toxic and disperses quickly. So little gaseous hydrogen is available in a hydride storage system (and heat is needed to liberate gas from the metal matrix) that such systems are inherently far safer than gasoline storage in today's cars.

A Hydrogen Economy

A hydrogen powered car needs a means to refuel. This could take the form of hydrogen refilling stations where hydrogen is piped or trucked from central generating sites. These "gas" stations will be worthy of their name. Hydrogen is produced in large quantities today from natural gas via a reforming process. This is the cheapest source at present. In future, we can look forward to large scale photovoltaic/electrolysis power stations in the southern U.S.A. producing hydrogen for the whole country. Pipelines, including the existing natural gas network, could be used for distribution.

Hydrogen can also be produced from water and electricity via electrolysis. This could be done actually at the "gas" stations, or alternately, small electrolysers could be installed in cars, or in home garages, to provide a means of refueling from grid electric power. In the short term, home or onboard electrolysers are the only alternative, despite higher fuel costs, as a network of hydrogen gas stations will take some time to evolve.

Economics

Dr. John Appleby of Texas A&M University's Center for Electrochemical Systems & Hydrogen Research has calculated that a fuel cell car powered by hydrogen made from natural gas could cost as little as 1.5¢ per mile in fuel cost, compared to 4.4¢ per mile for gasoline. A fuel cell car could cost one third as much to run as the car of today! Maintenance costs would be minimal with no engine oil changes, no spark plugs, no exhaust system, and with the regenerative braking reducing the mechanical brake wear. The fuel cell life could be as long as 100,000 hours. Appleby puts the cost of electrolytic hydrogen fueling at 5.6¢ per mile, and straight battery electric vehicles at 3.5¢ per mile plus 2 - 5¢ per mile in battery replacement costs.

The benefits of zero-pollution vehicles, such as the fuel cell car, should also be included in economic comparisons. Estimates of the social and health costs of burning gasoline in our cities range from $1.15 up to $4.50 per gallon of fuel.

Another researcher at Texas A&M, Dr. David Swan, has predicted that fuel cell system costs can drop to $272 per kW with mass production. He estimates a complete 75 kW peak, 25 kW continuous fuel cell/battery hybrid drive system would cost $8,550, about $1000 more than a conventional gasoline drive. Other estimates are as low as $4,450 for a complete drive system.

TOC

How long to Market?

While government and car manufacturers' predictions of fuel cell cars range from 2005 to 2050, recent advances have made practical cars possible within a few years. Many small companies are working on fuel cells for vehicles. Ballard Power Systems in Vancouver, B.C. plans to have a fuel cell powered bus on the road by 1992 and are also working with General Motors on automobile applications. Dr. Roger Billings of the American Academy of Science, Independence, MO, has developed fuel cells that are not only small, light and efficient, but can operate in reverse as electrolysers. He plans to deliver a demonstration fuel cell vehicle to the Penn. Energy Office in mid-1991.

We are about to leave oil behind, and enter the age of the fuel cell.

Access

Author:

Dr. Robert Wills, Skyline Engineering, Potato Hill Road, RR#1, Box 220-C, Fairlee, VT 05045 • 802-333-9305. Dr. Wills is a consulting engineer who specializes in photovoltaic system design and Co-Director of the American Tour de Sol, the Solar & Electric car race.

Fuel Cell Makers:

Ballard Power Systems, Inc., 980 West 1st Street, Unit 107, North Vancouver, B.C. V7P 3N4, CANADA • 604-986-9367.

Ergenics, 247 Margret King Ave., Ringwood, NJ 07456 • 201-962-4480.
Skyline Engineering AD

Direct Solar-Thermal Hydrogen Production From Water Using Nozzle/Skimmer and Glow Discharge

by W.R. Pyle, M.H. Hayes, A.L. Spivak

Originally published as IECEC Proceedings 1996 #96535

H-Ion Solar Company
6095 Monterey Avenue
Richmond, California, 94805
Tel: (510) 237-7877 FAX: (510) 232-5251
info@hionsolar.com
www.hionsolar.com

Abstract

An investigation of direct solar-thermal hydrogen and oxygen production from water is described. Nozzle jets and skimmers have been used for separation of the products and suppression of recombination. The dissociation of water vapor and the separation of its products was conducted in plasma-enhanced, non-equilibrium glow discharges.`

TOC

◀ ▶

Summary

In this report we describe the status of our work with a solar water dissociation gas phase reactor:

Solar radiant energy was concentrated by a parabolic mirror to produce high temperatures on a nozzle inside a solar reactor fed with water vapor (steam) at low pressure, to produce hydrogen and oxygen.

- A ceramic dissociator-nozzle was used as the target (absorber) for the concentrated solar-beam image. Water vapor was fed to the hot dissociator-nozzle by a feed-ring. Expansion of the water and its dissociation products into a lower pressure region was employed to provide quenching.
- A conical skimmer was used to separate the dissociated water vapor products, hydrogen and oxygen, from the unconverted water vapor in the expanding dissociator-nozzle jet. The objective is to separate the hydrogen and oxygen products from one another before they recombine.
- The dissociator-nozzle is operated with an electrical glow discharge between the water vapor feed-ring and the nozzle inlet. In this way the steam flow field, where the radiation and convection heat transfer takes place, was populated with free electrons, ions and molecules in the excited state. The radiation absorption capture cross-section for water vapor was altered by the plasma glow discharge.

- The product gas stream (containing hydrogen, oxygen and water) from the dissociator-nozzle's exhaust jet flow field was operated in a glow discharge. This affects the flow-field between the dissociator-nozzle jet and a conical-skimmer. The expanding jet flow-field downstream of the dissociator-nozzle separates the water decomposition products spatially, enriching the core of the jet flow-field with the heavier oxygen and water, and enriching the periphery of the jet flow-field with the lighter hydrogen. Transverse diffusion of hydrogen appears to be responsible for the separation.
- Progress to date includes:

  a) Operation of the reactor for over 50 hours "on-sun" at 2600-2900° K nozzle surface temperature without failure of materials.

  b) Dissociation of water and separation of hydrogen at 1 to 2% overall efficiency (solar to hydrogen.)

Introduction

A sustainable, non-polluting energy currency is required to provide for human needs such as cooking, heating, transportation, electricity production, and refrigeration. An economically viable method for producing large quantities of hydrogen from water using sun-light would satisfy this need, in a "Hydrogen Economy".

Pioneering studies of solar hydrogen and oxygen production from water occurred throughout the world during the 1970s and early 1980s as a response to the oil shocks of 1973 and 1978/1979. After a lull in activities during the mid and late 1980s, interest in direct water dissociation and other hydrogen production technologies has again increased during the early 1990s due to increasing environmental problems.

Water Dissociation to Produce Hydrogen and Oxygen

Our research objective is to develop a process that can attain a high level of water vapor dissociation and efficiently separate the hydrogen from the oxygen and un-converted water vapor.

At high temperatures, above about 1800° K, water vapor (steam) begins to dissociate into a mixture of H_2, O_2, H_2O, O, H and OH. The extent of dissociation increases with increasing temperature and decreasing pressure. The water and the diatomic hydrogen and oxygen species completely dissociate into H (atomic hydrogen) and O (atomic oxygen) above about 3500° K under equilibrium conditions at 1 mm Hg absolute pressure.

Endothermic Water Vapor Dissociation Reactions

Endothermic reactions can be carried out with the aid of electricity, as in electrolysis. However, thermal power from concentrated solar radiation can be used without any mechanical or electrical input, and without the aid of any catalyst, to achieve water dissociation. The direct thermal method has two advantages: it is very simple in its principle, and it is versatile and adaptable to many endothermic gas-phase reactions. This method does not suffer from the corrosive reagent problems of various multi-step lower temperature thermo-chemical cycles. New problems arise, however, in finding reactor materials capable of withstanding the higher temperatures required with one-step concentrated radiation water-thermolysis. The materials used in the reactor must be capable of withstanding the thermal cycling and shock brought about by the intermittent nature of solar diurnal and weather cycles.

TOC
◀ ▶

The chemical reactions associated with high temperature dissociation of water vapor are shown below, along with their pressure equilibrium constants:

Chemical Reactions

$H_2O \longrightarrow H_2 + 1/2O_2$

$H_2 \longrightarrow 2H$

$O_2 \longrightarrow 2O$

$O + H \longrightarrow OH$

Pressure Equilibrium

$K_1 = XH_2 \sqrt{P * XO_2} / XH_2O$

$K_2 = P * X^2H / XH_2$

$K_3 = P * X^2O / XO_2$

$K_4 = XOH / (P * XO * XH)$

Mole Fraction Equation

$XH_2O + XH_2 + XH + XO_2 + XO + XOH = 1$

Where P is the total pressure and X is the mole fraction.

Equation (1) above is an over-simplification of the primary reaction, because surface reactions in this reactor are significant. The surface reactions have been well characterized by Lede et al (1982).

TOC

Water vapor dissociation has an activation energy threshold of about 135 kcal/mole (5.9 electron volts). Atomic hydrogen and oxygen are formed and then recombined to diatomic hydrogen and oxygen, losing about 78 kcal/mole in the recombination process.

In this investigation we are studying the non-isothermal low-pressure glow-discharge region shown in Figure 1 (Bockris et al, 1985). It can be seen that the enthalpy change may be greater than the water dissociation activation threshold of 135 kCal/mole(5.9ev).

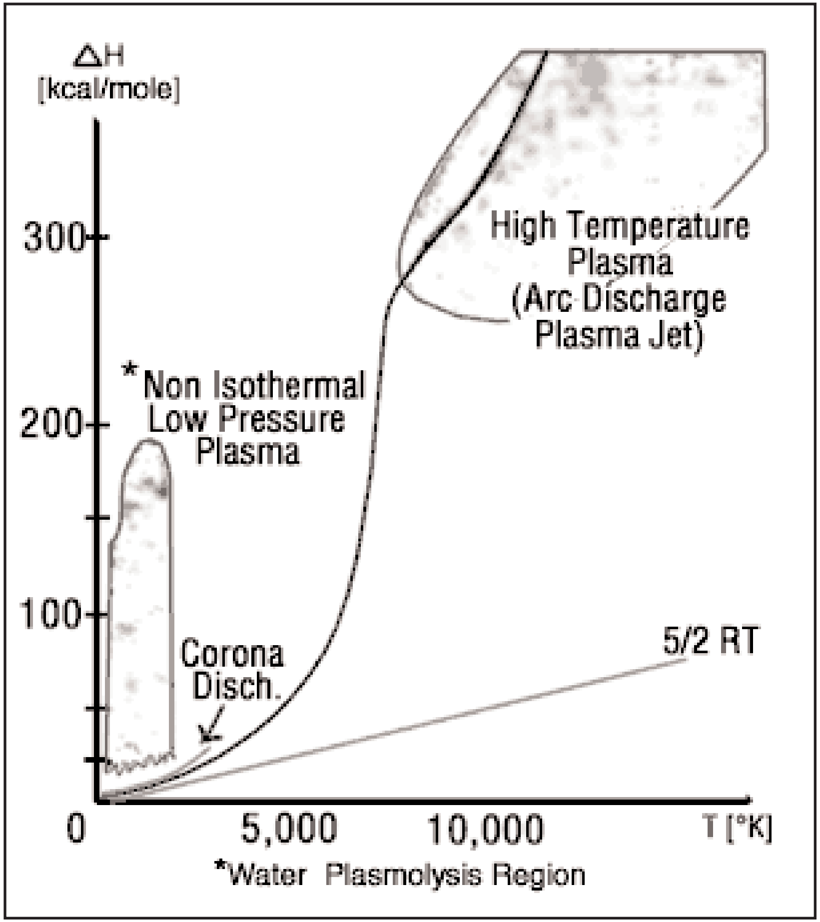


Figure 1. Glow Discharge Region Between Feed Ring and Nozzle

Non-Equilibrium Plasma-Chemical Reactions Associated with Water Vapor Glow Discharges

The process of decomposition of water in the plasma state can be accomplished at highest efficiency where the electron temperature is not sufficient for intense excitation of the electron states, and the larger portion of the electron's energy contributed to the discharge is expended for excitation of vibration modes and for dissociative attachment (Melik-Asloanova et al, 1978).

Dissociation of water vapor molecules is accomplished by successive stages of water oscillative excitation, population of highly excited states and, finally by reactions with participation of H2O* (where the * denotes the vibrationally excited state of water). The reaction is initialized in the bi-molecular act:

$$H_2O^* + H_2O^* \Rightarrow H + OH + H_2O$$

The radicals H and OH initiate a reaction with participation of the oscillatively excited molecules:

$$H + H_2O^* \Rightarrow H_2 + OH$$

$$OH + H_2O^* \Rightarrow H + H_2O_2$$

Water decomposition by dissociative attachment requires that in each reaction an electron disappears and a negative ion is produced. Plasmochemical

TOC

dissociative attachment reactions become energetically effective when each electron produced in the plasma can repeatedly participate in the dissociative attachment process. Multiple use of the electron becomes possible due to a high rate of negative ion collapse by electron impact. The chain process initializes:

$$e + H_2O \Rightarrow H^- + OH$$

$$H^- + e \Rightarrow H + e + e$$

Termination of the chain results from recombination with water and OH in a three-body collision:

$$H + OH + H_2O \Rightarrow H_2O + H_2O$$

The parallel channel of the chain extension has poorer kinetics because of a higher activation barrier of the limiting process:

$$OH + H_2O \Rightarrow H_2 + HO_2$$

$$HO_2 + H_2O \Rightarrow H_2O_2 + OH$$

The total efficiency of the process depends on the energy losses in the discharge, the efficiency associated with the negative contribution of the chain-breaking reaction, the heat losses of the excited-state reactions, and finally on the efficiency of the reaction relative to the oscillative relaxation.

The energy transfer efficiency of vibrational excitation by electron impact is a function of the energy contribution to water: oscillations, translational motion, rotation, and dissociative attachment. The energy transfer efficiency of the chain process depends on the chain length.

Dissociator-Nozzle Application to Production of Hydrogen and Oxygen from Water Vapor

A block diagram of the Photo-separatory Nozzle reactor (Pyle 1983) and the process under investigation is shown below:

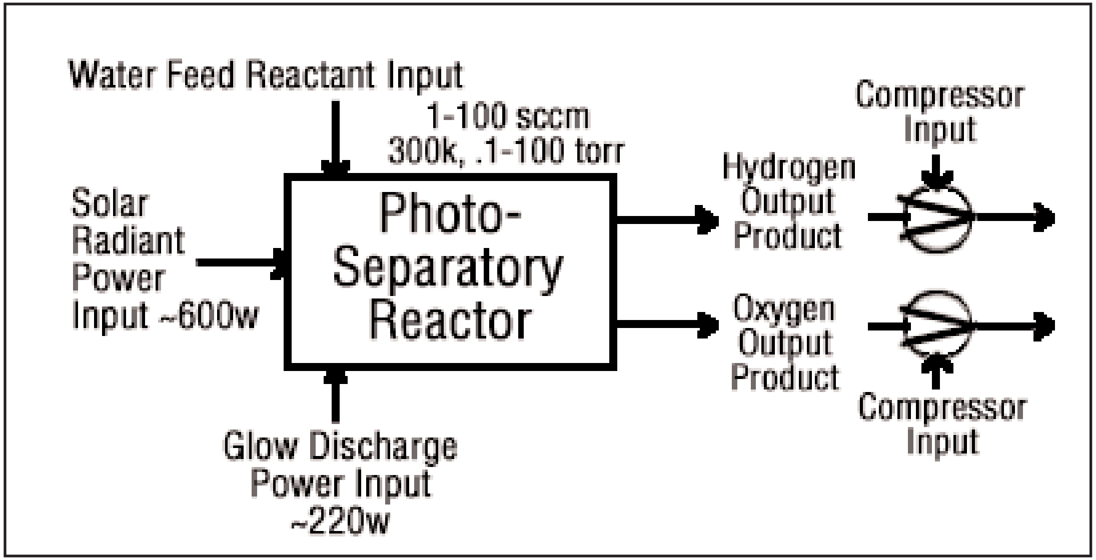


Figure 2. Block Diagram of Solar Reactor

Concentration and Absorption of Sunlight in Solar Reactor

Sun-light was concentrated using a parabolic mirror and directed through the entrance window of a high-temperature gas-phase reactor. Inside the solar reactor the concentrated radiant energy was focused onto a trumpet-shaped ceramic dissociator-nozzle. An optical pyrometer with a video camera looks through a prism and a hole in the concentrator mirror, then through the quartz reactor window to view the dissociator-nozzle surface and obtain nozzle surface temperatures.

The solar spectrum, at sea level on Earth with air mass of 1, loses some energy bands due to the water vapor absorption which occurs as the light is passing through the atmosphere, especially in the near UV. This absorption limits the energy spectrum available for water dissociation at the earth’s surface. We used re-radiation from a hot surface (the nozzle) to enhance gas heat transfer and create a surface reaction site.

Solar heat source temperature can be calculated as a function of the concentrator optical concentration ratio, reflection coefficient, and arriving solar power density.

By raising the temperature of the nozzle surface to a sufficiently high value (using the nozzle as a target for concentrated sunlight) and dropping

TOC

the water vapor pressure to a sufficiently low value, we are attempting to produce significant water vapor dissociation.

Glow-Discharge Enhancement of Radiation and Convection Heat Transfer at Nozzle Entrance

A high voltage DC electric power supply (PS-1) was used in some of the experiments to create a water-vapor glow-discharge between the water vapor feed-ring and the entrance to the ceramic dissociator-nozzle to enhance dissociation (Pyle et al, 1994). See Figure 3.

The applied voltage was measured with volt-meter V and the current with ammeter A, shown in the upper right of Figure 3. The circle shown in Figure 3, between the feed ring and the dissociator-nozzle, is where the solar image "fireball" and the water vapor glow-discharge region are located.

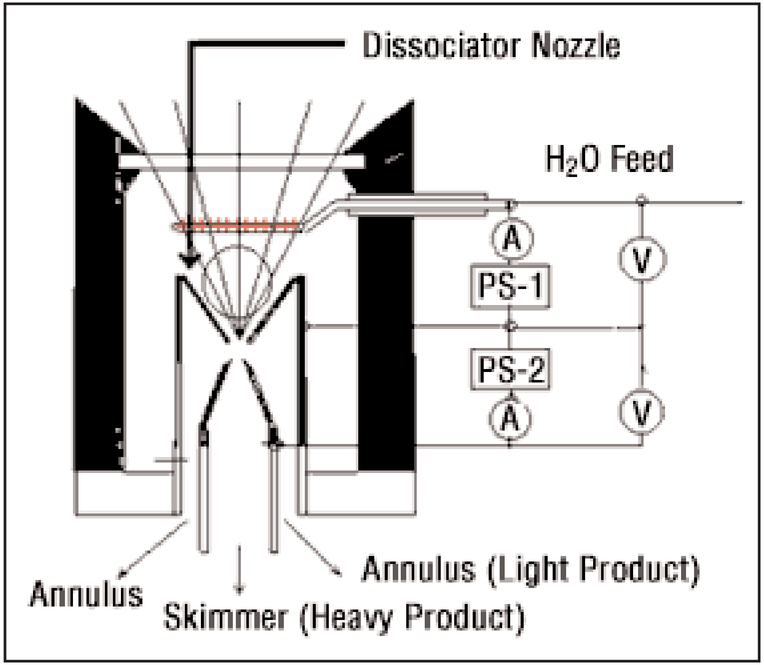


Figure 3. Photo-separatory Nozzle Reactor

The partially dissociated water vapor was allowed to pass through the dissociator-nozzle throat and expand into a lower pressure region. The pressure inside the dissociator-nozzle tube (downstream) must be lower than at the entrance (dissociation region) to create the driving force for sonic flow through the nozzle throat (pressure ratio > 0.55) , and produce a jet and shock-wave down stream.

In our application, a sonic dissociator-nozzle geometry was used because this was the easiest to fabricate using quartz tubing in the laboratory.

All gases at room temperature are excellent electrical insulators. In order to make them electrically conducting, a sufficient number of charge carriers have to be generated. If a sufficiently high electrical field is applied to a pair of electrodes separated by a volume of the gas, an electrical breakdown of the originally non-conducting gas establishes a conducting path through the electrode gap, producing an array of phenomena known as gaseous discharges.

We desire a steady-state dc glow discharge for our solar plasma reactor, to obtain a higher electron population density with relatively low electrical power consumption.

After breakdown, the current A rises and voltage V drops to steady-state values. The discharge voltage depends on the current and certain properties of the discharge tube, such as gas type, gas pressure, electrode material,

TOC

and electrode temperature. A current suppression (or ballast) resistor is needed to limit the current through the gas-plasma after breakdown occurs. We used 10,000 to 18,000 ohm suppression resistors in the Photo-separatory Nozzle reactor.

Heat is supplied to the dissociator-nozzle (which is also the cathode electrode for the glow discharge) by the concentrated solar beam, and it operates in glow discharge with low cathode fall. Cooling of the nozzle surface by electron boil-off occurs under direct thermionic emission process conditions at very high temperatures. Indirect emission processes (secondary emission processes) are also important to consider: electrons are ejected from the surface of the nozzle by energetic particles such as ions and photons in the glow discharge.

Glow Discharge Applied Between Dissociator Nozzle and Skimmer Separator

A supersonic beam skimmer was installed behind the shock wave to separate hydrogen and oxygen from the partially dissociated water vapor (Becker et al 1955). See Figure 3 (p.241).

The supersonic beam skimmer used was a knife-edged cone. The skimmer was positioned with micrometers so that its entrance was at the downstream edge of the shock-wave envelope produced inside the dissociator -

TOC

nozzle. An appropriate pressure ratio was applied between the low pressure dissociator-nozzle jet region and the beam skimmer interior to improve the separation factor for hydrogen and oxygen production. This jet separator functions by transverse gas diffusion. The hydrogen and oxygen (plus unconverted water vapor) are separated because the hydrogen gas diffuses transversely (relative to the jet flow axis, more rapidly than oxygen or water), due to its lower mass.

A second high voltage DC electric power supply (PS-2) was used to create a glow discharge between the sonic dissociator-nozzle and the conical skimmer nozzle to study separation enhancement by cataphoresis. Cataphoresis is the spatial gas density gradient which forms near a cathode within a glow discharge. Cataphoretic efficiency has been observed to decrease with increasing temperature, however.

The glow-discharge between the dissociator-nozzle and the skimmer-nozzle also allows shock-wave visualization by a video camera which is aimed through a viewing slit in the reactor wall. The video camera is attached to a coherent optical fiber bundle and illuminated with a He-Ne laser through another incoherent optical fiber bundle to allow observation of the dissociator-nozzle and skimmer separation distance, as the skimmer is moved in or out of the jet.

TOC

Enrichment of heavier-mass species occurs in the core of the gas jet. Enrichment of the lighter-mass species occurs in the periphery of the gas jet.

The free molecular diffusion separation arises from the disparity in the thermal velocity of light and heavy gas molecules, for gases with the same mass flow velocity and local temperature. The heavier species have a lower thermal velocity and expand less (laterally) after the transition plane, remaining more concentrated at the beam center.

In moving the skimmer transversely, a qualitative measurement of the degree of beam spreading is obtained. A much broader spreading is observed for light species (hydrogen) than for heavy species.

In the case of a fixed skimmer-orifice dimension, an axially movable skimmer is necessary to achieve comparable beam intensities for different gases. The mass separation factor is approximately proportional to the mass ratio when the skimmer-interference and background-penetration effects are minimized.

Separation Factor =

[(Heavy Core Gas, M%) (Light Peripheral Gas, M%)] /
[(Heavy Peripheral Gas, M%) (Light Core Gas, M%)]

Glow Discharge Power Supply Requirements

In the dark (no concentrated sunlight), with water vapor pressures in the Photo-separatory Nozzle reactor's normal pressure regime, the power supply voltage required for sustaining normal glow may be about 700, whereas under concentrated sun-beam illumination the normal glow voltage is only about 200. The current requirement is on the order of 1-3 ma under either dark or illuminated conditions. The use of higher pressure requires the use of higher current. The glow-discharge power is only a small fraction of the power arriving via the concentrated sun-beam, about 1 to 2 watts typically. This electrical power requirement can easily be met by a small photovoltaic cell array.

The glow-discharge power for the lower pressure gas region between the dissociator-nozzle and the skimmer is of the same order as for the feed-ring to dissociator-nozzle power, 1 to 2 watts.

Description of Experimental Apparatus

The complete Photo-separatory Nozzle reactor assembly is shown in Figure 4, next page.

A computer program, called Iontrack, calculates the elevation and azimuth of the sun based on the time of day, and the latitude and longitude of the

TOC
◀ ▶

mirror on the planet's surface. Iontrack reads the actual elevation and azimuth positions of the mirror from the two analog sensors, and determines the movement required for each axis to reduce the error to zero. Iontrack directs the two stepper motors to make the necessary movements to keep the tracking error under 0.10 degrees.

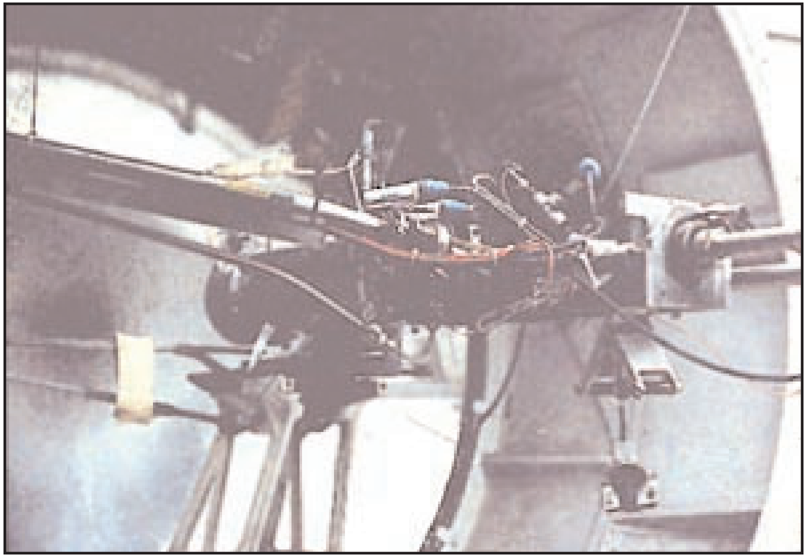


Figure 4. Photo-separatory Nozzle reactor

Photo-Separatory Nozzle Reactor Construction

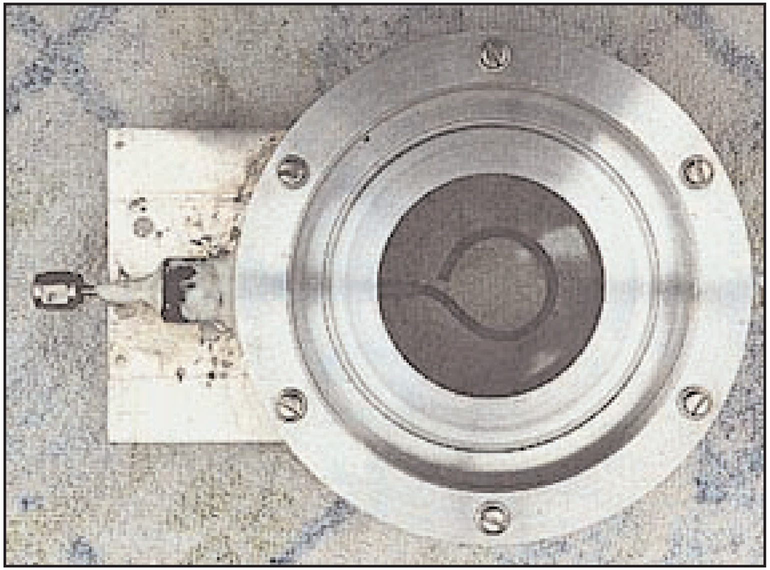
The Photo-separatory Nozzle reactor was constructed from concentric quartz tubes and surrounded by a convection and conduction barrier with radiant energy reflecting properties. See Figure 5, next page.

An aluminum housing protects the quartz tubes, aligns and holds the silicone o-ring seals in place, and serves as a mounting fixture on the stage of the searchlight concentrator. An optical viewing slit in the reactor containment vessel was provided for studying the transonic flow region, between the dissociator-nozzle and the skimmer.

Above, Figure 5.
Reactor Containment Vessel

Solar Beam Entrance Window

A quartz window admits the concentrated solar beam to the interior of the reactor. Inside the reactor, the gas feed-ring/electrode is positioned so that the converging solar beam passes through the feed-ring and the solar image "fireball" lands in the center of the trumpet-shaped dissociator-nozzle. See Figure 6.



Right, Figure 6.
Solar Beam Entrance Window
with Feed-Ring

Gas (Water Vapor) Feed-Ring Electrode

The feed-ring electrode was made from a loop of stainless steel tubing. The tubing was welded closed at one end and drilled with feed holes 0.508 mm (0.020 inches) diameter chamfered 1 mm (0.040 inches) periodically at 1.27 cm (0.5 inch) intervals along its length. The tubing was then rolled around a mandrel to form the feed-ring electrode. A quartz tubing sleeve was used as a feed-through insulator at the reactor window retainer wall to supply reactant gas and electrical power. The electrical power supply connection to the feed-ring electrode is made outside the reactor on the stainless steel gas feed tube.

It is important to operate the reactor when it is "on-sun" with water vapor flowing to the feed ring. In one experiment, water vapor feed was interrupted and the stainless steel feed-ring was evaporated. The feed-ring turns black after operation on-sun for a few hours, but is not damaged by the beam as long as the water vapor feed is continuous.

Sonic Dissociator-Nozzle/Electrode Fabrication

The dissociator-nozzle is a sonic nozzle with a trumpet-shaped converging entrance section made from a cylindrical quartz tube. A sealing flat flange was fused to the opposite end of the tube. A conductive thin film of

TOC

platinum was applied to the outside of the quartz cylinder to provide an electrical connection (negative ground) for the dissociator-nozzle. The quartz tubing (General Electric Type 204 clear fused quartz) was coated with an yttria and calcia stabilized zirconium oxide refractory (Aremco Products Inc. Ultratemp 516 high temperature ceramic adhesive, Osining, New York) for the reaction zone and solar beam target. The sonic quartz dissociator-nozzle is shown in Figure 7.

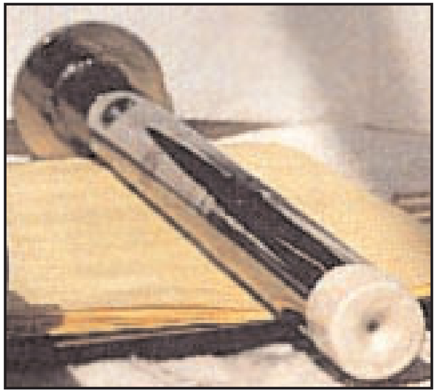


Figure 7. Sonic Quartz Dissociator-Nozzle with Ceramic Zirconia Coating

After 10 to 20 hours of on-sun operation, samples of a broken zirconia-on-quartz dissociator-nozzle were analyzed by x-ray diffraction. Zircon (zirconium-silicon oxide) micro crystals were detected, indicating a new conductive interface layer had been formed between the quartz tube and zirconia coating. Better thermal-expansion matching of materials seems to be obtained with a zircon layer. A glassy surface finish is produced on the heat-affected portion of the dissociator-nozzle coating after "break-in".

Skimmer Nozzle/Electrode

The skimmer nozzle/electrode is a conical nozzle that is mounted on the end of a cylindrical stainless steel tube which fits coaxially inside the cylindrical dissociator-nozzle tube. See Figure 8.

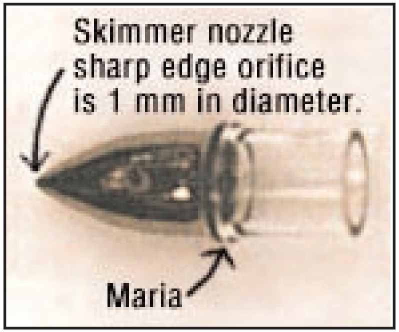


Figure 8. Conical Skimmer Nozzle/Electrode

The conical skimmer-nozzle/electrode entrance faces the dissociator-nozzle's exhaust jet. The conical skimmer-nozzle was fabricated from a sharp-edge truncated cone made of quartz tubing and ground to a knife-edge using a diamond abrasive wheel. The quartz skimmer-nozzle was coated with platinum for electrical conductivity and connected (via a feed-through) to an electrical power supply (PS-2 in Figure 3, p.241) on the outside of the reactor.

Product Separation Control System

A scissors jack is used to move the skimmer in and out with respect to the dissociator-nozzle exhaust axis. The scissors jack counteracts the forces on the skimmer caused by atmospheric pressure exerted on one side of the skimmer and the lower process pressure on the inside of the skimmer. An electronic proximity sensor and a dial gauge are used to provide axial position information. The spacing between the dissociator-nozzle and skimmer is of the order of one nozzle diameter (about 1mm.) The skimmer can be moved from about 0.1mm to about 2.0mm downstream of the dissociator-nozzle. Depending on the pressure in the region between the dissociator-nozzle and the skimmer, this distance is approximately 1 mean-free-path (between atom/molecular collisions).

An eccentric is used to move the skimmer from right/left and up/down around its pivot point. The pivot point is located about 22 cm downstream from the dissociator-nozzle's exit orifice. The pivot point is made from 3 dimples inside the dissociator-nozzle tube. Two more proximity detectors and dial gauges provide up/down and right/left skimmer position information.

Product Gas Sampling System

Sampling valves are located in the two product discharge lines. Each sampling valve can admit product gas into the mass spectrometer. The spectra from each product line are alternately taken; then the mass spectrometer background gas pressure spectrum is subtracted from each. The mass ratios for the light and heavy products are calculated and used to obtain a separation factor.

TOC

Mass Flowmeters

The mass-flow rates of the water vapor feed and the skimmer (heavy product) and annulus (light product) were measured with Teledyne Hastings-Raydist model ST and model HFM-200H mass flow meters.

Using the three mass-flow meters allowed us to perform a mass balance across the reactor to obtain measurement closure with the flow meters (as a calibration and leak check.)

Optical Pyrometer for Nozzle Surface Temperature Measurement

A Pyro Micro-Optical Pyrometer made by the Pyrometer Instrument Company Inc. (Northvale N.J.) was used to measure the temperature of the dissociator-nozzle surface under different operating conditions. We used an EC-6 high temperature range filter and a 90° M-14 prism to view the dissociator-nozzle. Corrections to the indicated temperature were made for the prism, the filter, the range selection, and the reactor window transmission loss for any given temperature.

We normally measure temperatures in the 2300° K to 2800° K range at the nozzle surface, depending on the water vapor feed pressure and the solar beam flux. Stagnation temperatures as high as 3250° K have been measured on the nozzle surface (somewhat higher than the published melting point of zirconia.)

Pumping requirements

Pumping the products from low pressure to atmospheric pressure or higher requires compression work, which is a parasitic loss in the overall efficiency of the process. The losses for the oxygen-rich stream compressor and the hydrogen-rich stream compressor must be minimized by selecting reactor pressures no lower than necessary, and by the use of efficient compressor designs.

The net power required to pump the process fluids in this reactor was about 18 watts.

To compress the products adiabatically (no cooling) from 1 Torr to one atmosphere with an inlet temperature of 300° K would require about 50 kJ/g-mole (11.9 kcal/g-mole). Isothermal compression (with intercooling) would require only about $^1/_3$ as much compression work.

Energy Balance

An energy diagram which gives estimates for the losses in the process, both to the surroundings, and to parasitic power requirements is shown in Figure 9, right.

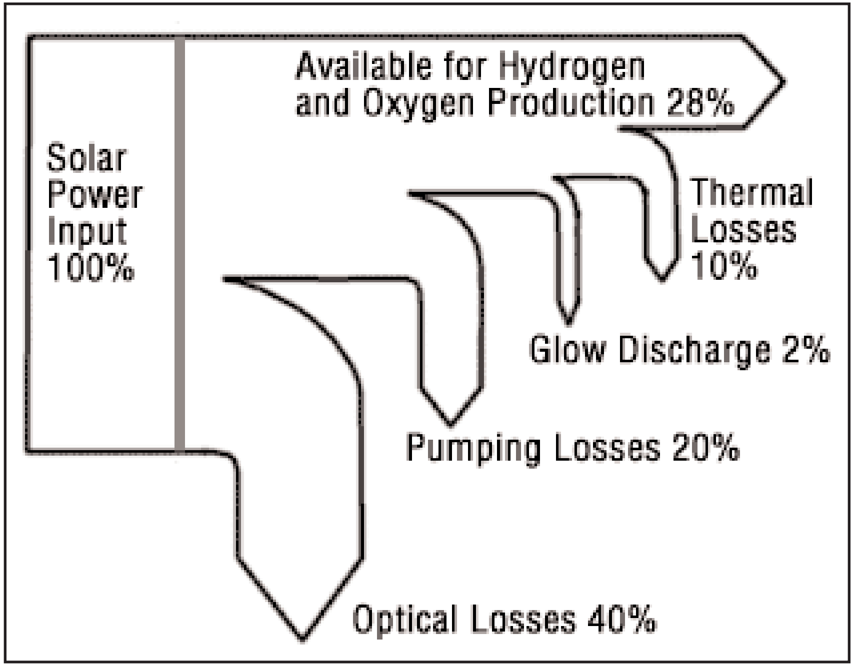


Figure 9. Energy Diagram for Process

The optical losses can be reduced through:

- Use of a higher quality solar concentrator mirror.
- Use of a dome shaped solar-beam entrance window instead of a flat window.
- A receiver geometry resembling a cavity.

The pumping losses and glow-discharge losses are, in reality, electrical power requirements, which, if met by photo-voltaic means, can be considered a capital cost.

Experimental Separation Efficiencies and Solar-to-Hydrogen Efficiencies to Date

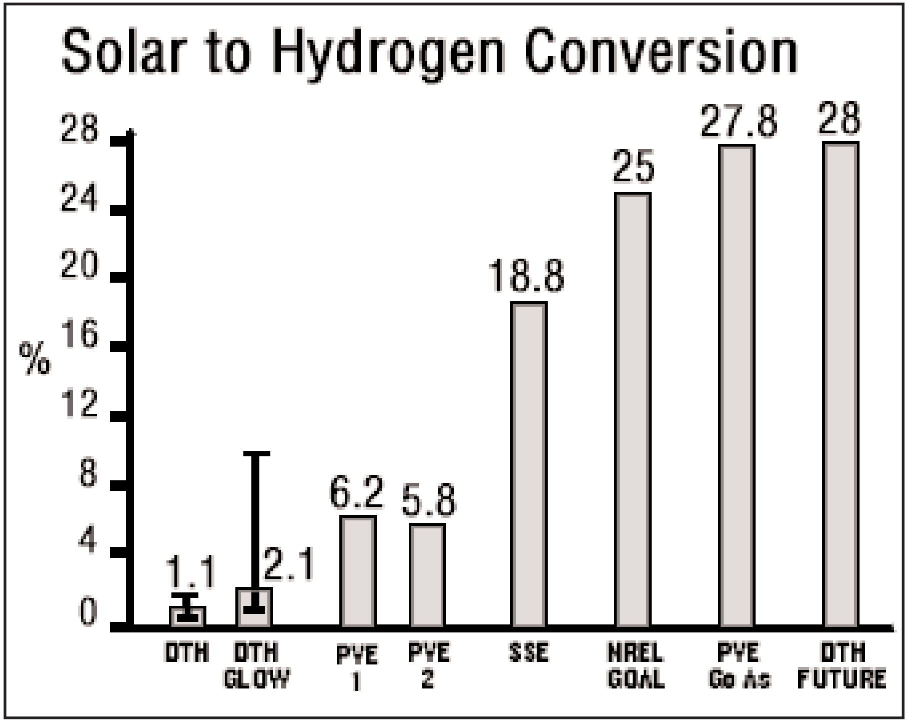


Figure 10.
Efficiency of Solar-Hydrogen Processes

Experimental solar-to-hydrogen efficiencies to date are shown in Figure 10.

The first bar on the left (labeled DTH) is the direct thermal hydrogen conversion efficiency obtained by analyzing the dissociator-nozzle jet flow-field without the use of a glow discharge or skimmer. About 1.1% solar-to-hydrogen (higher heating value) conversion was obtained.

The second bar (labeled DTH Glow) shows an improvement in solar to hydrogen conversion to about 2.1% when a glow discharge was applied and the skimmer and annulus hydrogen production was added together. The maximum and minimum measured values are shown about the mean.

The third bar (labeled PVE1) shows the solar-to-hydrogen efficiency obtained using silicon photovoltaic cells and an alkaline electrolyzer. The fourth bar (labeled PVE2) shows the results of another photovoltaic electrolysis system.

The conversion efficiency for a solar dish Stirling generator combined with an alkaline electrolyzer [75% efficient] is labeled SSE in Figure 10.

The next bar (labeled NREL Goal) shows the long term solar-to-hydrogen efficiency goal established by the National Renewable Energy Laboratory, for reference purposes.

Multi-junction single crystal gallium arsenide solar cells with future 37% solar-to-electrical efficiency combined with a 75% efficient alkaline electrolyzer is labeled PVE Ga As.

The bar (labeled DTH Future) indicates that the future direct thermal hydrogen process may compete with other known methods on an efficiency basis. It may have the further advantage that it does not use expensive single crystal materials.

Micro-Nozzle Arrays and Scale-Up

Micro-nozzle arrays may allow scale-up of the process for a wide area solar reactor receiver. With smaller nozzles, the mean-free-path dimensions will also be smaller, and higher operating pressures will be allowable in principle. The higher operating pressure will result in a reduction of parasitic compression work required .

The arrays can be arranged in matrices or linearly. We can envision arrays of solar-hydrogen reactors along two parallel pipe lines, running from an area with high insolation, to supply cities. Existing natural gas pipelines could be used to transport the hydrogen and oxygen products separately to their point of use. Alternatively, one pipeline could be used to transport hydrogen to the point of use and the oxygen could be vented.

Recommendations for Future Research and Experimentation

We have seen that some direct thermal hydrogen production can be obtained in this reactor simply by passing water vapor through a hot ceramic nozzle (1.1%). We have also found that impressing a glow-discharge across the dissociator-nozzle almost doubles the conversion (2.1%). The separation factor for the skimmer has not yet been optimized. More work remains to obtain accurate spatial calibration of the skimmer, and investigate the effect of pressure, flow separation, and glow discharge on the separation efficiency. At this time, the amount of recombination which occurs after dissociation is unknown. However, we feel there are very exciting possibilities for improvement of the process.

Further improvements in product gas analysis (mass spectrometer) calibration and skimmer nozzle position calibration are needed to remove uncertainty from the measurements and provide real-time data during "on-sun" experimental runs.

Acknowledgments

We are grateful for the suggestion by John Green to consider the separatory-nozzle, as applied in mass-spectroscopy, to the separation of dissociated water-vapor in a solar reactor.

We thank J.D. Healy, E.C. Petersen, and R. Cortez for their assistance in constructing and trouble-shooting the apparatus for these experiments.

References

Becker, E.W. et al, 1955, *The Separatory Nozzle: a New Device for Separation of Gases and Isotopes*, Z. Naturforschg, Part A, Vol.10a, pp565-572.

TOC

References (continued)

Bockris, J.O.M. et al, 1985, *On the Splitting of Water*, International Journal of Hydrogen Energy, Vol. 10 No. 30, pp.179-201

Lede, J., Lapique, F., Villermaux, J., Cales, B., Baumard, J.F., and Anthony, A.M., 1982, *Production of Hydrogen by Direct Thermal Decomposition of Water, Preliminary Investigation*, International Journal of Hydrogen Energy, Vol.7, No.12, pp.939-950.

Melik-Asloanova, T.A., Abbosov, A.S., Shilnikov,V.I., 1978, *Dissociation of Water Vapor in Supersonic Flow of Non-equilibrium Plasma*, Proceedings World Hydrogen Energy Conference 2, pp.1063-1069.

Pyle, W.R., 1983, *Photo-separatory Nozzle*, U.S. Patent No.4,405,594.

Pyle, W.R., Hayes, M.H., Healy, J.D., Petersen, E.C., Spivak, A.L., Cortez, R., 1994 *Direct-Thermal Solar Hydrogen Production from Water Using Nozzles/Skimmers and Glow Discharge in the Gas Phase at Low Pressure and High Temperature*, H-Ion Solar Company, NREL Task No. HY413801, Subcontract No. AAP-4-14240-01, Richmond, California, pp.1-63.

Links

Home Power Magazine
www.homepower.com

Dr. Robert Wills
Advanced Energy Systems

A full product line of grid-tied, battery back-up, and stand-alone inverters as well as data monitors, string combiners, and battery enclosures
www.advancedenergy.com

Walt Pyle
H-Ion Solar, Inc.

Consulting, design, and installation of solar photovoltaic and thermal systems; and products for the use of hydrogen fuel including the Double-Bubbler™ and Hydro-que™.
www.hionsolar.com

Hydrogen Wind Electrolyzers .
www.fuelcellsvt.com

TOC
◀ ▶

Links

Other e-book titles available from

Wheelock Mountain Publications:

Build Your Own Solar Panel
by Phillip Hurley

Build Your Own Fuel Cells
by Phillip Hurley

Tesla: the Lost Inventions
by George Trinkaus

Chinese Firecracker Art
by Hal Kantrud

Wheelock Mountain Publications
is an imprint of

Good Idea Creative Services
324 Minister Hill Road
Wheelock VT 05851