THE HYDROGEN ENERGY SYSTEM

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ABSTRACT

Because of diminishing reserves of convenient to use fossil energy sources, as well as environmental considerations, a serious research effort is underway worldwide to develop alternative long-term primary energy sources. Most of these alternative sources have the disadvantages of providing energy in forms which are difficult to store and transport. One possible solution to this problem is to convert the primary energy into chemical potential energy by decomposing water to form hydrogen which can be stored and transported with relative ease. The hydrogen energy system offers many attractive features including minimal environmental impact as well as a steady-state cycle.

Introduction

Fuel cycles have become of more and more obvious importance in light of environmental problems and diminishing reserves of fossil fuels. The fossil fuel cycle is illustrated in Figure 1. There are several things inherently wrong with this cycle. The most obvious is that fossil energy is being used at a much higher rate than it is being produced by fossilization. Most of the fossil energy created over the past several million years will have been used up in a period of a few hundred years. In other words, the fossilization step is rate limiting and for all practical purposes this is not a closed cycle since it will take millions of years to recreate new fossil fuel reserves. Other problems with the cycle relate to its impact on the environment. Fossil fuels are dirty. They are usually combusted in devices which result in the production of chemical pollutants such as unburned hydrocarbons, oxides of nitrogen, and

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Figure 1. Fossil fuel cycle.

oxides of sulfur. In the atmosphere these components combine in complicated chain reactions to produce photo-chemical smog as well as irritants to the eyes and respiratory system. Carbon dioxide, though not chemically active in the environment, may be accumulating to the point of creating a solar energy trap by the "greenhouse effect." Some scientists believe that this is resulting in gradual global temperature increases, ultimately affecting the climate. Finally, as is obvious from Figure 1, this cycle has been a mechanism over millions of years of storing solar energy. The rapid utilization of this energy, all of which is ultimately rejected to the environment, results in increasing the energy flux to the environment beyond the daily solar irradiation. Though this may not have far-reaching global effects, it affects localized areas such as large metropolitan areas, which have high energy consumptions.

Environmental factors, and particularly shortages of conveniently produced and utilized fossil fuels (natural gas and petroleum) have recently resulted in considerable research into alternative energy sources. Nuclear fission has been developed to the point of practical usage, but a controversy still rages over safety and the advisability of extensive use of a system which creates dangerous radioactive byproducts which may have to be stored for hundreds or thousands of years. Nuclear fusion holds much promise for providing clean energy indefinitely into the future but crucial break-throughs which will make this possible may be decades away. More recently there has been a reawakening to the potentials of using solar energy, especially for space heating and cooling applications. The use of solar energy has the advantage of not increasing local energy fluxes above the solar insolation.

It is becoming obvious that if the United States is to become energy independent in the immediate future, it will have to rely more on domestic coal and oil shale reserves as well as to implement solar energy where practical. The development and use of these reserves is currently receiving much attention in Congress and in many research laboratories across the country. However even though coal and oil shale will provide additional years to develop the ultimate, nondepletable energy source, they too will one day be exhausted. Estimates for the expected lifetime of coal reserves range from a hundred years or so to several hundred years. Since much of the coal reserves are not convenient to mine, their use will be expensive and mining may permanently scar the local environment. A switch from them to a more desirable form of energy generation should be made as soon as practical.

Nuclear and/or solar energy may ultimately provide most of our requirement, but they have two serious drawbacks. They cannot be transported or stored and so must be converted from their primary energy form into some secondary energy form to allow for ease of storage and transportation. A good example of a secondary energy source used today is electricity, but which does not have the advantages of ease of storage and can be expensive to transmit over long distances. A serious research effort is underway worldwide to explore the possible use of hydrogen, created by water decomposition, as the ultimate energy storage and transportation medium.

Hydrogen Cycle

The "hydrogen economy concept" is based upon the hydrogen cycle in Figure 2. While the cycle has the same appearance as the fossil fuel cycle, there are some important differences. Hydrogen burns very cleanly over a very wide range of mixtures with air. In lean mixtures (low ratio of hydrogen to air) the combustion temperature is low enough that little or no oxides of nitrogen are formed. Since there are no hydrocarbons or sulfur present there is no problem with unburned hydrocarbons or with oxides of sulfur. There still is waste energy produced as the result of process inefficiencies and thermodynamic limitations, but combustion efficiencies tend to be higher with hydrogen than with more chemically complicated fuels such as hydrocarbons. If solar energy





is utilized as the primary energy source there would be no problems of energy rejection increasing the local energy flux above the solar insolation.

A major advantage to this cycle is that the energy intermediate (hydrogen) can be produced from the product of combustion (water). The water returns to the environment from whence it came in a matter of days to weeks. There is no step, such as fossilization, with a long characteristic time scale to prevent a steady state from being achieved. An additional feature of the cycle is that oxygen is another by-product of water decomposition which can either be transported along with the hydrogen for ultra-clean burning or which can be used in other ways.

Hydrogen Utilization

The reaction of many to the notion of using hydrogen as a fuel is that it is much too dangerous, recalling the destruction of the Hindenburg airship. This response is termed the "Hindenburg Syndrome" to those working in the area. In fact there is an informal organization called the Hindenburg Society, comprised of individuals who believe that hydrogen may play an important role in the future. The fact is that any energy medium, including natural gas and gasoline, are dangerous if improperly handled. Much has been learned about handling hydrogen during our space program. Hydrogen even has characteristics which make it safer in some ways than more conventional fuels. For one thing, being lighter than air, it is dispersed very rapidly away from a point of leak or spill. It also burns with a nonluminous flame which minimizes any possible burn damage by radiation such as can occur with hydrocarbon fires.

The energy consuming sector most easily converted to hydrogen use is industry. Essentially all energy consuming devices used in industry such as furnaces, turbines, and various other combustion applications, could be converted just as today many are converting, or already have converted from natural gas to fuel oil because of natural gas shortages. Industry is also more likely than any other sector to have the technical capability required to maintain strict safety standards. Industry consumes as fuel some 30 per cent of all energy consumed in the United States.

The sector least likely to convert to hydrogen use is transportation. This is primarily due to the low volumetric energy density of the hydrogen requiring large high pressure tanks or sophisticated cyrogenic systems. Commercial transportation, trucks, busses and trains may be exceptions since storage space is less of a problem. Another exception may be air transportation, since the mass energy density of liquid hydrogen is very high, more than twice that of conventional jet fuel.

The sector impacting on most persons is that of residential and commercial, amounting to some 25 per cent of the total domestic energy consumption. Most of this consumption is for space and process heating. Fossil fuel burners may be converted to hydrogen by changing burners, controls, and pilot lights. Such a wholesale change-over is not practical considering the lifetime of such devices. Direct replacement with a hydrogen burning device is more practical. The use of hydrogen cannot be directly extended to systems which operate on electricity such as motors, radios, and such even though fuel cells utilizing hydrogen could generate electricity for such units. The practicality of having a fuel cell in each home is dubious at present with the high price of efficient electrodes, but larger community units supplying a city block might be more manageable.

The nature of hydrogen could result in new devices for home heating such as catalytic burners which operate at extremely low temperatures compared to furnaces. For such unvented devices, home humidity control might have to be exerted except in dryer southwest climates. Hydrogen may also prove adaptable to absorption type refrigeration and air conditioning units. Because of the costs involved in a large scale change to hydrogen, existing homes and businesses are less likely to make the change than new construction, or ideally, new communities altogether. The costs involved with new construction should be comparable to conventional natural gas or electrically implemented homes, and would have the added advantage of increased efficiency offered by unvented type combustors.

Since hydrogen is a colorless and odorless gas it may be desirable to add an oderant to aid in leak detection. It has been found that certain additives also have the effect of inhibiting hydrogen environment embrittlement, possibly allowing use of existing gas pipelines. Leak detectors for hydrogen are currently commercially available and could be mounted in the ceiling to detect gas accumulating from a leak. With such precautions hydrogen should not pose any more serious safety problem than conventional fuels.

Hydrogen Production

There are many ways that hydrogen can be produced. Today the principal means is by steam—hydrocarbon reforming. This process

combines steam with a hydrocarbon, such as methane, over a catalyst resulting in the generation of hydrogen by reactions such as those below:

$$CH_4 + H_2O \stackrel{\frown}{\leftarrow} CO + 3H_2$$
$$CO + H_2O \stackrel{\frown}{\leftarrow} CO_2 + H_2$$

This technology does not decouple the hydrogen source from the fossil fuel resources and thus cannot be considered a candidate for hydrogen production in a true hydrogen economy. Alternatively water can be decomposed into hydrogen and oxygen in a number of ways. Direct thermal decomposition requires excessively high temperatures to be a serious contender, but electrolysis is one technology which is promising. Present day high cost of electrodes and low current densities make this option costly. An additional factor is that electricity must be available to drive an electrolyzer. It would be better to utilize primary energy to produce hydrogen directly if possible rather than to subject it to the Carnot efficiency to produce an intermediate such as electricity for electrolysis.

An area of the hydrogen energy concept receiving much attention today is the production of hydrogen by multi-step thermochemical water decomposition. Some thirty such schemes have been suggested in the literature and development work is in progress worldwide in such labs as the Euratom facilities at Ispra, Italy [1-4]; the Nuclear Research Center in Julich. West Germany, Los Alamos [5], Brookhaven and Argonne National Laboratories; the Institute of Gas Technology [6, 7]; General Electric [8-10] and several universities in the United States. These schemes produce hydrogen from water with theoretically no net consumption of other chemical species. Major advantages are an infinite supply of raw material (water) which is recycled rapidly back to the environment, smaller work requirements than exist with other schemes with resultant higher thermal efficiencies, and heat requirements at temperatures which are available with foreseeable advances in primary energy technology.

The process receiving the most attention to date is the "Mark 1" calcium bromide process developed at Euratom.

$CaBr_2 + 2H_2O \rightarrow Ca (OH)_2 + 2HBr$	730°C
$\mathrm{Hg} + 2\mathrm{HBr} \rightarrow \mathrm{HgBr}_2 + \mathrm{H}_2$	$250^{\circ}C$
$\mathrm{HgBr}_2 + \mathrm{Ca(OH)}_2 \rightarrow \mathrm{CaBr}_2 + \mathrm{HgO} + \mathrm{H}_2\mathrm{O}$	$200^{\circ}C$
$HgO \rightarrow Hg + \frac{1}{2}O_2$	600°C

A process schematic is shown in Figure 3. Each block in the



Figure 3. Mark 1 multistep water decomposition schematic.

diagram would consist of a chemical reactor, a separation device, and heat exchangers. For each mole of water entering the process one mole of hydrogen and one-half mole of oxygen would be produced. The other constituents are internally recycled. The highest temperature required by this scheme is well within the range of capability of high temperature gas cooled fission reactors and possibly advanced linear solar collectors, the preferable primary energy source. Other process possibilities are reviewed elsewhere [11].

Cost predictions and comparisons for various energy alternatives have been made for the next fifty years or so. The accuracy of such predictions is questionable due to the nature of assumptions which must be made. In particular, the societal costs associated with health and the environment are difficult to assess. In all likelihood we will never have a single unique source of energy, but will utilize a mix based upon a variety of considerations. Hydrogen figures to play an important role in whatever develops.

REFERENCES

- 1. G. De Beni and C. Marchetti, "Hydrogen, Key to the Energy Market," *Eurospectra*, 9:2, p. 46, 1970.
- 2. ____, "Mark 1, a Chemical Process to Decompose Water Using Nuclear Heat," presented at the Symposium on Non-Fossil Chemical Fuels, ACS 163rd National Meeting, Boston, Massachusetts, April 10-14, 1972.
-, "Hydrogen Production from Water Using Nuclear Heat," Report No. 1, EUR 4776e, December, 1975; Report No. 2, EUR 4955e, December, 1971; Report No. 3, EUR/C-IS/35/73c, December, 1972.
- 4. C. Hardy, "Thermal Decomposition of Water Using Cycles of the FeCl₂ Family," Report EUR 4958f, 1973.
- D. P. Macmillan and J. D. Balcomb, "Nuclear Reactors for High Temperature Process Heat—A Survey of Reactor Types and Temperature Regimes," LASL Paper LA-UR-73-877, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, paper presented at 166 National A.C.S. Meeting, August 27, 1973.
- 6. D. P. Gregory, "The Hydrogen Economy," Scientific American, 228:1, pp. 13-21, 1973.
- , "A Hydrogen-Energy System," Publication No. L 21173, Institute of Gas Technology, Chicago, Illinois, August, 1972.
- G. P. Kerns, "Hydrogen Production for Eco-Energy," G.E. Publication 72 TMP-53, General Electric Company—TEMPO, Santa Barbara, California, November, 1972.
- 9. W. Hausz, et al., "Hydrogen Systems for Electric Energy," G.E. Publication 72TMP-15, General Electric Company-TEMPO, Santa Barbara, California, April, 1972.
- G. G. Leeth, "Nuclear Power Plants for Hydrogen Production," G.E. Publication 72TMP-52, General Electric Company—TEMPO, Santa Barbara, California, November, 1972.
- R. L. Savage, et al., "A Hydrogen Energy Carrier," 1 and 2, Summary and Systems Analysis, 1973 NASA-ASEE Engineering Systems Design Institute Report, University of Houston, NASA, Johnson Space Center, Houston, Texas, October, 1973.