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Hydrogen as a Navy Fuel

A Study Paper Prepared by the NRL Hydrogen Panel

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Hydrogen has desirable properties as a fuel. It can be burned in all burners and engines in widespread use today and is a superior material for fuel cells. A high heat of combustion makes hydrogen attractive, but its low density negates much of the advantage obtained by the heat of combustion, particularly for volume-limited vehicles. Thus, the use of hydrogen in major ships and carrier aircraft is not promising. Hydrogen is not a prime fuel; it is produced by putting energy into chemical reactions. Hazards with gaseous hydrogen are greater than with most combustible gases, but suitable handling techniques are available. Experience with liquid hydrogen		

is limited, however, and explosion hazards must be examined. The increase in crude oil prices coupled with the decreasing oil reserves-to-production ratio indicates that hydrogen will not be at as large an economic disadvantage as it is today. The cost of hydrogen should not be a deterrent to its use in the Navy if system performance shows significant advantages.

CONTENTS

INTRODUCTION	1
PROPERTIES OF HYDROGEN AS A FUEL	3
Chemical Oxidation	3
Electrochemical Oxidation	6
HYDROGEN PRODUCTION	12
Fossil Fuels	13
Nonfossil Fuels	14
Electrolysis	14
Thermal Energy	15
Production—Cost Summary	16
Commentary	17
HYDROGEN STORAGE	18
Storage as a Gas	18
Storage as a Liquid	19
Unconventional Storage Methods	20
H ₂ Liquefaction Energetics	20
LIQUID HYDROGEN USAGE IN THE NAVY	20
Comparison of LH ₂ and Petroleum Fuels for Today's Fleet	20
Usage in Fleet After Year 2000	21
Other Factors	23
Other Concepts	23
Special Applications	23
HAZARDS IN THE STORAGE, TRANSPORTATION, HANDLING, AND USE OF LIQUID AND GASEOUS HYDROGEN	24
History	24
Nature of the Hazard of Hydrogen	25
TOXICITY AND EFFECT ON THE ENVIRONMENT	29
Engine Exhaust	29
Thermal Pollution	29
Toxicity	29

CONTENTS—Continued

CONCLUSIONS	29
REFERENCES	30

HYDROGEN AS A NAVY FUEL

INTRODUCTION

Hydrogen (H_2) is one of several fuels available for the long term. It offers a means of energy storage, particularly when environmental sources (sun, wind, tides, geothermal and ocean thermal gradients, ocean currents, etc.) are tapped, since these energy sources are restricted geographically and may be intermittent. Hydrogen is not a source fuel, however, and must be produced from energy from some other source. It can be produced and used either chemically or electrochemically and is also the ideal nonpolluting fuel. Its potential use on a large scale by the Navy will of necessity be tied closely to its general application in the civilian economy.

Enormous quantities of hydrogen would be required to replace completely fossil fuels. For the years 1975 and 2000, the projected electrical demand needed to produce the required H_2 by electrolysis of water would amount to 14 to 15 trillion kWh at a rate of 1.7 to 5.1 million MW. Since the projected production of U.S. production of electrical energy for those years is 1.96 trillion and 10.9 trillion kWh, full conversion to electrically produced H_2 by 2000 is unrealistic even from the most optimistic viewpoint.

A major problem with hydrogen is storage. A cylinder containing 1 lb of H_2 at 2000 psi weighs about 125 lb. A cylinder containing H_2 would produce 51,600 Btu. Thus, about 40 cylinders would be equivalent to 20 gal. of gasoline when used in an internal combustion engine. In liquid form the element has an energy density of 30,000 Btu/gal. Thus a 73-gal. tank would be required for an automobile, instead of the normal 20-gal. gasoline tank, as shown in Table 1. Hydrogen has about three times more energy per unit of weight than gasoline.

Liquid hydrogen (LH_2) must be stored at a temperature below $-431^\circ F$, and a vacuum-insulated tank is required to minimize boiloff. Large-scale transportation of LH_2 is now done by rail tank car, road tanker, and barge. The weight of 20 gal. of gasoline plus its storage tank on an auto is about 150 lb, whereas the equivalent amount of LH_2 plus a suitable cryogenic tank would weigh about 300 lb. The same amount of H_2 stored in a MgNi alloy hydride system [1] would weigh 625 lb, with its container.

Replacing an auto engine with a fuel cell improves the comparison of H_2 with gasoline considerably, since the efficiency of overall conversion in a spark-ignition engine is about 15% [2], and the electrochemical efficiency of known fuel cells ranges from 50% to 70% [3]. This means that H_2 may be cheaper than gasoline on a per-mile basis [2]. Fuel cells are not now competitive with the spark-ignition engine in price or performance, but with the development of cheap fuel cells synthetic fuels may become economically competitive.

Note: Manuscript submitted April 12, 1974.

Table 1
Comparison of Various Fuels, Based on 20 Gal. of Gasoline*

Fuel	Btu/lb	Btu/ft ³	Amount Equivalent to 20 Gal. of Gasoline	
			Gal.	Lb
Typical gasoline	19,080	835,700	20.0	117
Methane gas (CH ₄ , 2000 psia)	21,500	152,400	110.0	104
Methanol (anhyd CH ₃ OH)	8,640	429,400	38.9	258
Ethanol (anhyd C ₂ H ₅ OH)	11,550	572,900	29.2	194
Liquid hydrogen (at NBP)	51,980	230,300	72.6	43
Hydrogen gas (2000 psia)	51,980	34,650	482.0	43
Metal hydride (Mg ₂ Ni · H _x)	4,350	479,900	34.8	513
Liquid ammonia (at NBP)	8,000	384,800	43.3	279
JP-5	18,500	930,000	18.0	120

*From Ref. 1.

The thermal efficiency of a reversible heat engine working between temperatures T_1 and T_2 is given by the Carnot theory as

$$\text{efficiency} = (T_2 - T_1)/T_2.$$

Since practical heat engines are irreversible and normally operate with a lower temperature T_1 of more than 300 K, while the upper temperature T_2 is limited by the materials of construction, thermal efficiencies in excess of 40% are seldom achieved.

The efficiency of electrochemical conversion of chemical to electrical energy is not limited by the Carnot cycle. The theoretical thermal efficiency of an electrochemical cell is

$$\text{efficiency} = \Delta G/\Delta H = - \frac{nFE_r}{\Delta H},$$

where ΔG is the free energy change and ΔH is the enthalpy change of the reaction, n is the number of electrons transferred in one act of the overall reaction, F is the faraday constant (96.5×10^3 C mole⁻¹), and E_r is the reversible cell potential. Generally, $\Delta G \approx \Delta H$, hence the efficiency of ideal fuel cells is close to unity.

In a real fuel cell, however, energy losses due to solution resistance and electrode polarization reduce E_r to an operating potential E , such that

$$E = E_r - \eta_p - \eta_d - \eta_R$$

where η_p is the net voltage loss from chemical and charge transfer processes at each electrode, η_d is the net voltage loss from mass transport processes, and η_R is the voltage loss from the ohmic resistance of the electrolyte separating the anode and cathode. Hence, the real efficiency of a fuel cell is

$$\text{efficiency} = - nFE/\Delta H.$$

The magnitude of each voltage loss η increases with current drawn from the cell so that operating potential E and the efficiency of the cell decrease with increasing current.

There are many problems of transporting, distributing, and storing liquid H_2 . However, substitute synthetic fuels such as aluminum or aluminum alloys in fuel cells [4] would avoid the problems of H_2 storage and flammability and substitute a cheap light-metal fuel with a high energy content.

In the immediate future, H_2 can serve as a clean fuel for special naval purposes, such as storing wind-generated electrical energy at remote bases. The most important characteristic of H_2 is its versatility; it can serve as either a thermal or an electrochemical fuel.

PROPERTIES OF HYDROGEN AS A FUEL

Chemical Oxidation

The convenience and flexibility of general-purpose fuels are reflected in the current energy economy, in which about 80% of the energy resources [5] consumed are for uses other than electric generation. Proper use of nuclear and solar energy requires portable and storable synthetic fuels derived from abundantly available or recycleable resources. Hydrogen can become a secondary source of energy, derived from the primary source by the decomposition of water [6].

Comparative Physical and Chemical Properties—Table 2 [7] compares physical properties of H_2 with those of other fuels. A comparison of the "energy density" of the fuels with gasoline in Table 1 shows some major differences. For an energy content equivalent to gasoline, all fuels listed, except JP-5, occupy more volume, but methane and hydrogen are lighter. Comparative costs of fuels are listed below.

Fuel	Dollars per Million Btu
Gasoline	1.32 (at refinery)
Methanol	2.10
Ethanol	7.30
Hydrogen	0.78–3.00 (electrolysis, estimates for future)
Hydrogen	4.00–6.00 (fossil fuel processes)
Natural gas	0.20 (domestic gas at wellhead)
Natural gas	0.70 (liquid imported at port of entry)
Coal	0.15 (at mine mouth)
Navy distillate	1.00
Nuclear fuel	0.05

Table 2
Physical Properties of Hydrogen and Other Fuels*

Property	H ₂	CH ₄	CH ₃ OH
Molecular weight (g/g-mole)	2.016	16.04	32.04
Freezing point (°C)	-259.20	-182.5	-97.8
Boiling point (°C)	-252.77	-161.5	64.7
Heat of vaporization (cal/g)	106.5	121.9	262.79
Critical temperature (°C)	-239.9	-82.1	240
Critical pressure (atm)	12.80	45.8	78.5
Liquid density (g/l[temp °C])	71[-252.77°]	425[-252.77°]	792[20°]
Gas density (g/l)	0.082†	0.7174†	-
Specific heat at STP (cal/mole-°C)	6.89	8.16	18.3

*After Ref. 7.

†Ref. 8.

Methods of Combustion—H₂ burners and combustion chambers will be smaller [7] than those required for natural gas. Appliances convert gas into mechanical energy either by internal (piston, gas-turbine engines) or external combustion (burners).

1. Flame burners. Most burners mix air with gas prior to burning. The gas-air mixture must travel toward the open end of the burner at a rate higher than the rate of flame propagation in the mixture. This prevents "flashback," or ignition inside the burner. If the velocity of the gas flow exceeds the burning velocity at all points, the flame is blown off. Figure 1 [9] shows flame velocities for various mixtures of some typical fuel gases with air. H₂ has a very high flame velocity, particularly at less than stoichiometric air content, such as in the primary gas-air mixture, but the design and construction of appliances that use H₂ present no severe problems. H₂ burners are more prone to flashback than to blowoff [10]. Since the only product of combustion is water, a H₂ furnace does not need a flue unless the amount of water vapor produced is excessive.

2. Catalytic burners. Various gas research projects have demonstrated the advantages of using catalytic burners for cooking, heating [11], and other purposes. (Catalytic burners have been applied to specific Navy uses; for example, the removal of atmospheric contamination in submarines.) A catalytic burner for H₂ does not require preignition, but natural gas requires a pilot, or electrical preheating, to initiate combustion.

There are two types of catalytic burners for H₂. The low-temperature burner is about 70%-porous ceramic plate. The internal surface of the plate is coated with a catalyst; a platinum metal is best, but cheaper materials may be found. Air is mixed with the H₂ and fed through the porous plate. Flameless combustion occurs within the plate. At low output, the burner can operate at 300 to 500°F with no fire hazard. The high-temperature catalytic burner, which operates at temperatures above 1000°F, requires a backing for the catalytic surface [7].

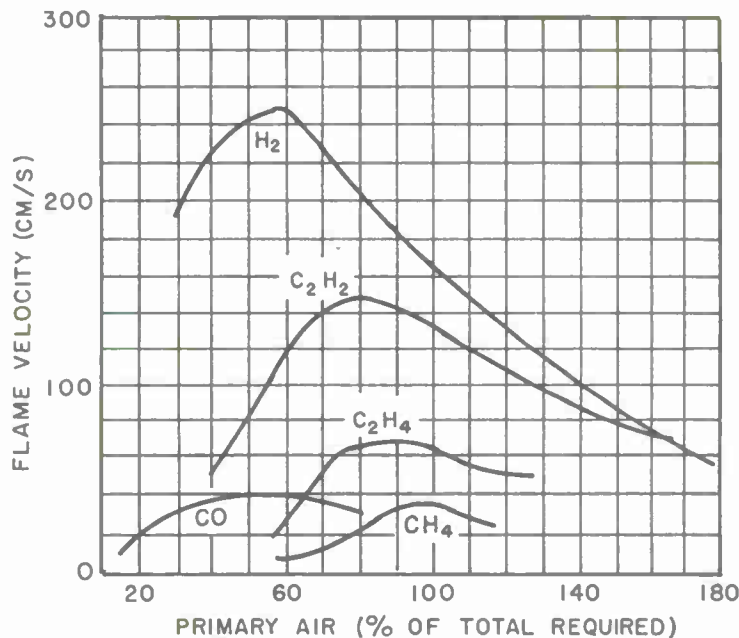


Fig. 1—Burning velocities of combustible gases mixed with air [9]

The generation of large quantities of heat for naval applications requires special consideration. The design and other technical problems of really large-scale H₂-fueled flame and catalytic burners have not been tackled to date.

3. Piston engines. One of the important factors in the choice of a fuel for a piston engine of the type used in land vehicles is the compression ratio. In general, high compression ratios favor higher outputs and higher thermal efficiencies. The permissible compression ratio is determined not only by the fuel characteristics, but also by such factors as mixture ratio, size and speed of engine, combustion chamber design, ignition timing, and mechanical strength. The important fuel characteristics are the flame speed and the limits of flammability [7].

Hydrogen has very wide limits of flammability when mixed with air (4% to 75% H₂), which enables an engine to operate with the mixture far from the stoichiometric proportion of 29.6%. The very high flame speed of H₂ leads to a marked tendency to "knock." However, flame speeds for all fuels are lower near the limits of flammability, and a fuel-air mixture that has an inherently high flame speed (H₂-air) exhibits an acceptable burning rate at a relatively lean mixture ratio. The tendency of H₂ to knock and to backfire can be eliminated if the mixture is adjusted to contain at least 25% excess air [12]. King et al [13] used H₂ in a test engine at a compression ratio of 10:1 without knock provided carbon deposits were absent. In an engine designed for and operated with H₂, engine deposits will not build up from the combustion of fuel, but deposits from engine oil are possible. Tests [14] using H₂ showed very small quantities of oxides of nitrogen in the exhaust.

Besides lubrication, there seem to be no significant obstacles to using H_2 in a conventional piston engine. Such an engine could be a high-performance, high-compression-ratio engine with a clean water-vapor exhaust and an extended life resulting from the absence of deposit buildup.

4. Gas turbine engines. Although optimal engine parameters have not been determined for an H_2 -burning engine, NASA successfully flew a B-57 aircraft with one of the J65 engines fueled with H_2 [15]. Combustion problems should be minor for turbine engines because H_2 has a very high flame velocity and can be prevaporized and premixed with air. These facts point to smaller, lighter engines than are possible with petroleum fuels.

Carbon deposits in combustors would be greatly reduced and possibly eliminated if bearing lubricant leaks could be minimized. Because of this and because the H_2 -air flame radiates at low intensities, radiation to the combustor walls could be reduced. Hence, the materials problem for higher temperature combustors would be greatly relieved, since the cooling of convective and conductive hot spots is more amenable to secondary airflow distribution.

Aircraft heat exchangers would have longer life because of the lack of fuel deposits from H_2 , and combustor nozzle life would be extended for the same reason. Furthermore, H_2 has a unique advantage for hypersonic flight because it has a high specific heat and can be heated to high temperatures without degradation or decomposition.

5. Rocket propulsion. NASA has exploited the properties of H_2 for large rockets. The military, on the other hand, give priority to readiness in weapons design, sacrificing the high performance which is possible with LH_2/LOX missiles. Thus, although LH_2 cannot be matched in some ways, it is likely that readiness will continue to dominate the military rocket design criteria to the exclusion of this propellant.

Electrochemical Oxidation

Despite the time that has elapsed since the principle was established in 1839 [16], no fuel cell has yet been exploited commercially. The key to the economically useful fuel cell is an overall cell reaction with a high electrical potential; cheap, stable electrodes with low overvoltages; cheap, stable fuel; and a stable, noncorrosive electrolyte of high conductivity. The difficulty is in getting all of these desiderata into a compact package that will last long enough. Unfortunately, reactions with high free energies involve reactive chemicals that are not normally stable. Stable electrodes with low overvoltage must of necessity be good catalysts for the electrode reactions and must have a large electrode area (high porosity). The best and most stable catalysts are usually the platinum metals and the cost of both the electrode materials and the porous construction is high. The most suitable electrolytes are usually corrosive strong acids or bases.

Much progress has been made in developing useful fuel cells, but the progress has been too dependent on costly trial and error. There is no complete theory of either catalysis or electrode processes that allows prediction of the necessary characteristics. A large number of thermodynamically favorable chemical reactions have not been realized

because there are no methods for catalyzing them. Table 3 [17] gives thermodynamic data on some H_2 fuel-cell reactions.

Table 3
Maximum Performance of Various H_2 Fuel-Cell Reactants*

Reaction	ΔG° , kcal/mole	E° (volts), 25°C	W-hr per pound of reactants
$1/2 H_2(g) + 1/2 F_2(g) \rightarrow HF(aq)$	66.1	2.87	1740
$O_3(g) + H_2(g) \rightarrow O_2(g) + H_2O(l)$	95.8	2.07	1010
$H_2O_2(l) + H_2(g) \rightarrow 2H_2O(l)$	85.2	1.85	1240
$1/2 H_2(g) + 1/2 Cl_2(aq) \rightarrow HCl(aq)$	33.0	1.43	476
$H_2(g) + 1/2 O_2(g) \rightarrow H_2O(l)$	56.7	1.23	1660
$1/2 H_2(g) + 1/2 Br_2(aq) \rightarrow HBr(aq)$	25.6	1.11	168
$Fe^{3+}(aq) + 1/2 H_2(g) \rightarrow Fe^{2+}(aq) + H^+(aq)$	17.77	0.77	164
$H_2(g) + I_3^-(aq) \rightarrow 2HI(aq) + I^-(aq)$	24.7	0.53	51.0

*Ref. 17.

Working H_2/O_2 Fuel Cells—In terms of electrochemical reactivity and energy content per unit weight, H_2 remains pre-eminent. The H_2/O_2 fuel cell operates best with either a strong acid or alkali electrolyte because these solutions are good ionic conductors and their large buffer capacity maintains constant pH and potential. The anode reactions are



The cathode reactions are



Since reactions involve three phases, fuel cells require a highly porous, solid structure in which a stable gas-liquid interface can be established. Both anode and cathode reactions require catalysts to promote the electrode processes. These catalysts must also be electronic conductors, be resistant to corrosion, and not be poisoned by impurities.

A small amount of direct reaction of H_2 with O_2 occurs because of solubility in the electrolyte. This generates heat and reduces efficiency. As current is increased, efficiencies decrease from about 90% to 50% at maximum power levels. This directly affects mission times, especially for space and undersea applications, where size and weight impose severe limitations.

As design temperature increases, heat rejection becomes easier, reaction rates increase, and the need for catalysts decreases. However, corrosion and stability problems increase.

For continuous operation, products must be removed at the same rate that reactants are introduced. For pure H_2 and O_2 , the cell is self-regulating, requiring only a constant-pressure gas feed. For an air-fed cell, air must be pumped at a rate proportional to the current drawn, and the excess air must be vented to prevent accumulation of nitrogen. Water can be evaporated into the vented airstream, but in an H_2/O_2 cell an alternative method for removal is required, such as recirculation of the moist H_2 in the cell through a condenser or a wick.

The fuel-cell battery [18,19] is a multiple stack of electrochemical cells connected in series to yield the required voltage. Each cell is fed with gas at the same rate. The cell stack is equipped with a heat-removal system, temperature control, fuel supply, oxidant supply, water-removal system, and electrical output. A control device coordinates all these operations. The power output is a variable low-voltage direct current and is conditioned to the required output. Thus even a simple H_2/O_2 fuel-cell battery is a complex chemical engineering system requiring far more than just electrochemical components. Table 4 [20] lists a variety of H_2/O_2 fuel cells that have been developed.

Table 4
 H_2/O_2 System Accomplishments*

Corporation	Item	Power	System	Date
Allis-Chalmers	Tractor	15 kW	$H_2/KOH/air$	1959
General Electric	Manpack, military	200 W	$H_2/IEM^\dagger/air$	1961
General Electric	Gemini, power source	1 kW	$H_2/IEM^\dagger/O_2$	1964
Westinghouse	Cell stacks	100 W	$CO-H_2/SE^\ddagger/air$	1965
Pratt and Whitney	Apollo, power source	1.5 kW	$H_2/KOH/O_2$	1966
Allis-Chalmers	Field power, military	5 kW	$H_2^\S/KOH/air$	1966
Union Carbide	Minibus	32 kW	$H_2/KOH/O_2$	1966
Texas Instruments	Field power, military	1 kW	$CO-H_2^\parallel/M_2CO_3/air$	1969
Pratt and Whitney	Residential power	10 kW	$H_2^{**}/H_3PO_4/air$	1971
Pratt and Whitney	Power module, DSSV	20 kW	$H_2/KOH/O_2$	1972

*Ref. 20

$^\dagger IEM$ = ion exchange material.

‡ Solid electrolyte; $(ZrO_2)_{0.85}(CaO)_{0.15}$.

§ Steam-reformed hydrocarbons and Pd-Ag diffusion.

$^\parallel$ Partial oxidation of hydrocarbons.

** Steam-reformed natural gas and shift reactor.

The GE Gemini cell (Fig. 2) [18] used as the electrolyte an ion-exchange resin in the form of a thin sheet of a sulfonated polystyrene that behaved as a strong acid. The electrodes were platinum black embedded in the surfaces of the sheet and in contact with cooled current-collector plates made of titanium or tantalum. The Gemini system

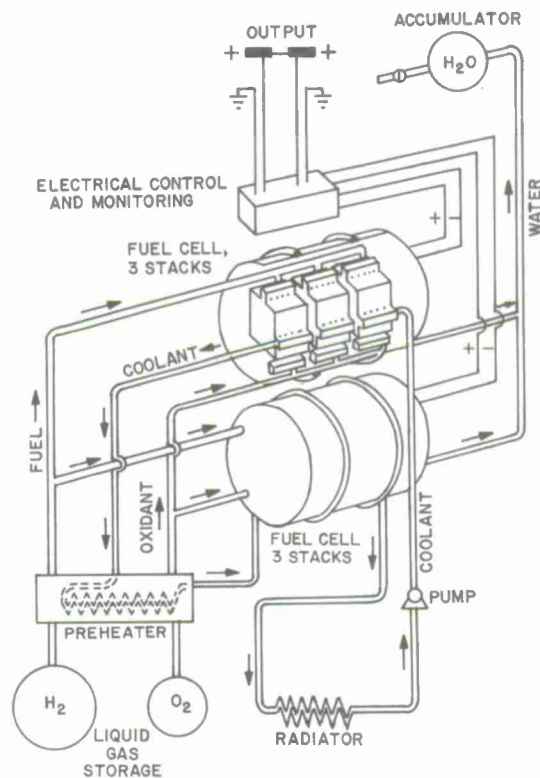


Fig. 2—Schematic arrangement of Gemini fuel-cell system [18]

contained 96 cells, each 8 in. by 7 in., arranged in three modules of 32 cells. The 1-kW unit was 25 in. long and 12.5 in. in diameter, and it weighed 68 lb. In addition, auxiliary pumping and control equipment was provided for the H₂, O₂, and coolant.

Both the Gemini and Apollo fuel-cell batteries were designed specifically for space operation, where fuel efficiency and reliability are crucial. Similar batteries for earth use are likely to have different characteristics. Because fuel cells operate with relatively few moving parts, they are quiet and can be installed close to the user.

An extensive test program for fuel cells powered with H₂ generated from reformed natural gas is now under way. This is the TARGET program, which uses the Pratt and Whitney 12.5-kW fuel cell and is sponsored by 32 natural gas companies. About 60 experimental fuel-cell powerplants are being installed to generate electricity onsite in apartment buildings, offices, banks, light-industry buildings, and single-family homes. Another major program, being conducted jointly by Esso Research and Development Company and France's Compagnie General d'Électricité [21], concerns the French-developed Alsthom thin-electrode fuel cell.

Comparison Among Fuel Cells and Other Energy Converters—Figures 3 and 4 [19]
compare energy with volume and weight for several electrical devices. Figure 5 gives

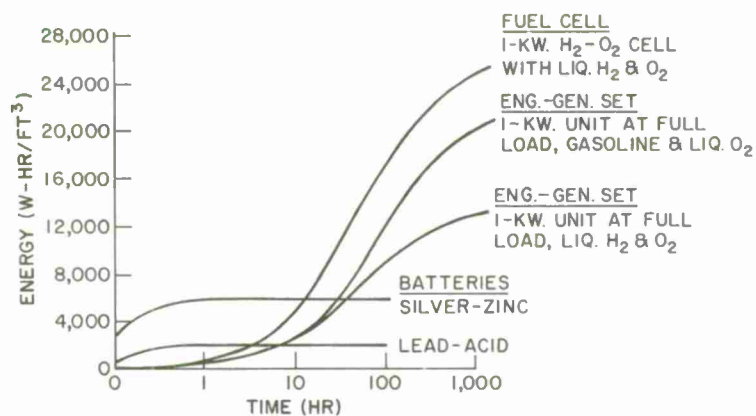


Fig. 3 — Energy-volume ratios for fuel cells, batteries, and engine-generator sets [19]

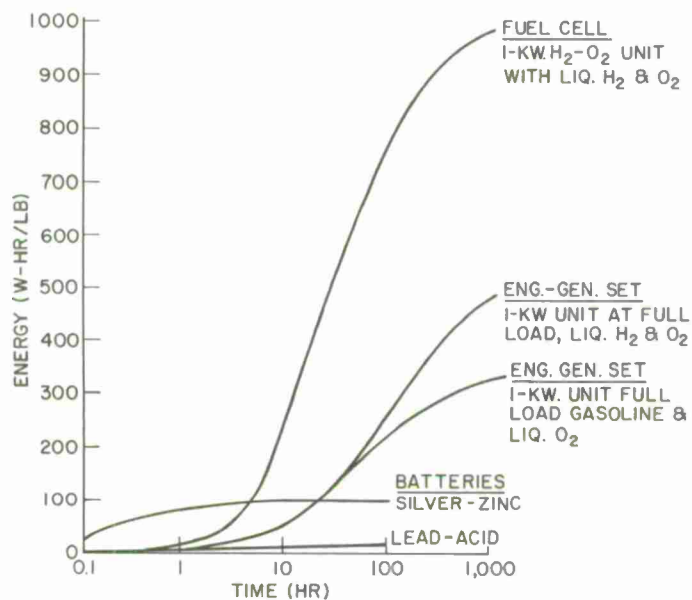
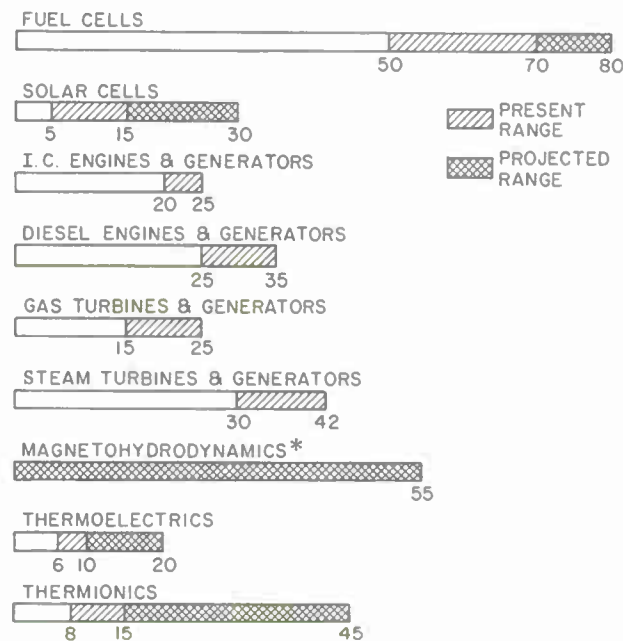


Fig. 4 — Energy-weight ratios for fuel cells, batteries, and engine-generator sets [19]



*Efficiency as topping stage with steam turbine;
demonstrated efficiency is 8% (Ref. 22)

Fig. 5—Efficiencies of energy-converting devices
in percent [19]

efficiencies of conventional engines using fossil fuels and fuel cells using inorganic fuels. The prices of inorganic fuels and fuel cells are still a long way from being economically competitive with those of heat engines using organic fuels. Fuel cells will become competitive with conventional energy sources only when a number of economic and technological objectives have been reached. A review [23] of the prospective use of fuel cells for surface naval propulsion concluded that although low- and high-temperature H_2 cells are potentially favorable economically, the requirements for surface naval propulsion are a long way from being met. The use of fuel cells must await the improvement of power-to-volume ratio and the construction of fuel-battery assemblies that have outputs in the megawatt range. In the long term, the potential for fuel cells is promising.

Small submarines and other submersible vessels equipped with H_2/O_2 low-temperature cells [23] will have operating times 10 to 30 times those of submarines propelled by the same volume of conventional lead-acid batteries. Fuel cells are competitive with batteries in small- and medium-sized submarines for operating times of less than a month.

Figure 6 [24] compares the weights of the most promising candidates for powering deep-ocean vessels as a function of mission duration and design depth. The three top-ranked fuel-cell systems— H_2/O_2 gas reactants stored in hard tanks at 6,000 psi; H_2/O_2 cryogenic liquid; and hydrazine/oxygen (N_2H_4/O_2) stored in soft tanks at ambient sea pressure—were shown to be relatively competitive at the Deep Sea Submergence Vehicle (DSSV) design depth (Fig. 6). Of the many chemical dynamic systems studied, the

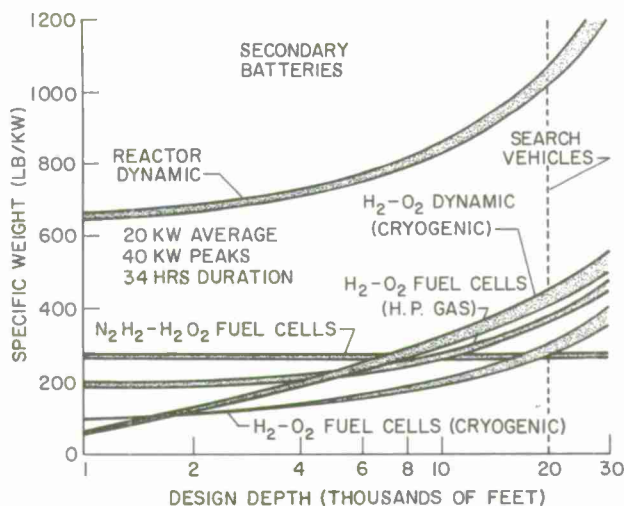


Fig. 6—Power system specific weight vs design depth [24]

closed-loop LH_2/LOX system stored in hard tanks was best. For these dynamic systems, both Rankin and Brayton cycle conversion systems were studied. Rich and Schmidt [24] concluded that fuel cells are the best power system for DSSV.

The problem for DSSV now reduces to selecting the best fuel-cell system. Much work on the $\text{N}_2\text{H}_4/\text{O}_2$ and hydrogen/peroxide ($\text{H}_2/\text{H}_2\text{O}_2$) fuel cells for underwater use has been done at the Naval Ship Research and Development Laboratory in Annapolis, Maryland [25]. The NSRDC work included simulated deep submergence to 6000 ft, using a $\text{N}_2\text{H}_4/\text{H}_2\text{O}_2$ system with an output of 1.8 kW at 18 V. Further work on both the cryogenic H_2/O_2 and the hydrazine fuel cells is necessary before a final selection of the best system can be made.

HYDROGEN PRODUCTION

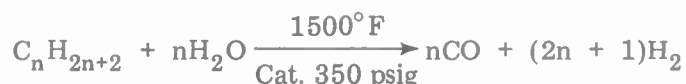
Since elemental H_2 is not found in our environment in significant amounts, it must be manufactured by applying energy to a hydrogen-containing compound, usually water. One generally chooses the least expensive available manufacturing process, but for the Navy's needs, convenience can also influence the choice [5]. For example, if nuclear energy is available, one may choose to produce H_2 by theoretically economical thermal processes, or the thermal energy could be converted to electricity for electrolysis of H_2O . Each Navy problem must be evaluated in terms of each energy source; the economics of the various processes are compared in the "Production—Cost" section.

About 3×10^{12} SCF of hydrogen is manufactured each year, most by the economical method of steam reforming of natural gas, but some by electrolysis where inexpensive energy (e.g., hydroelectric power) is available. However, future methods and costs will depend on the acceptance of the H_2 economy by the nation and world. Furthermore, dwindling fossil-fuel resources will limit the production of H_2 from these materials in the long term.

Fossil Fuels

Today, fossil fuels are the most economical source of large volumes of H_2 . The same technology is applicable to other sources of organic matter. The specific process used depends largely on the physical state of the raw materials: gases, liquids, or solids. All these techniques use the thermal splitting of H_2O molecules, deriving the energy from fuel oxidation.

Steam Reforming of Volatile Hydrocarbons—This will likely be the major process for producing H_2 until 1980 [26]. A desulfurized hydrocarbon gas is combined with steam in a reformer furnace to produce H_2 , carbon monoxide (CO), and carbon dioxide (CO_2) over a catalyst bed (generally Ni). The CO is removed by subsequent reaction in a catalytic shift converter to form more H_2 and CO_2 . The reactions are as follows



The reaction is endothermic, requiring heat. CO_2 is removed by standard techniques. The process would be greatly improved by the development of rugged catalysts that would be less susceptible to feedstock poisoning, yet effective at lower temperatures and pressures.

Partial Oxidation of Heavy Petroleum Fractions—This process can work with any petroleum fraction, but cannot compete economically with steam reforming where the latter can be used. It seems likely that this process will be a major source of H_2 between 1975 and 1985 [26]. A partial oxidation of the petroleum stock produces a synthesis gas of H_2 and CO while releasing the heat required for the shift reaction of CO to H_2 and CO_2 as follows:



The reaction is less efficient than steam reforming because some of the heat generated by oxidation cannot be used effectively. In addition, the oxidation requires, instead of air, pure O_2 , which requires additional energy and cost to produce.

Coal Gasification—The abundance of coal in the United States makes coal-conversion processes attractive. Processes to produce pipeline gas (CH_4) are in the pilot-plant stage [8,27], and the feasibility of H_2 production has been established [26]. As in steam reforming, the feedstock is reacted with H_2O at elevated temperatures (the reaction is endothermic) to form a synthesis gas which is subsequently treated with steam (shift reaction) to produce more H_2 . Physical preparation and heating of the coal feedstock are costly. The main reactions in a steam-oxygen process are as follows, for bituminous coal

represented as carbon:



The synthesis gas composition is more complex than shown because coal contains S and N compounds. The production plant is also complex because of the necessity of converting from solid to gas and the need for expensive pure O_2 .

Nonfossil fuels

Since H_2 can be produced in many ways, imaginative suggestions have emerged from diverse sources.

Plants—These can be the source of organic molecules for production of H_2 , as in coal gasification above. On the other hand, combustion of plants can provide the necessary energy for thermal or electrolytic production of H_2 . The plant sources include, but are not limited to, mariculture, agriculture, and municipal rubbish.

Bioconversion—It has been proposed that microorganisms may be developed that can synthesize H_2 directly using solar energy [28].

Decomposable Compounds—Many compounds decompose when heated to yield H_2 (e.g., NH_3 and metal hydrides). Since these systems could be considered as H_2 storage, they are discussed later under "Storage."

Exothermic Reactions—Since the heat from any exothermic reactions can be used to produce H_2 , one must consider an enormous list of reactions as candidates for H_2 production or storage. Some specific systems that release H_2 directly (e.g., $Al + \text{alkali}$) have special importance for consideration as H_2 storage.

Electrolysis

A General Electric water-electrolysis process based on solid-polymer electrolytes (SPE) has been proposed [29]. It was assumed that beyond 1985 an inorganic solid electrolyte would replace the solid-polymer electrolyte and that between 1985 and 2000 the system would operate at about $1000^\circ F$ with an electrical input of about 84 kWh per 1000 SCF of H_2 . The conventional electrolytic process requires 150 kWh/1000 SCF.

Commercial water-electrolysis processes now require about 8 gal. of makeup water per 1000 SCF of H_2 . Based on this, the water necessary to produce enough H_2 to meet projected energy requirements from 1985 until 2000 will range from 500 to 2400 billion gal. of water a year. This represents only a small fraction of our present water consumption, which is about 400 billion gal. each day for the entire United States.

For every ton of H_2 , 8 tons of O_2 are produced by electrolysis of water. Therefore, if large quantities of H_2 are produced, the O_2 production will be many times the present world consumption. However, some of this O_2 could be used for specific naval applications such as rocket and submarine propulsion.

Seawater or concentrated seawater (a byproduct of desalting) can be used in an electrolysis process to produce H_2 , but yields Cl_2 and $NaOH$ rather than O_2 . However, the power required per unit volume of H_2 would be doubled, and disposal of the Cl_2 and $NaOH$ would pose a problem.

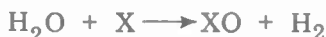
Thermal Energy

All sources of energy can be converted to thermal energy with a theoretical conversion efficiency of 100%. However, thermal processes for producing H_2 are Carnot limited and do not have high energy efficiencies. Yet, thermal processes have tremendous potential for energy sources that begin as heat since the efficiency of conversion of heat to other energy forms is itself limited by thermodynamic principles. Nuclear, solar, and geothermal sources of energy could provide this heat directly.

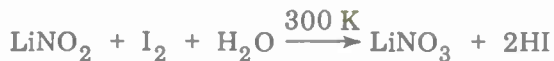
High-Temperature Water Decomposition—At temperatures around $4000^\circ C$, H_2O is split into H , H_2 , O , and O_2 , but no process exists for separating these species efficiently before they can recombine. Solar furnaces may provide the required temperatures, but currently envisioned nuclear reactors will operate at temperatures below $700^\circ C$ [30].

Low-Temperature Water Decomposition—Since heat is commonly available directly from many sources, multistep closed-reaction systems are being considered for H_2 production from H_2O [30-33]. These cycles are Carnot limited to efficiencies of about 85% in theory and perhaps 65% in practice [32], but ecological advantages of regenerating all materials except H_2O are significant.

Thermodynamic constraints make two-step processes such as the following unlikely:



where X is any appropriate atomic species. However, multistep processes are not only possible, but commercially interesting [32], though none have been run in large-scale tests. Numerous reaction schemes are being compared by computer analysis [30] and by chemical reasoning [31-32]. A typical three-step suggestion is as follows [31]:



The overall efficiency is limited by the temperature range 300 K to 750 K because each step of the process must occur in a separate reaction chamber with the usual complexities of operating a chemical plant.

Thermal processes are in such an early stage of development that further research is needed before they can be evaluated properly.

Production—Cost Summary

Today's price for LH_2 is \$4 to \$6 for 10^6 Btu (20-30 cents/lb), depending on the size of the plant [6,34]. This price makes H_2 cost \$24 to \$36 for an amount that has an energy content equivalent to a barrel of fuel oil. Steam reforming of oil or natural gas, the cheapest method for H_2 production, is the process now used commercially. Increasing the reforming plant size from 30 to 2500 tons per day might reduce the price to \$1.60 per million Btu [26]. Steam reforming is not a practical, long-term, large-scale process, however, since it requires natural gas as a raw material.

The proposed "hydrogen economy" will produce H_2 by electrolysis, the electricity coming from large nuclear reactor plants. Thus, the cost for electricity will determine in a major way the cost of LH_2 . Winsche, Hoffman, and Salzano [5] formulated the effect of electrical cost on H_2 production cost. Putting their formula in terms of one million Btu of H_2 (thermal equivalent), we obtain

$$\text{cost of electrolytic } \text{H}_2 = 0.38 g,$$

where g is the cost of electricity in mills/kWh. The cost of transportation and distribution, which is higher for H_2 than for distillate fuels, must be added. Cost at the plant site is tabulated below for several electricity rates.

g (mills/kWh)	Cost for 10^6 Btu (dollars)
1.0	0.38
2.0	0.76
4.0	1.52
6.0	2.28
10.0	3.80

Predictions of rates for electricity from nuclear power plants cover a wide range. Further, the influence of potential power sources, such as liquid-metal fast-breeder reactors and fusion reactors, on rates cannot be defined.

CDR Moore of the Navy Petroleum Office reported the following prices being paid in 1973 for distillate fuels [35]

Fuel	10 ⁶ Btu (dollars)	Barrel (dollars)
Navy Distillate	0.95	5.50
JP-5	1.17	6.80
JP-4	1.09	6.30
Diesel	1.17	6.80

Distillate fuel prices have increased drastically in recent years, and further significant but unpredictable increases will occur by the year 2000.

Thus, although the current price of H_2 far exceeds that of distillate fuels used in the Navy, this may not be the case in 10 to 20 years. The price per energy unit is certain to be higher, however, for any fuel, and the Navy fuel bill will be 2 to 3 times the 1973 bill if operations are continued at current levels. Development of alternate liquid fuels from oil shale and coal could stabilize the price at the lower value.

Figure 7 shows the historical pattern for relative costs for H_2 and JP fuel, with the JP cost in 1950 taken as 1 [36]. The dramatic decrease for H_2 since 1955 is levelling off, but projected costs [26,37] indicate that H_2 and JP may cost about the same in 2000.

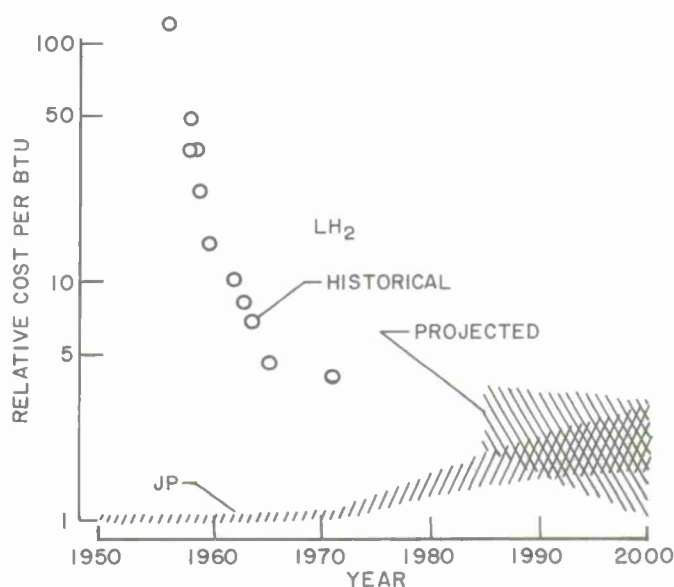


Fig. 7—Future fuel cost [36]

Commentary

The Navy may pursue special applications for H_2 fuel. For instance, small submersibles could be powered with H_2/O_2 fuel cells, and remote bases may use environmental energy sources to generate hydrogen for heating or energy storage. These limited uses do not depend on large-scale conversion to H_2 fuel by the civilian sector. Adequate supplies of H_2 fuel for DSSV's is commercially available today in the United States, but continuous

operation with such craft in distant areas would require H_2 production on a mother ship. Seawater electrolysis is a preferred process in this situation in spite of the higher power requirements. Remote bases could also produce H_2 by electrolysis, using wind power or solar energy to generate the electricity.

If the Navy converts major elements of the fleet to LH_2 , U.S. production must be increased. Since the Navy is a minor consumer in the total fuel picture, Navy conversion to H_2 might appear feasible. However, because of the complex interactions with national fuel factors we feel that significant use in the Navy could come only with national adoption of the "hydrogen economy."

Since large Navy usage of H_2 cannot be envisioned before 1990 because of the capital investment in current ships and aircraft, steam reforming and partial oil oxidation processes will not be important to the Navy fuel picture. Coal gasification will probably be the major H_2 production process from 1980 until the time when nuclear energy contributes a large fraction of our national power.

HYDROGEN STORAGE

Despite its high energy content per unit weight, the low energy content per unit volume of H_2 increases the size and cost of storage facilities. Storage as a gas for industrial and residential purposes can be handled much like natural gas storage, but storage as a liquid on craft such as ships and planes requires significant departures from current practice with liquid fuels.

Storage as a Gas

If the nation converts to an H_2 economy, many natural-gas storage facilities can be adapted for H_2 . The Institute of Gas Technology [30] states that depleted gas and oil fields as well as aquifer rock formations can be used for high-pressure H_2 storage, as they are for natural gas. Mined caverns and salt cavities show less promise.

Natural-gas storage vessels can also be converted to H_2 use, but the effects of hydrogen embrittlement at higher pressures (3000 psi) must be considered. The low volumetric heating value of hydrogen can be increased by increasing the pressure. However, this increase is not as great as it is for natural gas because of the difference in compressibility factors. Thus the ratio of Btus per unit volume for H_2 /natural gas decreases from 0.32 at 1 atm to 0.21 at 2400 psi. A potential Navy interest in H_2 gas is its use at shore facilities. A station would tie into a commercial H_2 distribution system, and only limited onbase storage facilities would be required. Vehicular storage of H_2 gas for fuel use need not be considered because of the low volumetric heating content.

Embrittlement in the transport and storage of hydrogen was recently reviewed by Bever [38]. Liquid hydrogen appears not to cause hydrogen embrittlement of steel. Systems of steel pipelines and storage tanks, based upon current technology, that are now in use are

1. high pressure hydrogen tanks
2. processing equipment for hydrogen in the chemical and petroleum refining industries
3. distribution of manufactured gas which contains more than 50% H_2
4. two pipelines, one in Texas and one in Germany, reported to carry H_2 over appreciable distances.

A body of technology for transport of H_2 is available, but an intensive investigation of industrial experience should be made. According to the *Metals Handbook* [39] at temperatures under $400^\circ F$, carbon steels are satisfactory at least up to 10,000 psi. These are the steels now used in long distance pipelines and gas distribution systems in cities. The special problems of welds are well known and even though further studies are required, real systems are now in operation. Recent papers [40a-40c] review the current state of knowledge of hydrogen embrittlement.

Storage as a Liquid

NASA pioneered LH_2 usage in the space flight programs. Two 900,000-gal. spherical vacuum-jacketed containers are part of the Apollo complex at the Kennedy Space Center. Daily boiloff losses from these tanks are 0.05% [30]. This type of design is limited in size to about 3 million gal., and the vacuum-jacketed insulation required in the construction is much more expensive than the dry-gas-purged perlite insulation which is satisfactory for liquefied natural gas. Boiloff losses from the latter construction would be 1-3% per day for tanks with capacity of 400,000 to 5 million gal. [26] and boiloff cost would be in the range of \$500,000 to \$2,500,000 per tank per year. In addition, this type of tank requires a purge gas which will not condense at the boiling point of H_2 . Helium is too valuable to assign to this purpose and H_2 , the only other gas noncondensable at this temperature, has a high thermal conductivity.

Hallett [26] considered the design of aboveground, nonspherical, single-wall storage tanks. External insulation affords better performance than internal insulation, but the boiloff losses are high, similar to those for the gas-purged spherical tank design. Hallett also considered underground LH_2 storage. Internally insulated prestressed concrete tanks have been used for liquefied natural gas (LNG) and have the most advantages for underground LH_2 storage.

The Chicago Bridge and Iron Co. designed and built LH_2 -carrying barges for NASA [41]. The capacity of the storage tanks was 240,000 gal., and the thermal barrier between two concentric cylinders was 23 in. of evacuated perlite. This insulation limits boiloff to 0.25% of capacity per day. Large liquefied natural gas tankers (12 million gal.), which use nonevacuated insulation, exhibit boiloff rates of 0.25% per day [42]. The gas boiloff provides a portion of the engine fuel for some tankers. Since evacuated tanks cost too much for LNG storage, no background information is available for the potential use of evacuated, insulated tanks on large LH_2 tankers.

Vehicle storage tanks, even on new construction, would exhibit larger boiloff than the LH_2 tanks just described. Factors that account for this are (a) smaller capacity tanks

with higher surface/volume ratios, (b) impracticality of spherical tank design, and (c) the problem of maintaining vacuum in vehicle tanks. We estimate that boiloff losses on large ships such as aircraft carriers would exceed 3% per day and losses of greater than 10% per day would be expected for Navy fighter planes, assuming single-wall, externally-insulated, nonspherical tanks. Witcofski [36] states that flightweight, evacuated LH_2 tank construction has not been successful.

Unconventional Storage Methods

At normal temperatures, greater quantities of H_2 can be stored per unit volume by means other than conversion to liquid. The most exciting concept is the reversible addition of H_2 to specific metals or alloys such as Mg_2Ni . This alloy can absorb twice the amount of H_2 per ft^3 as can be stored as LH_2 [43]. Although only a modest pressure is required, a tremendous weight penalty is imposed. Naval carrier aircraft, which are weight limited, cannot accept such an increase in operating empty weight. The metal-hydride concept exhibits more promise for shore and ship storage of H_2 . A severalfold improvement in adsorption capacity would spark new interest in this type of storage, and continued study on metal hydrides is in order.

Hydrogen can be chemically combined as a means of overcoming cryogenic storage problems. The most likely chemical, ammonia, has a low energy content on a weight basis as well as a volume basis and is much inferior to hydrocarbon fuels from both standpoints.

A third concept involves storing an active metal that produces H_2 by reaction with water. Thus aluminum, lithium, boron, and other metals might relieve the problems of LH_2 handling in some applications. These three metals have H_2 volumetric energy contents equal to or greater than that of LH_2 . This type of H_2 storage faces weight penalties just as the metal hydride idea does. In addition, regeneration of the metal oxide is impractical in most Navy systems, refueling procedures are unfavorable, and cost is prohibitive. However, it should be considered for special, volume-limited, short-range missions.

H_2 Liquefaction Energetics

Cooling H_2 gas to its boiling point and converting the cold gas to liquid theoretically require 1600 Btu/lb of energy [30]. Since H_2 liquefaction processes operate at very low temperatures, overall efficiency is very low. Hallett [26], assuming some technological advancements over the present state of the art, predicts that even after 1980 liquefaction energy consumption will be 4.46 kWh/lb (15,000 Btu/lb). This processing energy amounts to 29% of the energy released (51,571 Btu/lb) from H_2 combustion.

LIQUID HYDROGEN USAGE IN THE NAVY

Comparison of LH_2 and Petroleum Fuels for Today's Fleet

Most fuels used by the Navy have high flashpoints. Fuels for primary ship propulsion, Navy Special Fuel Oil (NSFO) and Navy Distillate (ND) fuel, have a minimum flashpoint of

150°F, whereas the major aircraft fuel, JP-5, has a minimum flashpoint of 140°F. The use of fuels with such low volatility brings distinct safety advantages to Navy operations. For instance, military aircraft using JP-5 have a lower percentage of fires during crash landings than aircraft using JP-4, a fuel used by the Air Force which has a flashpoint of 0°F or lower [44]. Also, the Navy ship and aircraft turbine fuels may be stored almost anywhere a tank can be built into a ship since the vapor concentration in the space above these fuels is too low to be flammable. The Navy even stores fuels in the skin tanks of ships to provide protection against torpedo attack. The flexibility of locating fuel tanks in many parts of a ship increases fuel capacity and hence reduces the limitations on tactical and strategic operations.

Storage of LH_2 on today's ships would greatly increase the fire and explosion hazard, cut the storage capacity on an energy basis by a factor of four, and require major overhaul of all fuel storage, pumping, piping, dispensing, and burner facilities. Installing the required insulation on storage tanks and pipelines would be prohibitive in cost even though these changes are not completely impossible on a physical basis.

Fuel tank capacity on the "Forrestal"-class aircraft carriers is 7,828 tons of boiler fuel and 5,882 tons of aviation fuel [45]. If the same tanks were used for LH_2 storage, the weight of H_2 would be only 1160 tons because of its low density (even without reducing tank volume by addition of insulation). On an energy comparison, LH_2 stored on a "Forrestal"-class carrier could supply only 25% of the fuel value available from current fuels. To maintain the same current state of readiness, the Navy would have to refuel at sea four times as often. Thus, this hazardous operation would be needed every day in many operational situations if H_2 replaced current petroleum fuels.

With respect to current aircraft, use of H_2 fuel would be structurally impractical and tactically unwise. To minimize evaporation losses, LH_2 tanks must have low surface/volume ratios. Further, the required insulation precludes the use of integral tanks which combine the dual purpose of fuel storage and structural strengthening. Only fuselage and/or pod tanks could store LH_2 in fighter and attack aircraft [46]. These factors, in addition to the low density of LH_2 , restrict the capacity for energy storage. The low density of LH_2 is a major restraint by itself and would reduce the range of current carrier-based aircraft by a factor of three.

Thus, we conclude that a change to LH_2 would severely compromise current Navy fleet operations. Present ships and aircraft would require drastic overhaul and would have significantly decreased military capability.

Usage In Fleet After Year 2000

In new construction, the Navy could integrate a novel fuel usage, such as LH_2 , into ship and aircraft design. Fuel storage and piping systems, including cryogenic insulation, would be a major design consideration.

Ships—Although a ship designed and built for H_2 fuel would present no unique structural problems, energy capacity comparable to present vessels would require radical new

concepts and/or operations. A naval vessel is limited in volume since it must be sized to accomplish a specified mission and attain a minimum performance. It would be necessary either to:

1. Retain current vessel sizes but increase the volume available for fuel storage and/or increase propulsion efficiency or to
2. Increase vessel size but develop methods to reduce drag.

Without enlarging vessels, instrumentation and automation could be increased to perform ship functions and hence reduce crew space, and the functions of each vessel could be specialized so that space assigned to other types of storage or operations could be converted to fuel storage. The propulsion efficiency could be improved by raising pressure in ship boilers and raising temperature in gas turbines to attain more effective use of fuel, and by developing other conversion devices, such as H_2/O_2 fuel cells, which have inherently greater efficiencies.

Increasing vessel sizes would require extensive development of recent vessel design innovations, such as hydrofoils and surface-effect machines, and vigorous research in the field of drag-reducing agents.

For safety, LH_2 fuel should be stored far from the skin in any new ship design. In addition, heavy armor plate is needed to protect H_2 storage areas, a design principle used for aviation gasoline storage on aircraft carriers.

Operation of naval ships on LH_2 would be marginal from many aspects—logistics, tactics, safety, cruising range, and strategy.

Aircraft—The aircraft industry and NASA have developed many proposals for vehicles burning LH_2 [47-49]. These proposals cover a wide speed range (subsonic through hypersonic) and capitalize on hydrogen's high heat of combustion per pound. This property of hydrogen is most beneficial for craft with high fuel-to-gross-takeoff-weight ratios and long ranges. Considering Navy operations, this advantage would be greatest for aircraft operating from shore stations—long-range patrol, transport, and reconnaissance planes. Short-range aircraft, fighter and attack vehicles, lose the advantage predicted for LH_2 -fueled systems.

Harris at NASA Langley [46] studied the use of LH_2 in two military aircraft, a V/STOL similar to the Harrier and a supersonic interceptor with F-15, F-14 level of performance. Mission radii of the study vehicles were identical to the Harrier and F-15. The Harrier, a small plane of 13,000 lb empty weight, failed to show any performance benefit by conversion to LH_2 although the maximum takeoff weight was decreased.

The study for the fighter plane showed that use of LH_2 would be detrimental to aircraft performance. Since the fuel storage volume must be increased by a factor of four and the fuel tanks must be located in the fuselage, the fuselage must be lengthened or increased in diameter. Either change increases drag; consequently this design aircraft of about 40,000 lb empty weight could not attain supersonic speed.

These preliminary studies show that aircraft fueled with H_2 designed for operation from carriers would be severely handicapped compared to those fueled with JP fuel. Long-range planes, transport and patrol, would exhibit advantages in takeoff weight, empty weight, and fuel efficiency if fueled with LH_2 .

Other Factors

Hazards associated with LH_2 fuel impose increased vulnerability probabilities during operations on both ships and aircraft. These hazards result from the volatility, flammability, and ignition properties described elsewhere in this report.

Fleet use of LH_2 would require conversion of tankers to cryogenic storage, a significant modification. If future naval operations are at the same level as today, new tankers with combined capacities several times that of the current total tanker capacity would have to be built. The Navy would also have to drastically revise refueling procedures to overcome strategic and tactical operational limitations.

Other Concepts

Since fuel logistics and capacity at sea are major problems in LH_2 usage, continuous production of this fuel on ships might be feasible. A large craft, with nuclear reactors for propulsion and H_2 generation, could supply LH_2 to onboard aircraft and to an accompanying task force. Although this concept was considered impractical in previous studies [50,51], it should be reexamined. Solar energy or other environmental energy sources need not be considered for such shipboard applications, since they are diffuse sources of power.

Metal-hydride storage of H_2 overcomes some of the difficulties of cryogenic storage. This concept could not be applied to aircraft, since these compounds would greatly increase the gross takeoff weight without materially increasing the fuel weight. Metal-hydride storage of H_2 on volume-limited ships may be feasible, but the influences of added weight, storage efficiency, and high cost of metals on the total system need careful study.

Stored LH_2 could be used to cool electric conductors to drastically reduce their resistance; thus, cables and electric motors could be much smaller and the possibility of ship propulsion by electric motors could be considered.

Special Applications

The discussion of the use of H_2 presented above has concentrated on major applications in the Navy—fuel for ships and aircraft. Some small-scale uses exhibit potential for earlier adaptation to H_2 .

Isolated shore bases could use gaseous H_2 for energy storage, provided an environmental energy source is available. Intermittent sources, such as solar and wind power, can supply an adequate amount of total energy, but not continuously. When electricity is being generated, the excess could be used to electrolyze water and the H_2 formed could be stored. Combustion of this H_2 would meet the electrical power and heating needs during darkness or slack wind periods.

Some small submersibles, particularly those designed to operate on advanced, high-efficiency fuel cells, may benefit from H_2 use. Liquid H_2 usage would be limited to short-duration designs because of boiloff losses, but improved metal-hydride storage systems would offer new flexibility to the designer. Careful volume and weight tradeoff studies are needed to define this H_2 application. Fuel cells or combustion devices burning H_2/O_2 should be considered for craft that must have nondetectable exhaust products.

Another potential use for H_2 is to power fast surface-effect vehicles. Liquid H_2 would be the preferred form, since weight is important for such craft. Again, high propulsive efficiency is essential. Evaluation based on craft mission, cruise range, and cruise duration would optimize vehicle size.

HAZARDS IN THE STORAGE, TRANSPORTATION, HANDLING, AND USE OF LIQUID AND GASEOUS HYDROGEN

History

Hydrogen is highly flammable, but despite the fact that it has been used with comparative safety for a variety of industrial purposes for many years, there is widespread fear of the hazards in its use. The Hindenburg airship disaster in 1937, because of its sensational nature, no doubt contributed to this fear which has been aptly referred to as the "Hindenburg syndrome" [52]. Nevertheless, both liquid and gaseous hydrogen can be used safely so long as its properties are known and understood and provided strict safety codes are developed and scrupulously observed.

Considerable experience over the years has resulted in safe handling procedures and safety codes for storing and piping heating gas to homes and industry. Manufactured gas has been extensively used for many years with relative safety despite its high flammability and toxicity. It consists of high concentrations of *hydrogen* (up to 60%) and carbon monoxide. Natural gas, which has largely replaced manufactured gas, consists chiefly of methane, with lesser concentrations of other gaseous hydrocarbons. Natural gas is also highly flammable and, as in the case of manufactured gas, must be used with great care. The flammability concentration limits in air of four representative gaseous fuels are shown in Table 5. Note that hydrogen has a wide flammable concentration range compared to natural gas (and other hydrocarbons). Acetylene and water gas, an example of a gas manufactured from coal, also have wide flammability ranges. However, experience with hydrogen-containing gases to date suggests that a safe technology should be possible for pure hydrogen gas.

Liquid H_2 , because of its cryogenic nature, will require advanced safety procedures if it is to be used widely in industry and transportation. Some technology has been developed over the last two decades by NASA and the armed services for use of LH_2 as a rocket fuel [53,54]. Strict safety codes have been adopted and practiced, so that LH_2 has been used for rocket fuel with relative safety. The same would be required for any potential Navy use.

Table 5
Typical Flammability Limits in Air of Gaseous Fuels

Fuel	Flammability limits (% by vol)		
	Lower	Upper	Range
Hydrogen*	4.0	75	71.0
Acetylene†	2.5	81	78.5
Natural gas† (Average Data)	5.1	15.0	9.9
Water gas†	7.0	72.0	65.0

*Ref. 57.

†Ref. 55.

Nature of the Hazard of Hydrogen

Flammability Properties of Hydrogen—The important flammability properties of hydrogen are shown in Table 6. Methane data are included in the table for comparative purposes. As noted, the flammability concentration range of hydrogen in air is wide and is greater than that of methane and most other flammable gases. This means that hydrogen leakage into a confined space will form a mixture with a greater probability of ignition. In closed air spaces, these mixtures might even detonate, but the detonation concentration range in air (18 to 59%) [64] is narrower than the flammability concentration range. Detonation is less likely to occur in open air spaces unless ignition is caused by a high-energy source such as a shock wave or a blasting cap. Replacement of air in an H_2 —air mixture by oxygen increases the likelihood of detonation, and a weak spark could ignite it [53].

The burning velocity in air during deflagration (about 10 ft/s) is about ten times that of methane (Fig. 1). Hydrogen detonation speeds may be of the order of several thousand feet per second [53]. The limiting oxygen concentration which will support a hydrogen flame is 5% (if nitrogen is the inert gas), about 0.4 that required for methane. Thus, flame extinguishment is more difficult.

The minimum temperature necessary for hydrogen to ignite spontaneously in air (the autoignition temperature) is relatively high compared to methane and other hydrocarbons. Thus, under some circumstances hydrogen is less likely to be ignited if it comes in contact with hot objects. However, experimental autoignition temperature data, including those in Table 6, are obtained in glass vessels. If other surfaces (such as rust) which catalyze hydrogen-oxygen reactions are present, ignition of H_2 in air might occur at ordinary temperatures. Hydrocarbons do not experience similar catalysis. At reduced pressures, however (0.2 to 0.5 atmosphere) the autoignition temperature may be reduced to about 650°F [53].

The minimum spark ignition energy necessary to ignite hydrogen—air mixtures is about one sixteenth of that for methane, and the minimum igniting current for an arc (or "break spark") is about 38% of that for methane. This means that hydrogen—air mixtures can be very easily ignited by ignition sources such as electric motors and switches.

Table 6
Selected Flammability Properties of Hydrogen and Methane

Property*	Hydrogen	Methane
Oxygen concentration in nitrogen below which no mixture is flammable (% by vol) [55]	5	12
Net heat of combustion (Btu/cu ft of gas) [56]	274.9	914.5
Net heat of combustion (Btu/lb) [56]	51,571	21,502
Autoignition temperature in air (°F) [53-55, 57-60] †	1,072	1,001
Minimum spark ignition energy in air (mJ) [59]	0.018	0.29
Minimum igniting current (arc) in air (A) [61]	0.075	0.195
Minimum quenching distance (in.) [59]	0.024	0.08
Maximum laminar burning velocity in air at 25°C and 1 atm. (ft/s) [62, 63]	10.2	1.1
Flame temperature at stoichiometric concentration in air (°F) [64]	3,713	3,407

* Numbers in brackets refer to the References.

† Average data.

The minimum quenching distance to extinguish a hydrogen flame is about one-third that of methane, so that conventional flame arrestors intended for methane and other hydrocarbon flames would not be effective with hydrogen.

Other Fire Properties of Hydrogen [53]—Pure hydrogen flames are invisible, so that the problems of damage control and fire extinguishment are complicated by the difficulty of seeing the fire. Spills of LH_2 burn rapidly and steadily in a column that is vertical in still air and of the same diameter as the pool. Compared to ordinary fires, there is much less heat radiated to nearby objects. Hydrogen pool fires do not last long, since LH_2 evaporates very rapidly.

Although the prime danger of hydrogen leakage, or LH_2 spills, is fire, another hazard must be considered. Certain metals and nonmetals lose their ductility when subject to the low temperatures of LH_2 and may fracture as a result of thermal stress [54]. For this reason, large spills may present problems if the materials surrounding the spill are subject to this phenomenon.

Liquid H_2 is subject to contamination by condensation of liquid or solidified air from the atmosphere. Such mixtures are unstable and may explode in the presence of catalysts, ignition sources, or friction.

Hydrogen can react violently with oxidizers such as oxygen, chlorine, and fluorine, and contamination must be avoided. Containers for hydrogen must be purged with an inert gas, and containers that have been used for hydrogen must be purged of hydrogen before admitting air.

Finely divided platinum and some other metals will cause a mixture of hydrogen and oxygen (or air) to explode at ordinary temperatures [65]. If a jet of hydrogen in air impinges on platinum black, the metal becomes hot enough to ignite the gas [65].

Ship Damage Control [53]—The only positive way to extinguish hydrogen fires is to let them burn out under the best control possible until the flow of hydrogen can be cut off. If the flow is not stopped, measures to extinguish the flame temporarily may result in formation of highly flammable vapor mixtures which will explode when reignited. Carbon dioxide must not be used to extinguish hydrogen flames because the flame temperature is high enough to reduce the carbon dioxide to carbon monoxide, a highly toxic gas. Standard dry chemicals are preferred because they make hydrogen fires visible.

Other Hazardous Properties of Hydrogen [53]—Hydrogen is colorless, odorless, and tasteless and cannot be detected by the senses. For this reason, hydrogen leaks are likely to go undetected. Because of low viscosities and densities, both liquid and gaseous hydrogen have very high diffusion rates, and are particularly subject to leakage. The diffusion rate of gaseous hydrogen is about 3.8 times that of air. Liquid hydrogen leaks about 100 times faster than liquid nitrogen. The fast diffusion rate can be a virtue, because spills can diffuse to a nonflammable mixture in a relatively short time.

Hydrogen exists in two molecular configurations, orthohydrogen and parahydrogen. At normal temperatures, hydrogen gas is chiefly orthohydrogen, while liquid hydrogen at

the boiling point (-422.0°F) is mostly parahydrogen. Spontaneous conversion of ortho-hydrogen to parahydrogen may occur with a large generation of heat, and can cause considerable liquid boiloff. Hence, it is necessary to obtain the parahydrogen form early in the liquid-hydrogen production cycle.

Special Precautions in Hydrogen Storage, Handling, and Use—Recommended practices for hydrogen storage are listed below [53,54].

1. Leakage of containers, piping, and connections must be prevented by careful choice of construction materials and techniques.
2. The dewar flasks in which liquid hydrogen is transported and stored must be protected against breakage and puncture, such as that caused by shrapnel.
3. As with manufactured and natural gas, suitable odorants should be added to hydrogen gas so that leaks may be detected. This is of no value for LH_2 because the odorant would be frozen.
4. All pressure vessels should be equipped with suitable burst diaphragms or pressure-relief valves.
5. Containers that have held hydrogen must be purged with inert gases before introduction of air or other oxidizers, and containers in which hydrogen is to be stored must first be purged of air or other oxidants.
6. Ignition sources (sparks, flames, hot objects, etc.) must be removed from areas where hydrogen is stored or used.
7. Ventilation must be plentiful in areas where hydrogen is stored or used.
8. Because of its small quenching distance, conventional screen-type flame arrestors are not suitable with hydrogen.
9. Liquid H_2 , as a cryogenic liquid, can cause severe damage if it comes in contact with skin.
10. The disposal of large quantities of H_2 is best accomplished in remote areas by burning with air.
11. Damage control is best accomplished by shutting off the H_2 supply and letting any spilled or leaked H_2 burn itself out.

Because of its flammability, gaseous hydrogen must be handled with great care, but the technology will not be very different from that of handling manufactured gas. Liquid H_2 , however, because of its cryogenic properties, presents additional problems and will require special technology.

If hydrogen is to be used for ship or aircraft fuels, the hazards of handling and storing will be *considerably* more than those of handling the petroleum-derived liquid fuels of today's Navy, and these hazards will be compounded under combat conditions. The limited experience with LH_2 handling, especially spills, precludes a detailed assessment of hazards.

TOXICITY AND EFFECT ON THE ENVIRONMENT

Engine Exhaust

Burners and engines burning petroleum, or any fossil fuel, produce many undesirable products (carbon monoxide, partially oxidized hydrocarbons, sulfur dioxide, nitrogen oxides (NO_x), and smoke) which pollute the atmosphere. Hydrogen fuel drastically reduces this pollution problem, since NO_x is the only one of these contaminants produced. Moreover, H_2 -air combustors can operate in a premixed mode and at fuel-to-air equivalence ratios of less than one. Such conditions prevent high combustor temperatures on a local or overall basis, thus minimizing NO_x production. Ferri, who developed this proposal for aircraft turbines fueled with JP [66], has extended the concept to H_2 -fueled engines [67].

Thermal Pollution

Energy must be expended to produce H_2 . Fossil or nuclear fuels may provide the power, in which case the earth must absorb an extra burden of waste heat. Use of solar energy avoids this disturbance of the global heat balance.

Toxicity

Hydrogen is not toxic, but gross leakage into a closed space could cause anoxia as the oxygen partial pressure is reduced by dilution.

CONCLUSIONS

Hydrogen has many desirable properties as a fuel. It can be burned efficiently in all burners and engines in widespread use today. Furthermore, it is a superior material for fuel cells with potential for efficiencies higher than conventional types of combustion.

A high heat of combustion is the property that makes hydrogen attractive. However, the low density of liquid hydrogen negates much of the advantage obtained by the heat of combustion, particularly for volume-limited vehicles. Thus, the use of hydrogen in major ships and carrier aircraft is not promising. Special applications, such as fueling small, weight-limited craft, may be practical. Remote naval facilities, if located near environmental sources of energy, could use the hydrogen fuel storage and transport idea.

Hydrogen is not a prime fuel, but must be produced by putting energy into chemical reactions. The most promising reactions today are based on fossil fuels, with coal having long-term resource potential. An expected trend to large-scale nuclear power generators should make the electrolysis of water the favored H_2 production process in the long term.

The hazards of gaseous hydrogen are greater than those of most combustible gases because of the wide flammability limits and the high flame velocity. Considerable experience with hydrogen-containing gases (town gas) has shown that suitable handling techniques are available. Experience with liquid hydrogen is limited, however, and explosion hazards must be examined in detail.

Storage techniques for liquid hydrogen are not satisfactory, and high boiloff losses would be experienced with containers that are satisfactory for liquefied natural gas. Hydrogen tank design for irregular shapes, as on ships and aircraft, is inadequate.

The cost of hydrogen between 1990 and 2000 will be several times that of current Navy fuels for equal amounts of energy. However, the present trend in crude oil price increases coupled with the decreasing oil reserves-to-production ratio indicates that H_2 will not be at as large an economic disadvantage then as it is today. The cost of H_2 should not be a deterrent to its use in the Navy if system performance shows significant advantages.

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