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Toward a Liquid Hydrogen Fuel Economy

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Abstract

The replacement of hydrocarbon fuels for air and vehicular transport by liquid hydrogen is discussed as a long-term solution to problems of conservation and pollution. The economic and technical aspects of the problem are reviewed and extensions and options are discussed.

The possibility of using liquid hydrogen as an ultimate replacement for fossil hydrocarbon fuels in vehicular and aircraft transport was first considered by this author in casual conversation related to the logistics and use of liquid hydrogen in a cosmic ray experiment. In remarking on the drop in price of liquid hydrogen in recent years, it was noted that the cost per liter was about the same as gasoline. As other work in this area came to my attention, I recognized that although this idea was not original, it had an inherent self consistancy and appeal which warrented broader exposure and discussion. The conclusion I have reached is that the use of liquid hydrogen as a fuel is not only feasible technically and economically, but it is desirable and may even be inevitable.

Fossil fuel (coal, oil, natural gas) is finite, and any extrapolation of our present rate of consumption leads to the exhaustion of readily available reserves in about 100 years (or somewhere between 30 and 3000 years). Here it is academic whether new reserves are found or whether our rate of use increases or remains constant; it is abundantly clear that our rate of consumption so vastly exceeds the rate at which these materials are being laid down that an ultimate crisis is inevitable. As fossil fuels become depleted, their costs will certainly escalate.

Table I presents some relevant numbers for the "energy budget" of the United States. The energy consumed as food is representative of the fraction of the solar energy stored by photosynthesis in farm crops. Our consumption of energy from fossil sources exceed our consumption of food energy by orders of magnitude, although it is still very much less than the solar energy input to the earth's surface.

Pollution of the air as a result of the consumption of fossil fuels has been so widely discussed that nothing new can be added here. Suffice it to note that CO, CO_2 and unburned hydrocarbon fragments are major pollutants that are not products of hydrogen oxidation. However oxides of nitrogen, ozone, and hydrogen peroxide could remain as potential problems even with hydrogen burning.

It is taken as almost axiomatic that nuclear energy (fission in the immediate future, fusion perhaps in the next century) will eventually supplant fossil fuels as the primary energy source for stationary-station electric power. Plants currently under construction will already produce about 10% of this nation's power demands from nuclear energy in several years. On the other hand, there seems no serious possibility of using nuclrar energy as a direct source of power for vehicles or aircraft. The problems of critical mass, shielding weight, and the safety hazard conspire to leave nuclear energy in stationary installations and perhaps ships.

As a consequence, the source of energy for vehicular locomotion in the distant future must be chemical energy synthesized by fixed-station nuclear power. The present options appear to be, a) the electrochemical storage battery, b) the fuel cell, and c) the internal- and d) external-combustion engines. Chemical and electrochemical reactions are characterized by energies of the order of an electron volt per reaction. Consequently, the most promising energy sources on an energy per unit weight basis are those involving light elements, in particular hydrogen. At the other extreme lies the lead-acid storage battery[1]. Electrochemical cells using lighter metals (zinc, sodium, lithium) are more promising than lead-acid, but less attractive than hydrocarbon combustion. Exotic storage batteries often involve expensive components and dangerous chemicals operated at elevated temperatures. For example, two of the most attractive batteries from the standpoint of energy storage per unit weight are the sodium-sulfur battery operated at 500° F and the lithium-chlorine battery operated at 1100° F. Unfortunately fuel cells do not now appear to have the power per unit weight capabilities, let alone the economic feasibility, for them to be current serious possibilities. The situation regarding these various options for automobile propulsion is discussed in a review paper by J. Bolt[2], from which Fig. 1 is taken.

If the combustion engines are optimum, and if fossil fuels are not in the picture, the question is which fuel should be synthesized? Hydrogen appears to be the optimum choice.

Our utilization of resources on the surface of the planet is reaching scale where we are forced to cycle essentially all materials and resources, compatible with the utilization of energy and the second law of thermodynamics. Hence any fuel of the future should be part of a completely closed cycle, wherein its reaction products are identically reconstituted as fuel, while producing no deliterious effects on the evironment (e.g. pollution) in any portion of the cycle. Thus, while failing on other counts, the rechargeable lead-acid storage battery is ideally cyclic in that its stored energy is used with no effluent and it is later recharged with good efficiency from a source of stationary electric power. Liquid hydrogen likewise is nearly ideal in that its only combustion product is water vapor, and the earth's atmosphere is already in equilibrium with a surface consisting of over two-thirds open water. A hydrogen fuel economy would draw water for electrolytic seperation by nuclear power, releasing the oxygen and liquifying the hydrogen. The liquid hydrogen would then be transported and distributed as fuel, burned with oxygen from the air, and eventually return to the water systems as rain. Virtually any other fuel system would either discharge foreign substances into the environment or be constrained to retain and store its exhaust. The only exception to my knowledge would be ammonia, although here the nitrogen would not "carry its own weight" in the fuel system, and the possibility of less desirable substances in the exhaust is greater. A hydrogen-burning system might in some instances carry its own liquid oxygen. This would of course eliminate oxides of nitrogen in the reaction products. In principle, we should ultimately strive to use solar energy as a replacement for nuclear energy, but that is beyond the scope of this discussion.

Some pertinent physical properties of liquid hydrogen are given in Table II. A specific comparison between liquid hydrogen and gasoline on an energy per unit weight and per unit volume basis is made in Table III. Very clearly liquid hydrogen is interesting wherever weight is a major factor, as in jet aircraft for example.

It is in connection with a hypersonic aircraft liquid hydrogen fuel system that a rather thorough study was made of the large-scale economics of liquid hydrogen production[3] by Air Products and Chemicals, Inc. for the National Aeromatics and Space Administration. Prior to about 1958, liquid hydrogen was essentially a laboratory curiousity and was produced only in small quantities. Subsequently, demands of the space program have lead to the construction of production facilities totaling over 150 tons per day of capacity. The cost of liquid hydrogen (not including marketing, distribution, etc.) is currently $.20 per pound from a 30 ton per day plant operating near capacity. The Air Products and Chemicals study[3] indicates that the cost for liquid hydrogen from a plant of 2500 tons per day capacity could be about $0.08 per pound delivered when geared to the hypersonic aircraft transportation system. It so happens that the current most economical method of production of liquid hydrogen is not electrolysis, but steam reforming using hydrocarbons. Here the basic reactions are summarized by

$$CH_n + H_2O \rightarrow CO_2 + H_2$$

with the CO_2 removed by solvents. Technological developments could bring the cost of electrolytic production of hydrogen to 30% over the chemical process costs, or about $0.11 per pound. With the electrolytic production of dydrogen, about 1/5 as much power would be required for the liquification as for the seperation. Another estimate of the cost of liquid hydrogen ranges from $0.05 lb. to $0.10/lb., F.O.B. plant site[4]. An Allis-Chalmers Mfg. Co. study indicates a projected cost for electrolytic hydrogen produced by large breeder-type nuclear power reactors of $0.20/thousand standard cubic feet, or about \$0.04/lb.[5]. The costs of liquid hydrogen and gasoline are noted on a comparable basis (dollars per calorie) in Table III where the Air Products and Chemicals figures are taken for liquid hydrogen and the cost of gasoline is taken as \$0.12 per gallon not including marketing, taxes, etc. All figures are normalized to 1968 dollars.

In any discussion of the use of electricity to replace fossil fuels in our economy the figures noted in Table I should be borne in mind. The energy comsumption of fossil fuels for vehicular transport in the U. S. is (1968) more than twice the energy consumption of electric power. Hence the use of electric power to produce fuel as discussed here would require tripling the electric generating capacity of the country. These power figures presented do not account for efficiency. Where electricity is used directly as a source for vehicular power, as in electrified rail transport, a rather high efficiency should be realized. On the other hand, a battery-powered vehicle has been analized by Bolt[2] to be overall only 14% efficient, while the overall thermal efficiency of typical automobile powered by a gasoline engine lies in the range of 13% to 22%.

The hypersonic transport system study[3] considered an 8000 ton per day liquid hydrogen world-wide supply. The liquid hydrogen equivalent of the 1968 U. S. gasoline consumption corresponds to about 300,000 tons per day.

Part of the increasing appeal of liquid hydrogen as a fuel lies in the rapid advance of the cryogenics technology in recent years. Super-insulated vacuum dewars are able to store liquid hydrogen with loss rates of 2% per day for 150 liter containers. A liquid nitrogen-cooled jacket can reduce these losses to 1% per day. The same reduction could be achieved with a relatively inexpensive refrigerator. Larger storage vessels have correspondingly smaller losses, as the ratio of surface area (heat loss) to volume decrease, so that the fractional loss goes about as $(\text{volume})^{-1/3}$. Modern stationary storage dewars of 5000 liter capacity have a loss rate of 0.85% per day. More dramatic than the storage technology are the advances in cryogenic refrigerators recently. Liquifiers and refrigerators for 20° K service are available in ratings from 1-2 watts (at 20° K) on up. For example, a July 1969 survey[7] revealed 14 commercially produced refrigerators in the 12° K to 35° K temperature range with heat loads of 1-10 watts and costs below $11,000.00. The cryogenics art is now such that the cost of helium delivered in quantity in Denver, for example, is lower as a liquid than as a compressed gas. Targets of liquid hydrogen at large accelerators (Argonne and Brookhaven National Laboratories) are now made as closed systems with refrigeration rather than as continously boiling vessels filled from a reservoir. Liquid hydrogen is shipped overland by truck in semi-trailer dewar tanks of 8300 pound capacity currently, and are frequently closed during shipment so that the boiloff gas is permitted simply to build the static pressure. Heat loss rates in such trailers correspond to about 0.5% per day boiloff. Railroad tank cars of 17,000 pound capacity are also in current use for transcontinental shipment of liquid hydrogen. Natural gas (mostly methane) is currently shipped and stored in part as a liquid. The boiloff loss rates are clearly most serious for small units (private automobiles) but even here may be manageable with improving dewars and mass-produced refrigerators.

Hydrogen has been explored as a fuel in conventional reciprocating engines. It has the desirable feature of burning very efficiently in a lean mixture (more so than gasoline). On the other hand it is unfortunately more subject to preignition (knocking) than gasoline. A paper by R. O. King[8] summarizes the work on hydrogen-fueled engines. He reports that with a coolant temperature of 140° F and a clean combustion chamber, the correct fuel-air mixture could be used at a compression ratio of 14:1 without preignition. The use of hydrogen as a turbine fuel should present no problem. It should be recalled that a stocheometric mixture of hydrogen and air contains two parts hydrogen to one part oxygen or five parts air, as opposed to one part heptane vapor to eleven parts oxygen (55 parts air). Hence the combustion chamber volume for hydrogen burning would want to be somewhat larger than that of a gasoline-burning engine. The flame temperature of hydrogen-oxygen combustion is 4010° F, comparable to gasoline flame temperatures.

Inevitably, a major question in the use of liquid hydrogen is the fire and explosion hazard. Hydrogen is well known to form explosive mixtures with air over a broad range of concentration (4% to 75% by volume) and the use of liquid hydrogen in high energy physics has been punctuated with several minor and one major accident. It seems, however, that careful handling could hold such accidents to a very minimal level in large scale use. In many ways hydrogen is safer than gasoline in that any escaping hydrogen goes directly into the air rather than remaining as a slowly-evaporating liquid. Explosions of hydrogen are very rare in practice as opposed to rapid burning. Apparently in one potentially serious highway accident a semi-trailer liquid hydrogen tanker went off the road in the mountains and broke apart spilling its charge. However no fire ensued and the driver "walked away."

It is logical that large-scale use of liquid hydrogen would first be applied to jet aircraft as the boiloff loss and distribution problems would be minimized, and the weight advantage over hydrocarbons would be most significant. Long-haul motor freight and city buses would be the next most effective users; from the standpoint of pollution, the use of liquid hydrogen in city buses would be particularly welcome. The fueling of such vehicles would most logically be through replacement of the entire tank (dewar) will a previously filled tank. Simple, quick disconnects would permit these tank replacements in minimal time, and with almost no loss of liquid hydrogen. Weighing of standardized dewars would be used to credit unused fuel. The refilling of dewars would then be done with minimal loss at the "service station." It would be most important to adequately vent the ambient boiloff of hydrogen from the fuel tanks of parked vehicles. No discussion is given here of the use of liquid hydrogen by railroads, as it is assumed that trains would be totally electrified.

The private automible is the most difficult logistics problem for liquid hydrogen because of its infrequent use, small capacity fuel system, and the wide spectrum of technical sophistication of the operators. One would not be able to return from an extended holiday and drive off in the family car in view of the boiloff from even the best insulated tank. Local hydrogen refrigerators could conceivably be economically practical, or alternatively hydrogen could be available in "home delivery" by service stations. A potential solution to this problem of the small-scale user has been proposed by a Brookhaven group[8] through the use of metal hydrides. They point out that Mg_2Cu-H_2, Mg_2Ni-H_2, and MgH_2 can hold as much hydrogen per unit volume as liquid hydrogen. They are stable at the ambient temperature and pressure, but dissociate to hydrogen gas and metal at about 500° F. Thus a "fuel tank" of powdered or sintered magnesium or other metal alloy could be charged with hydrogen under the right conditions of temperature and pressure, and the hydrogen could be released through heat from the exhaust of the engine.

In conclusion, the use of liquid hydrogen as a long term replacement for hydrocarbon fuel for land and air transportation seems technically feasible. It is an ideal fuel from the standpoint of a completely cyclic system, serving as a "working substance" in a closed chemical and thermodynamic cycle. The factor of three energy per unit weight advantage over gasoline or any other hydrocarbon fuel makes it particularly advantageous for aircraft and long-range land transport. As a pollution-free fuel, it must be seriously considered as the logical replacement for hydrocarbons in the Twenty First Century.

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Table I

Energy Budget of the United States

Electric Power Production[*]	1.317×10^{9} kwh (about 750 watts per person)		4.75×10^{18} joules/yr.
Motor Fuel Demand[*]	1.87×10^{9} bbls. (about 7.5 gals. per person)		1.0×10^{19} joules/yr.
Crude Oil[*]	3.33×10^{9} bbl	1.7×10^{19} joules/yr.	
Natural Gas Liquids[*]	5.50×10^{8} bbl	$.28\times10^{19}$ joules/yr.	
Natural Gas[*]	1.93×10^{13} ft.^{3}	2.04×10^{19} joules/yr.	
Coal[*]	5.57×10^{8} tons	$.13\times10^{19}$ joules/yr.	
Total Fossil Fuel Consmption			4.2×10^{19} joules/yr.
Food Consumption	2000 Calories per person per day, or 100 watts per person		6.1×10^{17} joules/yr.
Solar Energy	Solar Constant 2.0 cal/cm^{2}min 3.55×10^{6} miles^2		1.0×10^{23} joules/yr.

[*] Figures are for the U. S., 1968 from the 1970 World Almanac and Book of Facts, L. H. Long (Ed.) Newspaper Enterprizes Association, Inc. (1969).

Table II

Properties of Liquid Hydrogen

Boiling Point	20.4° K
Liquid Density	4.418 lbs/ft^3 0.07078 g/cm^3 0.1557 lb/liter 6.42 liters/lb
Latent Heat of Vaporization	108 cal/g
Std. cu. ft. gas per liquid liter	29.95
Combustion Energy Release	290 BTU/ft^3 (gas) 29,000 cal/g 2050 cal/cm^3 1.21x10^5 joules/g 5.5x10^7 joules/lb 1.1x10^{11} joules/ton
Flame temperature	4010° F
Auto ignition temperature	1085° F

Table III

Energy and Cost of Fuels

	energy/mass	density	energy/Vol.	cost
Liquid Hydrogen	29,000 $\frac{\text{cal}}{\text{g}}$	0.07078	2050 $\frac{\text{cal}}{\text{cm}^3}$	6×10^{-9} \$/cal @8¢/lb. 8×10^{-9} \$/cal @ 11¢/lb.
Gasoline	11,500 $\frac{\text{cal}}{\text{g}}$	0.74	8500 $\frac{\text{cal}}{\text{cm}^3}$	4.2×10^{-9} \$/cal@12¢/gal.
Fuel Oil	10,500 $\frac{\text{cal}}{\text{g}}$	0.96	10,000 $\frac{\text{cal}}{\text{cm}^3}$	

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Vehicle Requirements (2000 Lb. Vehicle) and Motive Power Source Requirements

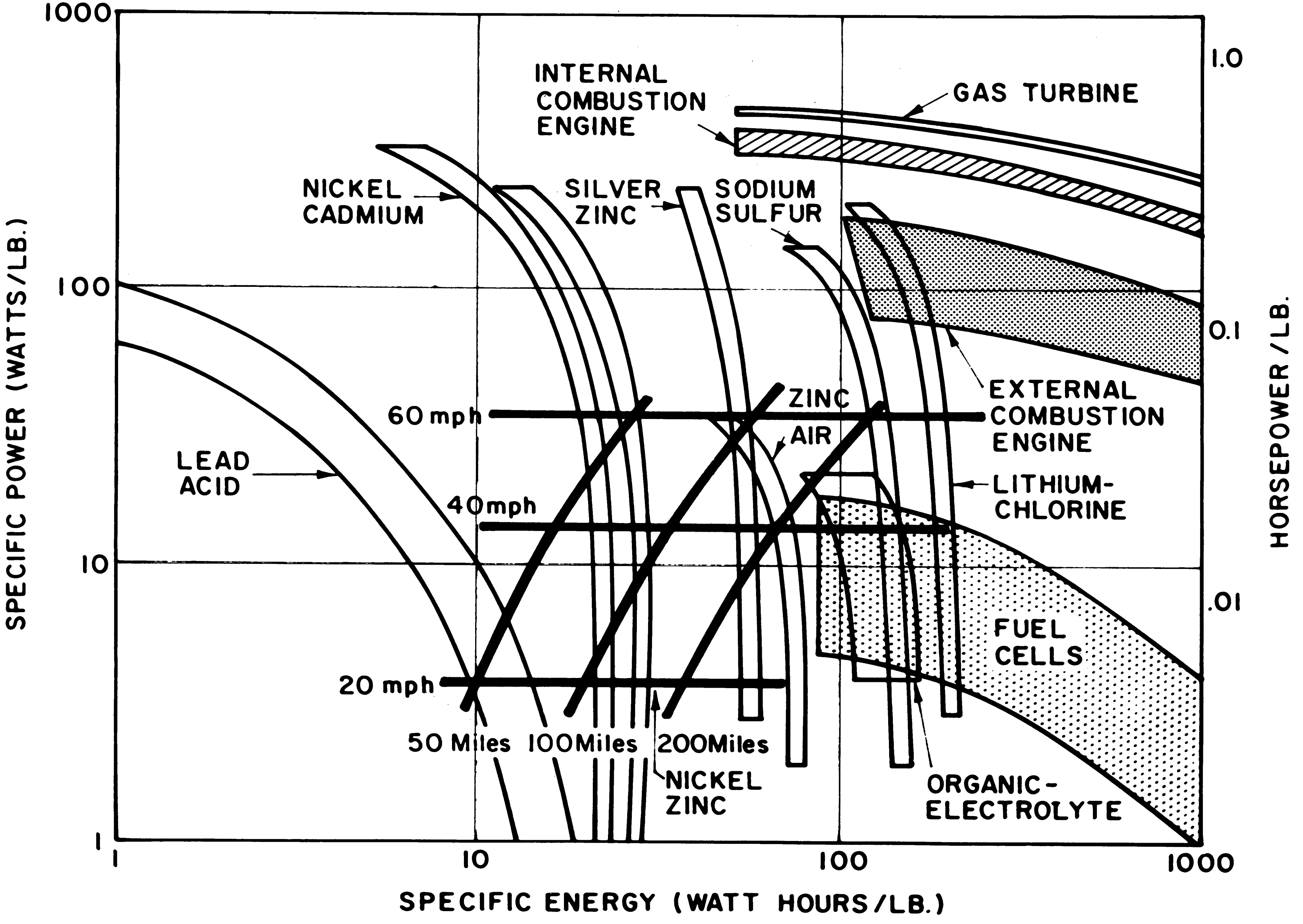

Figure 1