Apr 1st, 8:00 AM

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Tokio Ohta
Professor, Hydrogen Energy Research Laboratories, Faculty of Engineering, Yokohama National University, Ohka, Minami-ku, Yokohama, 233 Japan

T. N. Veziroglu
Director, Clean Energy Research Institute, School of Engineering and Environmental Design, University of Miami, Coral Gables, Florida 33124

Scholarly Commons Citation

Ohta, Tokio and Veziroglu, T. N., "Hydrogen Production By Solar Beam" (1976). *The Space Congress® Proceedings*. 4.
https://commons.erau.edu/space-congress-proceedings/proceedings-1976-13th/session-6/4

HYDROGEN PRODUCTION BY SOLAR BEAM

Dr. Tokio Ohta
Professor, Hydrogen Energy Research Laboratories
Faculty of Engineering
Yokohama National University
Ohka, Minami-ku, Yokohama, 233 Japan

Dr. T. Nejat Veziroglu
Director, Clean Energy Research Institute
School of Engineering and Environmental Design
University of Miami
Coral Gables, Florida 33124

ABSTRACT

Various methods of water-splitting with use of solar energy are reviewed and compared to each other. Direct thermal method has the highest efficiency, but the difficulty is the heat-resisting materials. Thermochemical method is promising if the corrosion-resisting materials are found. Electrolytic method is traditional, but the hybrid system combined with thermochemical and/or photochemical reactions are valuable and believed to be actualizing in the earist stage. Photolysis and biochemical methods are most environmental, but they are of low efficiency at present stage. Actually working system of so-called Yokohama Mark5 is introduced, too.

INTRODUCTION

The peoples of the world are aspiring to improve their standards of living. The standard of living is directly proportional to the energy consumption. Consequently, the people of the world are trying to increase their energy consumption faster than the population increase. The energy-resources in the world are finite in quantity and are being depleted at an ever growing rate. The energy-resources, the fossil fuels, have adverse effects on environment. An important type of pollution, air pollution, is caused mainly by fossil fuels used to obtain energy for transportation, power station, etc..

Solar energy is being seriously considered to satisfy part of the demand. If a convenient way of utilizing the solar energy can be found, it could be an answer to the aforementioned problems, since it is almost undepletable and is clean. The key of the solar energy utilization is undoubtedly how to store sunshine. Producing hydrogen fromwater by sunshine looks like an attractive solution to the above stated difficulties. Hydrogen can be used as a clean energy medium, can be used as a chemical raw material, and can be used to generate electricity. The most basic problem in the solar-hydrogen energy system is thus the hydrogen production using solar energy. In this paper, we review the promising some methods of such technologies and make some assesment on them.

HYDROGEN PRODUCTION BY HEAT ENERGY

If we wish to decompose water, $H_2O = H_2 + \frac{1}{2}O_2$, we need the energy equal to the enthalpy change given by

$$\Delta H = \Delta G + \Delta Q \ (=68.3 \text{ kcal/mol}), \qquad (1)$$

where ΔG and ΔQ ($= T\,\Delta S$, ΔS is the entropy change) are the change of Gibbs' free energy, and the change of heat energy respectively.

There are five main hydrogen production methods to which solar energy can be available, viz., Direct Thermal, Thermo-Chemical, Hybrid-Electrolytic, Photolytic, and Biochemical. These methods correspond to whether both of ΔG and ΔQ are used or one of them is used.

If the thermal process concerns, the efficiency is limited by the Carnot's efficiency

$$\eta_c = \frac{T_1 - T_2}{T_1}, \qquad (2)$$

where T_1 and T_2 are the highest and the ambient temperatures, respectively. On the other hand, there is no limit of efficiency when Gibbs' energy is supplied. Generally, Gibbs' free energy can be written as

$$\Delta G = \sum_i \Delta G_i, \qquad (3)$$

where ΔG_is can be contributed from optical, mechanical, electric, chemical, and other nonthermal energies.

Direct Thermal

If water vapor is heated up, hydrogen and oxygen will be decomposed after the equation:

$$H_2O + \text{heat} = aH_2O + bH_2 + cO_2 , \qquad (4)$$

where a, b, and c are the mole fractions. When the temperature is 4350 K , ΔG in eq.(1) is zero and the relationship:

$$a : b : c = 1 ; 1 : 1$$

is obtained and an appreciable fraction of hydrogen is available when the temperature rises above 3000 K. Fig. 1 shows the curve of mole fraction of dissociated hydrogen vs temperature(1).
It can be seen that very high temperatures are required for equilibrium dissociation of water to hydrogen and oxygen and that mole fraction or degree of dissociation increases with decreasing equlibrium pressure. The total thermal energy required, heat rejected and the thermal efficiency vs temperature of dissociation of water are shown in Fig. 2.
The energy for dissociation of hydrogen can be obtained from the solar radiation. For this purpose, an optical system which collects solar radiation and concentrates it into a small area could be utilized. If we use a parabolic mirror, the theoretical concentration ratio C is given as a function of rim angle r as (2):

$$C = 46200 \sin^2 r. \qquad (5)$$

The direct solar energy flux or the solar constant is about 0.1 W/cm^2 on the earth although it is somewhat variable. If the direct solar energy flux at normal incidence on the earth and concentration ratio are known, the heat flux in the image can be calculated and the maximum attainable temperature can be estimated from the Stefan-Boltzmann law of radiation.

In order to account for the reflection losses, the reflection coefficient η_r can be introduced (3). The attainable temperatures as a function of concentration ratio is shown in Fig. 3. Several optical concentration systems are also indicated in the same figure, viz., Mont-Louis, Odeillo, Natick, Algiers, and the proposed tower top point focous solar energy concentrators (4,5,6). For a reasonable yield in hydrogen production by direct decomposition of water, the temperature around 3000 K or above are required, and as a general rule, in order to operate at these temperatures, higher temperatures should be attainable at the image. High temperatures can be obtained in optical system such as in large solar furnances. Minimum requirements would be a concentration of the optical system necessitates a careful engineering design (6).

Another important process in direct thermal method is the separation of hydrogen from the mixed gas existing in the fraction such as given in eq. (4). Several methods have been studied. (1) The jet separation methods. If the mixed gas is jetted out, only the light gas goes on the curved path apart from the heavier gases. (2) The centrifugal method. (3) The membrane separation method. Some porous ceramics can be transparent only to hydrogen. (4) The magnetic separation method. Hydrogen is orth, but oxygen and water are para at high temperatures, therefore hydrogen goes straightforwardly while other do not in a strong transverse magnetic field.

The direct thermal method has high overall efficiency as high as 60 - 70 % because T_1 in eq. (2) is high, but the high heat-resistive materials are needed. No actual experiments are not carried out yet anywhere.

Thermo-Chemical

In direct thermal method, we use only heat energy, not Gibbs' free energy. Therefore it requires very high temperatures. This difficulty can be mostly removed by using chemical energy and mechanical energy in addition to the heat energy. Thermo-Chemical method is thus invented (7, 8).
The standard method can be written as a cycle:

$$\left.\begin{array}{ll} A + B + H_2O = AH_2 + BO & \text{(i)} \\ AH_2 = A + H_2 & \text{(ii)} \\ BO = B + \frac{1}{2}O_2 & \text{(iii)} \end{array}\right\} (6)$$

where the chemical substance A is an oxidation materials such as halogens (F, Cl, Br, I) or their compound and B represents a reduction materials such as transition metals (Fe, Cu, Ni, --) or their compound. More than 50 cycles with two steps, three steps, four steps,-- have been published so far. In Table I, some typical cycles, their steps, maximum temperatures, and the efficiencies based upon higher heating values of hydrogen are listed, leaving the values as they appeared in the papers. However, thermochemical cycles are intended mostly to combine with nuclear reactor, not with solar furnance up to now.
The evaluation of the overall practical efficiency of the thermochemical cycle is manifold. Optimistic is 50 %, while pessimistic is only 15 %. One should notice that not only the heat energy ΔQ but also Gibbs' energy ΔG are needed in this method. Gibbs' energy must be given

in the form of compression or depression in the reaction vessels.
The development of the corrosion-resistive materials in another important factor in this method. In a few years, a small scaled test plant will be constructed in some countries.

HYDRO-ELECTROLYTIC PRODUCTION

Electrolytic method of hydrogen production is not sophisticated but traditional and is so well-known that we would not describe the technologies. The weak point of this method is that the electric powers are mostly generated by burning petroleum. If solar energy is substituted, it could be a steady way in solving the energy problems.
The simplest method is the combination of power generation with electrolysis, and this is especially suited for coupling with ocean-thermal, wind, hydro and photovoltaic forms of solar energy since in these cases the solar energy is conventionally converted to electricity. Fig. 4 shows the tentative equipment of solid state device of producing hydrogen. This is called Yokohama Mark 4 and is utilizing a thermoelectric generation by semiconductors to electrolyze water. More profitable application of electrolysis to the hydrogen energy system is to combine it with thermochemical cycle, viz., uses of electric energy for ΔG and heat energy for ΔQ. An example is

$$\left.\begin{array}{ll} Cl_2 + H_2O = 2HCl + \tfrac{1}{2}O_2 & \text{(i)} \\ 2HCl = H_2 + Cl_2 & \text{(ii)} \end{array}\right\} \quad (7)$$

This first reaction is done by heat at about 700°C (9), and the second advances by electrolysis with o.54 V. It is an important point that the direct current with low voltage is easily obtained by solid-state-solar devices. In the above cycle, either Br or I can be replaced for Cl. Theoretical voltage necessary to electrolyze water is 1.23 V plus overvoltage and it is a great advantage to split water with only 0.5 V.

Solar beam has the wide range of wave length from ultra violet to infra red. The lights with shorter wave length are able to make advance some photochemical reactions (10). The products of the photochemical reactions are very easily electrolyzed. If the solar beam with longer wave length is converted to electricity which is to be supplied to the electrolysis , we have an effective conversion method of solar energy. This method means the utilization of two kinds of Gibbs' free energy, viz., electric and photon energies. Yokohama Mark 5 is an example of this type. It has been working to produce hydrogen about 90 l per hour per 1 m^2 of the surface area , at most. Fig. 5 is its picture (11).
The used photochemical reaction is

$$2FeSO_4 + I_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2HI \quad \text{(i)}$$

and the electrolysis achieves the reaction:

$$\begin{array}{ll} 2HI = H_2 + I_2 & \text{(ii)} \qquad (8) \\ Fe_2(SO_4)_3 + H_2O = 2FeSO_4 + H_2SO_4 + \tfrac{1}{2}O_2 & \\ & \text{(iii)} \end{array}$$

The overall efficiency of Yokohama Mark 5 is strongly limited by the low efficiency of the thermoelectric conversion (5 %) ; but if auxiliary electric energy is supplied, the efficiency can be attained to near 20 % (11).
More than 90 % of the input heat are wasted from the thermoelectric system, so the wasted heat ahould be effectively used if we wish to raise up the efficiency without auxiliary power. The wasted heat is used to make progress of eq. (8)-(ii), and the electrolysis takes place only for eq. (8)-(iii) in a new system of Yokohama Mark 6. The efficiency is estimated about 25 % (11, 12).

PHOTOLYTIC PRODUCTION

Photons on solar beam, under certain circumstance, can be absorbed by water molecules to release hydrogen when the photons have the wave length shorter than a certain value in ultra violet range. This phenomenon. photolysis, could be used to produce hydrogen directly from the sun's photon. Most of the ultra violet radiation is absorbed in the upper atomshere. Consequently, the intensity of the solar radiation reaching the earth is very low in the ultra violet region of the spectrum (about 5 % of all the solar energy) . On the other hand, water is almost transparent to the visible light. Hence photocatalysis must be used for the photolysis of water on earth. The function of such a catalysis is to absorb the solar radiation and then transmit the energy to water in order to decompose it. An example is due to Heidt (13):

$$\left.\begin{array}{ll} Ce^{4+} + \tfrac{1}{2}H_2O + \text{photon} = Ce^{3+} + \tfrac{1}{2}O_2 + H^- & \text{(i)} \\ Ce^{3+} + H_2O + \text{photon} = Ce^{4+} + \tfrac{1}{2}H_2 + OH^- & \text{(ii)} \\ H^+ + OH^- = H_2O & \text{(iii)} \end{array}\right\} (9)$$

The efficiency in such a case as above utilizing compound salts is generally lower than 0.01 %.

Another type of photolysis is to use a photolytis phenomenon at semiconductor electrodes. If two electrodes composed of TiO_2 and Pt are immersed in an aqueous electrolyte and are separated by a porous membrane, hydrogen and oxygen are evolved at Pt- and TiO_2-electrodes, respectively, and an electric current flows in a circuit between these electrodes (14). The electrode reactions are explained as

$$\left.\begin{array}{ll} TiO_2 + \text{photon} = 2e + 2p & \text{(i)} \\ 2p + H_2O = 2H^+ + O_2 & \text{(ii)} \end{array}\right\} \text{(10)}$$

at TiO_2-electrode, where electrons (e) and positive holes (p) yield. Electrons and protons migrate to another electrode via circuit and electrolyte, respectively, and at Pt-electrode, the reaction

$$2H^+ + 2e = H_2 \qquad \text{(iii)}$$

occurs.
The useful photons have to have the wave length less than 4150 A in so far as TiO_2 concerns and the utilization efficiency of solar beam is very small. (less than 1 % at most). In addition, most of good semiconductors are dissolved into the electrolytes and the mechanism can hardly work steadily. The fabrication of semiconductor to overcome the above two defects is required, we think this is not an easy task.

Biochemists (15) have found out that there exist biological photocatalysts too. These are intact cells of some species of blue-green, green , red, and other algae and some photosynthetic bacteria. Basically solar radiation is absorbed by a pigment in the cell, e.g., the light harvesting chlorophyll protein. This energy is transmitted to an electron through the reaction center chlorophyll protein. The source of this electron is a hydrogen atom donated by some electron donor compound such as water. Under some physico-chemical conditions, such energized electrons combine with $2H^+$ to form H_2. The efficiency of such processes is too low to be practical use in the present stage.

CONCLUSIONS

Most important thing in the solar-hydrogen energy system is to produce hydrogen from water by solar energy. We have investigated a several methods theoretically, and experimentally for a few methods. Among them, the direct thermal methods has the potential of the highest efficiency but has still a material problem. No remarkable experiments are undertaken by now. High efficient and actualizing are the hybri-electrolysis. In so far as the thermochemical methods are concerned, any definite conclusionas are not done yet on the energy economy in competition with the traditional electrolysis methods.
All the methods will benifit from further research and development works.

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ILLUSTRATIONS

Figure 1. Water Decomposition Temperature vs Mole Fraction of Dissociated Hydrogen.

Figure2. Water Decomposition Temperature vs Heat Absorbed and Heat Rejected per Mole of Hydrogen and Thermal Efficiency.

Figure 3. Black Body Temperature at Image vs Concentration Ratio.

Figure 4. Yokohama Mark 4. An Experimental Hydrogen-Producing Solid-State-Device Utilizing Thermoelectric Generation and Electrolysis.

Figure 5. Yokohama Mark 5. Hydrogen Production Installation Hybridized by Photochemical and Thermoelectric Systems.

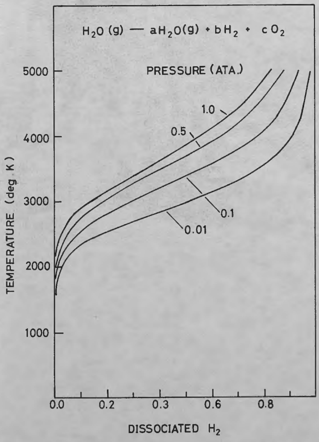

Figure 1

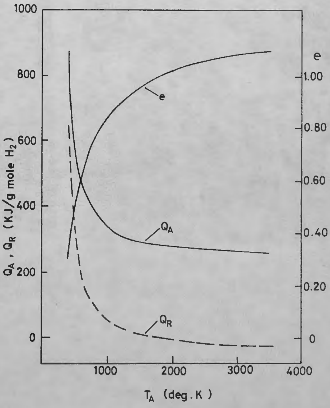

Figure 2

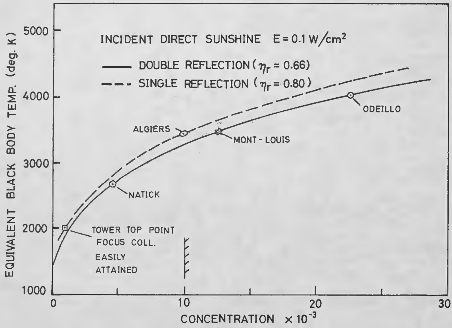

Figure 3

Figure 4

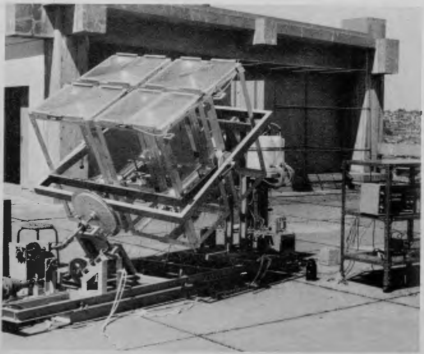

Figure 5