ENERGY CARRIERS AND CONVERSION SYSTEMS WITH EMPHASIS ON HYDROGEN

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Contents

Summary

This theme level article introduces the background and outline of hydrogen energy systems and the relevant elementary technologies. The most significant points are as follows:

- Energy, energy resources, and energy carriers are defined. The merits and the demerits of every energy resource are pointed out. It is emphasized that the combination of every traditional system with hydrogen systems must be considered.
- Hydrogen energy systems are introduced as an important option of future energy systems, and the elementary technologies are reviewed. The most important fundamental is how to produce hydrogen using renewable energy resources. However, it is too expensive to be realized at the present stage.
- Feasibilities for realizing the proposed application technologies are promising. Therefore, if hydrogen fuel can be produced at low cost and safely distributed, our energy systems will tend to move gradually towards the hydrogen energy systems.

Recently, environmental demands for clean fuel for driving vehicles have been promoting the application of PEMFC to cars to a practical level. A new age for hydrogen energy is coming now.

1. Energy Resources

1.1. Energy, Energy Resources, and Energy Carriers

The term ”conversion system,” which often appears in the contexts of energy essays, has two meanings. The first is scientific and technological as in the example of: ”mechanical energy conversion to electric energy has high efficiency, whereas thermal energy can be converted to mechanical energy with somewhat limited efficiency.”

The second meaning is economical and political as in the example of "conversion of the main systems of energy carriers from coal to oil have been going on since the 1960s." The term "conversion system" used in the present case has the second connotation. Putting this in concrete terms, "the present systems of energy carriers may be converted to advanced carrier systems—the hydrogen energy systems—in the twenty-first century."

Energy is defined as a capacity for motion, which is sometimes equivalent to work. Work is scientifically defined by the physical quantity that is given to a body when it is moved a distance by a force. The general meaning of energy includes every quantity that is equivalent to work as defined above. There are two kinds of energy: dynamic and static. Examples of the former are kinetic energy, electric current, photon, and sensible heat. The latter includes potential energy, electro- (magneto) static potential energy, latent heat, and chemical cohesion.

We shall next define the concepts of energy source, resource (the primary energy), and energy carrier (the secondary energy). Let us consider a domestic refrigerator. The cold generated by a conventional refrigerator is due to the adiabatic expansion of a heat medium that has been compressed with the use of a compressor and motor. Energy is provided to the latter in the form of electricity from an electric power plant, operates the compressor. The electric power plant gets the electric energy from a steam-power station where fuel oil is burnt. In this system, the oil is called the energy resource and electricity is called the energy carrier. Strictly speaking, the electricity provided to the refrigerator is called the energy source on the spot, and the initial provider of energy, the fuel oil in this case, is called the energy resource.

An innovative refrigeration energy conversion system is possible if the energy resource is a solar-hydrogen energy system (a system of hydrogen produced by solar energy), the energy carrier is hydrogen, and a metal hydride refrigeration system replaces the mechanical compressor system.

There are several kinds of energy carriers in present energy systems, for example, gasoline, kerosene, electricity, city gas, LNG, and LPG. Some advanced energy carriers, making use of hydrogen, laser beams, and microwave power transmission in space, may be realized in the near future.

The basic principles of energy are noted in the following paragraphs. First, "energy is conserved overall in the universe," where the term energy means the sum of conventional energy and mass, because mass is equivalent to conventional energy, that is to say, a mass of m kg can be converted to the conventional energy of mc^2 kJ, where c is the velocity of light in a vacuum. This equivalence is due to Einstein's special relativity. One important energy resource today, nuclear energy, is the result of precisely this equivalence. There are only negligible amounts of nuclear energy conversions globally, so that the energy conservation law holds among the conventional energies, kinetic energy, potential energy, electric energy, chemical energy, photon energy, and thermal energy.

Let us consider the case of lighting. If the energy resource is oil, the following conversion systems are realized:

- from oil (chemical energy) to burner (heat)
- from heat to heat energy (mechanical energy + waste heat)
- from mechanical energy to electric generator (electric energy + waste energy)
- from electric energy to light bulb (light energy + waste energy), where all the waste energies are converted finally to waste heat.

Less than 8.5 percent of the oil energy is used in the illuminating energy of the fluorescent lamp.

It should be noted that “energy is conserved,” but the useful (available) energy decreases at every step of energy conversion. Therefore, we obtain the second main principle: “available energy decreases whenever it is converted.” This principle is called the second law of thermodynamics: the law of increasing entropy. This is why energy is not always ability of work as indicated above; for example energy may be energy at ambient temperature.

Expressing the total energy (enthalpy), Gibbs’s free energy, entropy, and the absolute temperature, by E, G, S, and T, respectively, we arrive at the well-known formula:

$$G = E - TS \quad (1)$$

Free energy is the energy which can be converted to mechanical energy directly rather than via a heat engine; it has a higher value than heat energy, which is expressed by the term TS. Equation (1) shows that the useful energy G decreases as entropy increases. The lost heat q divided by T is the entropy increment in the energy conversion process.

It is understood that dynamic energy (kinetic energy and sensible heat) tends to generate entropy much more easily than static energy (potential energy and latent heat). Therefore, for energy storage, static energy systems become indispensable. Coal, oil, fuel gas, wood, and uranium are the materials wherein cohesive potential energies are stored stably. These materials are often called “energy media,” and are equivalent to energy carriers (secondary energy). One must be careful to use the term energy media, because all matter, even void space, can be the energy propagation medium.

1.2. Fossil Fuels

1.2.1. Coal

The ancient remains of plants that were subjected to a dry distillation under geothermal heat and great geological pressures several hundred thousand years ago, in due course became coal, of which the major constituent is carbon. Coal has been one of the most important energy resources since the Industrial Revolution in the eighteenth century. The kinds of coal are anthracite, bituminous, sub-bituminous, and lignite; however only anthracite and bituminous are used in practice, because they higher more energy density (about 32,400 kJ/kg) and are cleaner (with a sulfur component of about 3 percent) than the others. The world has very large coal reserves in the world are very large, with a lifetime estimated at 230 years in 1998. Moreover, these resources are fairly evenly distributed around the world. The major problem with coal utilization is the air pollution caused by coal combustion, which gives off more than three times the amount of sulfur oxide gas than is produced by oil combustion, and more than twice the amount of carbon dioxide gas, which is the main cause of the greenhouse effect. Other obvious economic disadvantages are that coal is not readily compatible with automatic combustion systems or with a pipeline transportation system. However, it is highly probable that the use of coal will be revived when oil resources are depleted in about sixty-four years time.

It is obvious that the disadvantages of coal can be overcome if it can be liquefied or gasified. The simplest way of getting liquefied coal is to mix oil with powdered coal. It is necessary to add a surfactant (surface active agent) to avoid the precipitation of the coal powder. This energy carrier is called COM (coal oil mixture), and is often used in order to save oil.

1.2.2. Coal and Hydrogen

The well-known and traditional coal fluidization technologies are coal liquefaction and coal gasification, which involve the addition of hydrogen to coal under high pressure and at high temperatures. If the added hydrogen can be supplied from the solar hydrogen energy system, then the energy quantity of the liquefied coal fuel will be comparable to that of oil, and the lifetime of the fuel will be greater than 230 years. This fuel could be one of the leading fuels in the post petroleum era.

1.2.3. Oil

Accumulated masses of ancient remnants of plankton were subjected to dry distillation under geothermal heat and high geological pressure about a billion years ago, resulting in the production of oil (petroleum). Oil is a stable liquid energy carrier with high energy density. For example, the energy density of kerosene is 40,850 kJ/kg, of burner oil 42,680 kJ/kg, and heavy oil 45,740 kJ/kg. Oil is believed to be the most practical energy carrier in human history. More than 30,000 oil-producing wells have been drilled so far. They produced, for example, 3.82 billion kl of oil in 1979 (this is a remarkable record). The vast amounts of oil produced lowers its price, and not only energy but everything in human civilization has benefited from oil. Today is said to be the golden age of oil.

There are three major problems with oil energy: the depletion of reserves, uneven distribution around the world, and pollution.

Depletion of Reserves: The most serious of these problems concern the world reserve of oil. The ultimate reserve is roughly estimated to be about 2 T barrel, ($T = 10^{12}$; 1 barrel = 0.159 kl). The production rates and global reserves of every energy resource are usually a function of time elapsed. For example, oil data for 1985 indicate a production rate of 3.48 T l/Y and total global reserves of 318 T l. Assuming a constant consumption rate, the total life of the reserve can be easily estimated. If oil is consumed at a constant rate, then it will be exhausted in ninety-one years from 1985. However, we know that the situation is not so simple. The production rate is sensitive to the global economy and the demands of exporting and importing countries. Since oil first began to play an important role in the economy, the production rate has been steadily increasing (although it is relatively stable at present). On the other hand, it is expected that the rate will decrease at some point, when about half of the reserves have been consumed. In order to express this trend, and to study the resource life cycle more exactly, we shall study a model.

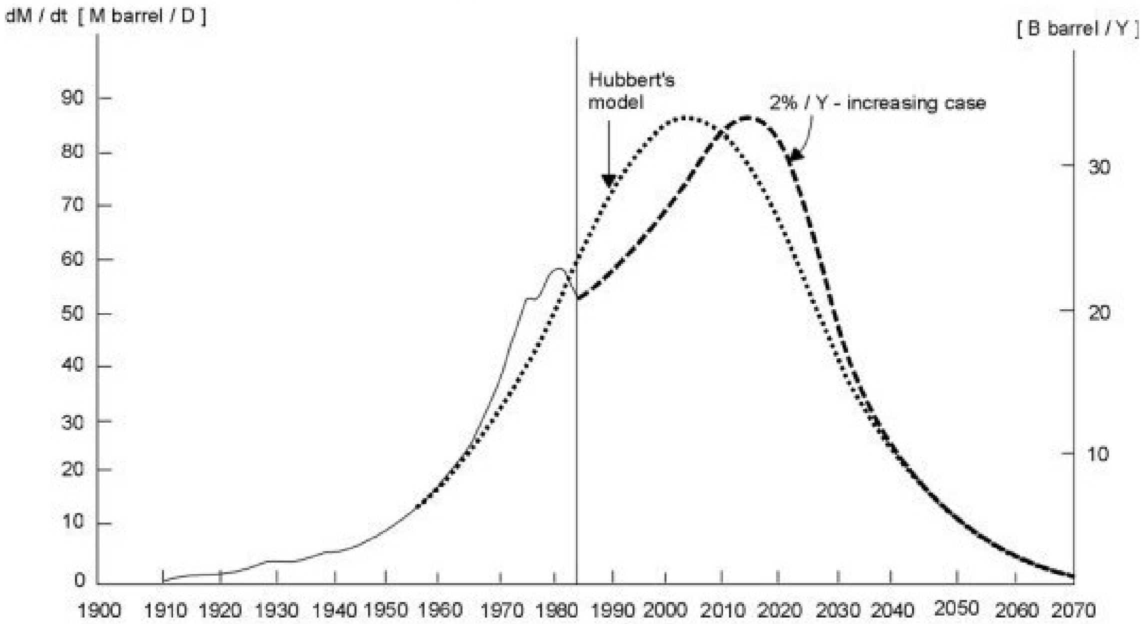

Figure 1. Hubbert's model for lifetime of oil reserve
Note: dM / dt is the production rate.

M. K. Hubbert proposed a life-cycle model for oil in 1956. This is shown in Figure 1, where the horizontal axis and vertical axes represent the oil production rate and the year, respectively. The model is based on the following three assumptions:

- The total initial oil reserve is 2 T barrel = 318 T l.
- The production rate increases to a maximum and then stabilizes for a short time before decreasing.
- The behavior of the production rate is predicted by an extension of empirical data and is assumed to be symmetrical with respect to the time when the production rate becomes maximum.

We extended the empirical data taken from 1910 to 1955 by Hubbert to 1985. The hump in the oil production is due to the oil crisis. Assuming a production rate increase of 2 percent every year, the production rate reaches a peak in 2010 and is estimated to be 5.22 T l/Y. In 1955 Dr Hubbert predicted that oil would be depleted in 2042. According to a recent publication by Deffeyes (2001) the depletion time has shifted to the beginning of 2100.

There are several other predictions about the year of the maximum production:

- 2000–5; F. Bernable, ENI SOA, 1998
- 2000–10; C. Campbell and J. Laherrere, Petroconsultants, 1998
- 2007–14; J. Makenzie, World Resources Institute, 1996
- 2010–20; OECD's International Energy Agency, 1998
- 2020; J. Edwards, University of Colorado, 1997
- After 2020; DOE's Energy Information Administration, 1998.

Geographical Distribution of Oil: The second problem is the uneven distribution of oil around the world, which can cause global economical confusion, as in the "oil crisis" of 1973 to 1980. According to a recent research report in *Science* (August 21 1998), about 50 percent of the initial total reserves of oil have been consumed, and the confirmed remaining reserves of 1.0376 T barrel (=164.91T l) is distributed as follows:

- North America: 12.18 T l
- South & Central America: 13.7 T l
- Europe: 3.2 T l
- former Soviet Union: 10.4 T l
- Middle East: 107.6 T l
- Asia Pacific: 6.725 T l
- Africa: 11.1 T l.

The Middle East contains 65.23 percent of the world's oil reserves. This situation is very different from coal distribution.

Pollution: The third problem of oil is related to polluting emissions. When oil is burned, it emits as many kinds of gases as the number of elements it contains. Most of the gases are oxides: NO_x, SO_x, CO_x, and H_2O.

Carbon dioxide (CO_2) has been recognized, for a long time, as a non-noxious gas resulting from fossil fuel combustion. However, the huge amount of CO_2 gas accumulated in the atmosphere year by year poses a serious problem for the global environment.

Figure 2 shows the change in global surface air temperatures. The standard level (0.0) is the average from 1950 to 1979. The tropical rain forests and seaweeds have very active photosynthetic actions in summer, and so the amount of CO_2 to the atmosphere decreases in that season.

The global damage due to the increase of surface air temperatures is obvious: rise of sea levels, enlargement of desert areas, changes of climate, and so on. All of these effects affect the sustainable development of human lives.

Agenda 21 was issued in 1992, setting out the aim of reducing carbon dioxide emissions to a level agreed by every country of the world.

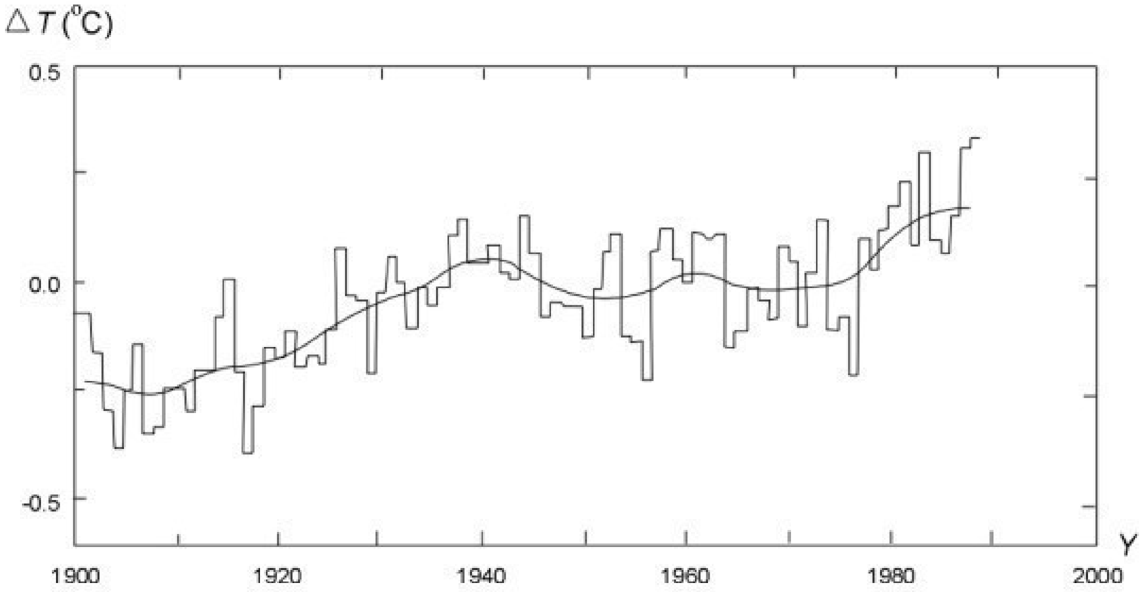

Figure 2. Global surface air temperature
Note: The standard (0.0) is the average temperature from 1950 to 1970
Source: University of East Anglia.

However, the underdeveloped countries such as China tend to increase their use of oil rather than coal. Thus, the developed countries will have to yield more of the oil reserve to the underdeveloped countries, and will have to develop and utilize more natural gas, nuclear energy, and pollution free fuels such as hydrogen generated from water by renewable energy sources.

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Bibliography

Barbir, F.; Veziroglu, T. N.; Plass, H. J. Jr. 1990. Environmental Damage due to Fossil Fuels Use. *International Journal of Hydrogen Energy*, Vol. 10, p. 739. [Environmental damage due to fossil fuel combustion is reviewed and the introduction of hydrogen energy systems is recommended.]

Chambers, A.; Park, C.; Baker, T. K.; Rodriguez, N. M. 1998. Hydrogen Storage in Graphite Nanofibers. *The Journal of Physical Chemistry B*, Vol. 102, No. 22, p. 4254, [This is one of the earliest papers that studied the hydrogen storage capacity of graphite nanofibers.]

Gregory, D. 1973. The Hydrogen Economy. *Scientific American*, Vol. 228, No. 1, p. 13. [This is the first review paper on the economical comparison of energy transports; the priority of energy transportation by hydrogen is stressed.]

Ikeda, S. et al. (Tokyo Institute of Technology Group headed by K. Domen.) 1998. *Mecano-Catalytic Overall Water-Splitting*, *Chemical Communications*. pp. 2185–6. [The discovery of mechano-catalytic water-splitting.]

Fujishima, A.; Honda, K. 1972. Electrochemical Photolysis of Water at a Semiconductor Electrode. *Nature, Vol.* 238, No. 37. [This is one of the earliest and most prominent reports of photolysis by TiO2 electrode.]

Fulkerson, W.; Judkins, R. J.; Sanghvi, M. K. 1990. Energy from Fossil Fuels. *Scientific American,* Vol. 263, No. 3, p. 129. [This is a fresh review of fossil fuels. Recent data are presented also.]

Hannond, A. L.; Metz, W. D.; Maugh II, T. H. 1973. *Energy and Future*. Washington, D.C., American Association for the Advancement of Science (AAAS). 97 pp. [Future of every kind of energy sources is discussed. Energy transmission-by-transmission lines, fuel cell, and hydrogen are compared with each other. Energy conservation and energy policy are also discussed for the future.]

NASA Technical Memorandum. 1968. *Hydrogen Safety Manual*. Washington, D.C., NASA. 79 pp. [This is the shrewdest condensed safety manual about hydrogen handling.]

Ohta, T. 1973. Clean Energy System by Hydrogen. *Science* (Japanese edition of *Scientific American*), Vol. 2, No. 5, p. 68. Tokyo, Nikkei. [This is the first review article in Japanese on Hydrogen energy systems. The prominent character of this paper is an introduction of cooperative systems between electric power and hydrogen.]

——. 1974. Hydrogen Energy Systems: How they Work. *Chemical Economy and Engineering Review*, Vol. 6, No. 7, p. 7. [A historical trend toward hydrogen energy systems is pointed out first by this paper and an experiment of hydrogen production by solar thermoelectric power is introduced.]

——. 1988. Photochemical and Photo Electrochemical Hydrogen Production from Water. *International Journal of Hydrogen Energy*, Vol. 13, No. 6, p. 333. [This is a report of most advanced technologies on photolysis, of which fundamental principles are discussed in detail.]

——. 1994. *Energy Technology, Sources, Systems, and Frontier Conversions*. Oxford, Pergamon. 235 pp. [Energy systems and their elemental technologies are introduced and evaluated from the viewpoints of efficiency and the global environment. Principles of effective conversion are explained with the use of reversible thermodynamics and energy.]

——. 2000. Preliminary of Mechano-catalytic Water-splitting. *International Journal of Hydrogen Energy*, Vol. 25, No. 4, p. 287. [This is the first theory on the mechano-catalytic water splitting at the present stage.]

——. (ed.) 1979. *Solar-hydrogen Energy Systems*. Oxford, Pergamon. 264 pp. [This is a compilation of scientific papers on hydrogen production methods, hydrogen storage by metal hydride systems, and ocean-based hydrogen energy systems.]

SCIENCE, News Focus. 1998. The Next Oil Crisis Looms Large: And Perhaps Close. *SCIENCE*, Vol. 281, p. 1128. [An interesting analysis of the global energy situation that discusses demand prospects. The earliest predicted peak in world oil production will be 2000.]

Veziroglu, T. N. 1987. Hydrogen Technology for Energy Needs of Human Settlements. *International Journal of Hydrogen Energy*, Vol. 12, No. 2. [This is an essay about the relationship between human settlements and hydrogen energy systems.]

——. (ed.) 1975. *Hydrogen Energy, Part A and B*. New York, Plenum. 1369 pp. [These are Proceedings of Hydrogen Economy Miami Energy Conference, 1976.]

Veziroglu, T. N. et al. (eds.) 1978–98. *Hydrogen Energy Progress*, Vols. I-XIII. Each set has about 2500 pp. Miami, International Association of Hydrogen Energy. [Those are the Proceedings of the World Hydrogen Energy Conferences, which have been held every two years since 1976.]

Biographical Sketches

Tokio Ohta was born in 1925 in Japan. He studied at the Department of Physics, University of Kyoto obtaining a Ph.D. in Solid State Physics. He has taught at the University of Kyoto, Portland State

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T. Nejat Veziroglu was born in 1924 in Istanbul, Turkey. He received an A.C.G.I. Degree in Mechanical Engineering from the City and Guilds Institute of London, a B.Sc. in Mechanical Engineering from the University of London, a D.I.C. in Advanced Studies from Imperial College, London, and a Ph.D. in Heat Transfer from the University of London. He has served as Chair of the Department of Mechanical Engineering, University of Miami (1971–5), and as Associate Dean of Engineering Research, University of Miami (1975–9); he is presently the Director of the Clean Energy Research Institute, the University Miami. Dr Veziroglu has published some 250 scientific reports and papers, edited 170 volumes of proceedings, and is the Editor-in-Chief of the monthly scientific journal, the *International Journal of Hydrogen Energy*. He is the Founding President of the International Association for Hydrogen Energy.