6. HYDROGEN PRODUCTION BY THERMOCHEMICAL METHODS –

J. C. Sharer and J. B. Pangborn

Introduction

During recent years, an interest has been generated in thermochemical hydrogen production methods.[9,13,17] Thermochemical hydrogen production is a means of splitting water into its elements, hydrogen and oxygen, via a series of chemical reactions. All chemical intermediates are recycled internally within the process so that water is the only raw material and hydrogen and oxygen are the products. This process must be driven by an external heat source, which could be a high-temperature, gas-cooled, nuclear reactor (HTGR) or a solar furnace. The maximum temperature requirements for heat for most proposed cycles lie within a temperature range of 650° to 1100°C, thus eliminating many of the lower temperature heat sources as potential energy donors.

The objective of using a closed-loop series of chemical reactions is established in order to utilize heat directly as the form of energy for hydrogen production and to use only water as a raw material. This approach differs from the major commercial practice of hydrogen production – i.e., steam reforming of natural gas – because a carbon source is not expended and carbon dioxide is not a coproduct. It also differs greatly from the less common commercial practice of producing hydrogen via electrolysis, where the majority of the energy requirements are supplied in the form of work (electricity). Because of practical limitations in the efficiency of converting heat from a primary energy source (e.g., HTGR or solar furnace) to work (electricity), it may be advantageous to utilize the heat directly at, hopefully, higher overall efficiencies. It should, however, be noted that water splitting processes, whether electrolytic or thermochemical, are limited by the second law of thermodynamics to the extent that heat is converted to the "free" chemical energy of hydrogen. This will be shown in more detail later in this section.

The general scheme of thermochemical hydrogen production is depicted in Figure 6-1, which includes a 2-step example – the cycle postulated by Emil Collett and patented in Great Britain in 1924 (probably the first thermochemical cycle for water splitting).[5]

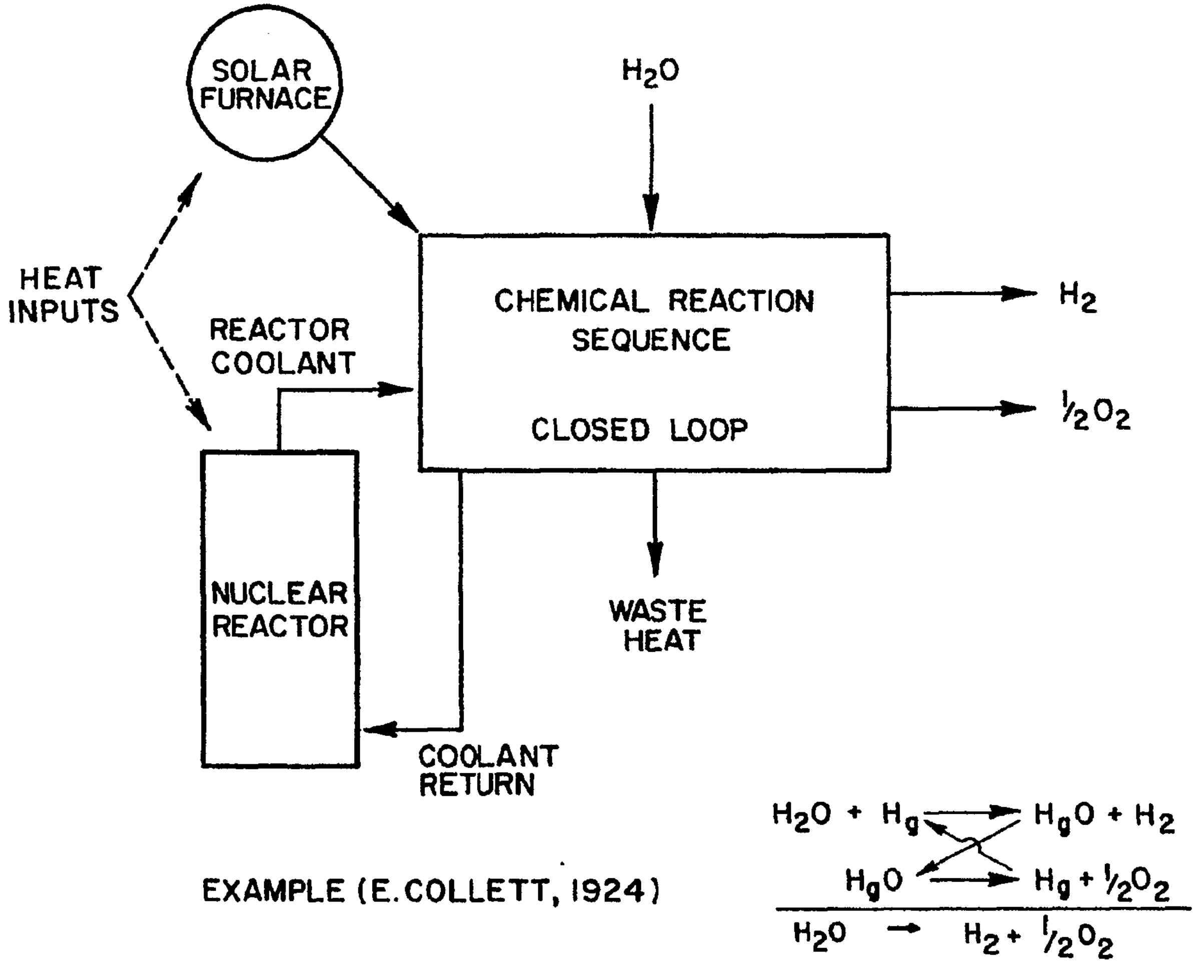

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Figure 6-1. THERMOCHEMICAL HYDROGEN PRODUCTION

Water may be chemically decomposed in a single-step reaction. This, however, requires a very high temperature thermal source because temperatures in excess of 2500° C are essential for reasonable reaction yields. Process heat sources are not available at these temperature levels, and the materials requirements for containment and high-temperature gas separations make techniques impractical for large-scale hydrogen production.

Theoretically, a series of two or more chemical reactions can be devised to react water with intermediates, liberate hydrogen and oxygen at different reaction sites, and regenerate all of the consumed intermediates. These (ideal) reactions would be selected so that they could be driven thermally and would not require work. In other words, the free-energy change for each reaction would be equal to or less than zero, and no work would be required for separation of the reaction products. The reaction cycle would be composed of only entropy (heat) requirements. If such a case existed, heat could be used directly, and it would be possible, with the proper choice of reactions, to produce a cycle with very high overall energy efficiency. As will be discussed later, an ideal thermochemical cycle requiring no work does not exist, and there are other considerations that must be examined to determine if a proposed cycle is feasible and practical.

Although thermochemical processes for the production of hydrogen are not in commercial practice today, considerable research is under way at research centers around the world to develop the chemical and engineering technology for thermochemical hydrogen production. Appendix B of this report describes the programs of 23 research groups that deal with thermochemical hydrogen. This information was compiled from the published literature and from private communications (both personal visits and telephone interviews). For each research organization, the appendix includes the organization's address, the duration of its program, a list of nonproprietary cycles, and a list of publications. Because of the proprietary nature of the many programs that are under private sponsorship, full disclosure of the organizations' work is impossible. Therefore, some of the cycles thought to be of high quality in terms of practicality and energy efficiency are not available for publication.

It should also be noted that the development of thermochemical hydrogen production processes is in its infancy stages. Therefore, it is premature to report in detail on process parameters, engineering flowsheets, and cost analyses of specific processes. Thermochemical hydrogen production on a large-scale basis is probably at least 20 years away. This is indicated by the variety of research organizations doing work in the field and the numerous approaches to this research. For example, an academic institution with governmental funding will have an entirely different approach from an industrially sponsored organization. In addition, an organization with a high level of funding has the opportunity for a more comprehensive program than those groups with programs that can support only one or two researchers. With the many degrees of freedom available in this area of research, almost every organization has a unique approach, with varying goals and abilities to publish or communicate its conclusions. Therefore, compiling and discussing all work done in the area of thermochemical hydrogen production is a difficult task. The information included herein is as complete and accurate as possible as of January 31, 1975.

Table 6-1 presents a summary of the information included in Appendix B. Each research organization is listed with the areas of research that it is involved in. Research activities are divided into seven categories. They are –

- Literature Surveys
- Derivation of Novel Cycles
- Analytical Evaluation of Cycles
- Experimental Evaluation of Cycles
- Comparisons With Electrolytic Hydrogen Production
- Nuclear Reactor Interface Studies
- Detailed Engineering Studies of Chosen Cycles.

Although the level of effort in each activity is not depicted, a notation is established to differentiate between published work, proprietary or unpublished work, and no work for each area.

Basic Thermodynamic Considerations

Because thermochemical hydrogen production schemes are in the early stages of development, a basic thermodynamic approach to prove feasibility is required. The following equation describes the overall system reaction

Table 6-1. AREAS OF RESEARCH ON THERMOCHEMICAL HYDROGEN PRODUCTION BY INTERESTED GROUPS

	Research Activities						
Group	Literature Surveys	Derivation of Novel Cycles	Analytical Evaluation of Cycles	Experimental Evaluation of Cycles	Comparisons With Electrolytic Hydrogen Production	Nuclear Reactor Interfaced Studies	Detailed Engineering Studies of Chosen Cycles
Aerojet-General Corp., El Monte, Calif.	Reply not received.						
Air Products and Chemicals, Inc. Allentown, Penna.	2	3	3	3	3	3	3
Argonne National Laboratory, Argonne, Ill.	2	1	1	2	3	3	3
Atomic Energy of Canada Ltd., Pinowa, Manitoba	1	3	3	3	3	3	3
Avco Corp., Wilmington, Mass.	Reply not received.						
EURATOM, Ispra, Italy	2	1	1	1	2	1	1
Gaz de France Paris, France	2	2	2	2	2	3	3
General Atomic Co. San Diego, Calif.	2	1	2	2	3	2	2
General Electric Co. Schenectady, N.Y.	2	1	1	2	2	1	1
Holifield Natl. Lab. Oak Ridge, Tenn.	2	2	2	2	3	3	3

Key: 1 = Published Results
2 = Proprietary or Unpublished Work
3 = No Work in This Activity as of January 31, 1975

Table 6-1, Cont. AREAS OF RESEARCH ON THERMOCHEMICAL HYDROGEN PRODUCTION BY INTERESTED GROUPS

	Research Activities						
Group	Literature Surveys	Derivation of Novel Cycles	Analytical Evaluation of Cycles	Experimental Evaluation of Cycles	Comparisons With Electrolytic Hydrogen Production	Nuclear Reactor Interface Studies	Detailed Engineering Studies of Chosen Cycles
Institute of Gas Technology, Chicago, Ill.	2	1	1	2	1	1	3
Iowa State Univ. Ames, Iowa	2	2	2	2	3	3	3
Japanese Govt. (Sunshine Program), Tokyo, Japan	2	2	2	2	2(?)	3(?)	3(?)
KFA (Nuclear Research Center), Jülich, W. Germany	2	2	1	2	3(?)	1	3
KMS Fusion, Inc. Ann Arbor, Mich.	2	2	2(?)	2	3	2	3
Lawrence Livermore Lab., Livermore, Calif.	2	1	2	1	3	3	3
Los Alamos Scientific Lab., Los Alamos, N. M.	2	1	2	2	3	3	3
Pechiney Ugine Kuhlmann, Paris, France	2	3	1(?)	3	3	3	3
Stevens Inst. of Tech. Hoboken, N. J.	1	3	3	3	3	3	3
Univ. of Kentucky Lexington, Ky.	2	2	1	3	3	3	3
Univ. of New Mexico Albuquerque, N. M.	1	3	1	3	3	3	3
Univ. of Puerto Rico Mayaguez, Puerto Rico	2	3	1	3	3	3	3
Westinghouse Electric Corp., Pittsburgh, Penna.	2	2	2	2	2	2	3(?)

Key: 1 = Published Results
2 = Proprietary or Unpublished Work
3 = No Work in This Activity as of January 31, 1975

for all processes producing hydrogen and oxygen from water:

$$H_2O(\ell) \rightarrow H_2(g) + {}_1/_2\, O_2(g) \text{ at } 25°C \qquad (6\text{-}1)$$

If we deal with electrolysis, direct thermal decomposition, or a thermochemical cycle, the net reaction is described by Equation 6-1. For this net reaction, we know that –

$$\Delta H = \Delta G - T\Delta S$$

where –

ΔH = enthalpy change for the reaction

ΔG = Gibbs free-energy change for the reaction

ΔS = entropy change for the reaction

T = temperature of the reaction

A basic proof has been derived that shows that water-splitting processes are subject to a Carnot-type limitation on the transformation of heat into free energy.[8,14] It applies to any water-splitting process in which water is the only raw material and in which the process is driven directly or indirectly by heat. These processes include thermochemical water-splitting cycles, electrolysis (including electricity generation), and direct thermal water splitting. The proof is as follows:

Consider a steady-state process that converts water into hydrogen and oxygen by obtaining heat, q_r, at a constant, elevated temperature, T_r (from a nuclear reactor, for example), and by rejecting heat, q_e, at a lower temperature, T_e, which may be the environment temperature. (See Figure 6-2.) Aside from hydrogen production, the only energy outputs from the process are the heat rejection and the displacement of the environment. The reactant water and product gases enter and exit at the fixed conditions, T_e and P_e.

Writing the first law for such a system, where ΔE is the internal energy change and ΔV is the volume displacement of the environment, Equation 6-2 is obtained:

$$q_e = q_r - Pe\Delta - \Delta E \qquad (6\text{-}2)$$

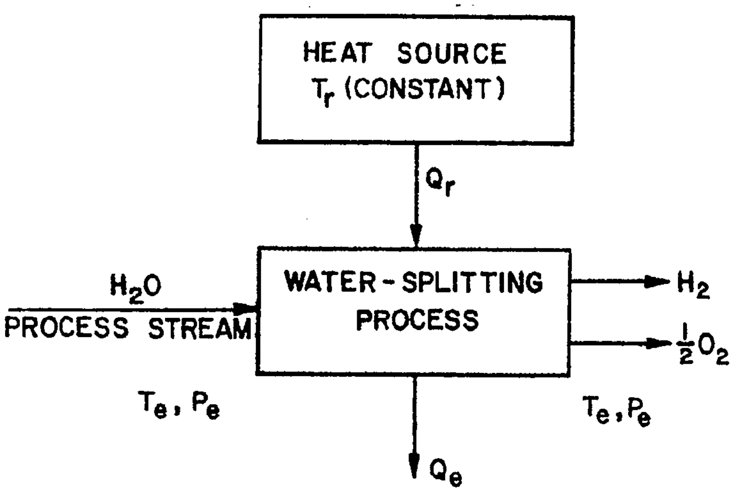

Figure 6-2. IDEAL STEADY-STATE PROCESS TO CONVERT WATER INTO HYDROGEN AND OXYGEN

Denoting the entropy change of the system by ΔS and writing the second law, we derive Equation 6-3:

$$\Delta S \geq \frac{q_r}{T_r} - \frac{q_r}{T_e} \tag{6-3}$$

Combining Equations 6-2 and 6-3 results in Equation 6-4:

$$\Delta E + P_e \Delta V - T_e \Delta S \geq q_r \left(\frac{T_r - T_e}{T_r}\right) \tag{6-4}$$

The corresponding equation for the process stream is —

$$\Delta E + P_e \Delta V - T_e \Delta S = \sum_i \mu_i \Delta n_i \tag{6-5}$$

where μ_i is the chemical potential of a component —

$$\mu_i = \left(\frac{\delta G}{\delta n}\right)_{T,\ P,\ n} \tag{6-6}$$

G denotes Gibbs free energy, and n denotes the number of moles of a component.

Substituting Equation 6-5 into 6-4, Equation 6-7 is obtained:

$$\Sigma \mu_i \Delta n_i \leq q_r \left(\frac{T_r - T_e}{T_r}\right) \tag{6-7}$$

From the definition of Gibbs free energy and the Gibbs-Duhem Equation, $SdT + VdP - \Sigma n_i d\mu_i = 0$ (where $dP = dT = 0$ because T is constant at T_e and P is constant at P_e), Equation 6-8 is obtained:

$$\Delta G \leq q_r\left(\frac{T_r - T_e}{T_r}\right) \quad \text{or} \quad \frac{\Delta G}{q_r} \leq \left(\frac{T_r - T_e}{T_r}\right) \qquad (6\text{-}8)$$

From this relationship, an ideal water-splitting efficiency can be written involving the enthalpy, Δ H, or heating value of hydrogen:

$$E = \frac{\Delta H}{q_r} \leq \frac{\Delta H}{\Delta G}\left(\frac{T_r - T_e}{T_r}\right) \qquad (6\text{-}9)$$

The efficiency of any given process or cycle should be compared with the best attainable, which is given by Equation 6-9. From the process –

$$H_2O(\ell) \rightarrow H_2(g) + {}_1/_2\, O_2(g)$$

at 1 atmosphere and 25° C, where $\Delta H = 68.3$ kcal/g-mol and $\Delta G = 56.7$ kcal/g-mol, we have calculated the ideal water-splitting efficiencies presented in Table 6-2.

Actual thermochemical water-splitting cycles cannot be evaluated by Equation 6-9; they can only be compared with it, and they cannot exceed it. Theoretically, a cycle might be written so that –

1. All the chemical reactions proceed as written, spontaneously, with no work inputs required (only heat inputs).
2. No gas separations need to be done, and no compression work is required.
3. All the heat required by the cycle is fed in at T_r, all the waste heat is rejected at T_e, and there is perfect internal matching of endothermic and exothermic processes.

When all these conditions are fulfilled, Equation 6-9 can be applied. However, no cycles known to us come close to fulfilling all these criteria. If a given cycle satisfies criteria 1 and 2, but not 3, a simple heat (entropy) balance is adequate, but very few cycles even approximate this circumstance.

For an electrolysis process that operates at 25 °C, we know that work must be supplied to the reaction and that, ideally, the quantity of work is equal to the Gibbs free-energy change for the reaction, 56.7 kcal/g-mol of hydrogen. There is also an ideal heat requirement that is equal to the entropy term, $T\Delta S$, which for this reaction is equal to 11.6 kcal/g-mol of hydrogen. We do produce hydrogen that has a high heating value equal to the

Table 6-2. IDEAL WATER-SPLITTING EFFICIENCIES

T_r	T_e	q_r	q_e	H/q_r	E, %
°C		kcal/g-mol			
125	25	222	154	0.307	30.7
225	25	140	72	0.487	48.7
325	25	113	45	0.605	60.5
425	25	99.8	31.5	0.692	69.2
525	25	90.3	22.0	0.757	75.7
725	25	80.7	12.4	0.846	84.6
1225	25	70.8	2.5	0.965	96.5
1725	25	66.6	–1.7*	1.025	100.0*
4025	25	60.9	–7.4*	1.122	100.0*
∞	25	56.7	–11.6*	1.204	100.0*

*Indicates negative heat rejection q_e at T_e (25°C). To have a process efficiency in excess of 100%, this negative q_e would have to be "free heat" input from the environment. An example would be a 25°C, 1 atmosphere reversible electrolyzer operating at 1.23 volts and supplying exactly 56.7 kcal of electrical energy for each mole of water decomposed. With 100% heat-to-work efficiency ($T_r = \infty$, $T_e = 25°C$), this overall process would be "120%" efficient, but it requires a free entropy input of 11.6 kcal/mole of water decomposed.

negative of the enthalpy change of this overall reaction, or −68.3 kcal/g-mol of hydrogen. The work that is required for the reaction in an electrolysis cell is supplied in the form of electricity, the generation of which is subjected to a Carnot limitation by the second law of thermodynamics. Electricity today has a practical generation efficiency usually in the range of from 30% to 40%.

Because work generating cycles are limited in efficiency by maximum operating temperatures (imposed by available heat sources) and by process materials for heat transfer or containment of working fluids, it would be advantageous to use heat directly in a chemical process, thus avoiding many of the mechanical limitations that cause the practical limitations on efficiency in electricity generation. By using heat directly, it is hoped that one step in an energy conversion process would be eliminated. This is the basic reason for trying to devise a thermochemical hydrogen production scheme.

In reality, there will be work requirements for thermochemical cycles. For example, work will be required to drive some reactions to completion, to perform separations of reaction products, for compression work for reactions that operate at elevated pressures, and to maintain mass transfer and sustain pressure drops in the system. These work inputs can and should be minimized to achieve the maximum operating efficiency of a thermochemical cycle, and this can be accomplished by selecting proper operating conditions for the various chemical reactions. The operating temperatures must be selected so that the heat requirements will fall within some feasible temperature envelope that could be supplied by a nuclear reactor or some other heat source (e.g., solar). From the literature, maximum temperatures in the range of from 900° to 1100°C may be attained by an advanced-technology, high-temperature, gas-cooled nuclear reactor (HTGR).[16,18,19] Limits on solar furnaces for this application have not yet been estimated, although, with concentration, 2000°C temperatures have been achieved for other purposes.[3]

Also essential for a thermochemical cycle is that the net overall reaction for the series of reactions selected be described by water-splitting Reaction 5-1 (i.e., that all intermediates be internally recycled within the process). For example, let's examine a cycle proposed by the Institute of Gas Technology and others,[13] as described below:

$$
\begin{array}{llll}
2CrCl_2(s) + 2HCl(g) \rightarrow 2CrCl_3(s) + H_2(g) & 25^\circ C & \Delta G_{Rx} = -8.5 & (6\text{-}10) \\
2CrCl_3(s) \rightarrow 2CrCl_2(\ell) + Cl_2(g) & 925^\circ C & \Delta G_{Rx} = +15.1 & (6\text{-}11) \\
\underline{Cl_2(g) + H_2O(g) \rightarrow 2HCl(g) + 1/2\,O_2(g)} & 925^\circ C & \Delta G_{Rx} = -5.41\,. & (6\text{-}12) \\
H_2O \rightarrow H_2 + 1/2\,O_2 & & &
\end{array}
$$

The net overall reaction "splits" water into hydrogen and oxygen. The temperatures are selected so that the Gibbs free-energy change for each reaction is minimized and so that the temperatures are within an envelope of 25° to $925^\circ C$. Reactions 6-10 and 6-12 have free-energy changes of -8.5 and -5.41, respectively, and theoretically will not require work inputs to generate appreciable quantities of reaction products. Admittedly, this does not include the work inputs necessary for product mixture separation. Reaction 6-11, however, does have a positive free-energy change, $+15.1$ kcal at $925^\circ C$, and will require a work input. We have, however, in theory reduced the work requirements for splitting one mole of water from 56.7 to 15.1 kcal.

This cursory look at the basic thermodynamic considerations for reaction and temperature selection can be summarized as follows. For a promising thermochemical cycle, reactions, and temperatures for those reactions, should be selected so that the free-energy change for each reaction is minimized and should fall within a tolerable range. (Most research organizations have selected a range not larger than -15 kcal to $+20$ kcal per reaction, per gram-mole of hydrogen produced.) Temperatures should be selected between $25^\circ C$ and some maximum temperature that could be supplied by a futuristic heat source. (This maximum temperature varies between 800° and $1000^\circ C$, depending on the research organization.)

There are other considerations that must be examined in evaluating thermochemical cycles. Some of these are work requirements for gas separations, the exchange of heat within the cycle, corrosivity of chemical compounds, interfacing the thermochemical cycle with a heat source, and reaction kinetics. These considerations are discussed in the following paragraphs.

Efficiency Calculations for Thermochemical Cycles

Although most research organizations have determined theoretical maximum (ideal) efficiencies for thermochemical cycles, relatively few groups have tried to calculate or estimate realistic values or process operating efficiencies. Each organization has devised its own method of efficiency evaluation that best suits the objectives of its program. To date, no one method has been established as the best approach, although it may be advantageous to determine a scheme that will allow each team of researchers to measure the quality of its cycle against those proposed by others.

Importance of Energy Efficiency for Thermochemical Cycles

The efficiencies of cycles may be the most important criterion in determining the most promising cycle. As in electrolysis, operating costs of thermochemical processes may contribute significantly to the hydrogen production cost. A consideration of the electrolysis process for hydrogen production is useful at this point: For example, Figure 6-3 shows the effect of the cost of electricity on the cost of hydrogen produced by electrolysis.[20]

In Figure 6-3, the abscissa intercepts are directly related to the capital costs for an advanced electrolyzer plant. The slope of the cost lines reflect the electrolyzer efficiency. Because the cost of nuclear electricity is in excess of 10 mills/kWhr, operating costs will be at least 65% to 80% of the production cost of electrolytic hydrogen. The more efficient the electrolyzer operation, the lower the hydrogen cost (after some power cost is assumed).

It is interesting to note that an estimated 67% or more of the proportion of capital costs associated with a nuclear heat supply versus those associated with an entire conventional nuclear-electricity generating plant is attributable to the nuclear heat supply.[11,15] Hence, the nuclear-heat portion of all plant capital costs for electrolytic and thermochemical hydrogen production will be relatively large for processes of reasonable and competitive costs. A recent study[15] that included projections of costs for thermochemical hydrogen placed the nuclear-heat portion of the hydrogen production cost at 44%. Evidently, efficiency of the use of nuclear heat will have a strong influence on both electrolytic and thermochemical hydrogen production — i.e., the greater the efficiency, the cheaper the cost of the hydrogen (for similar plant capital costs).

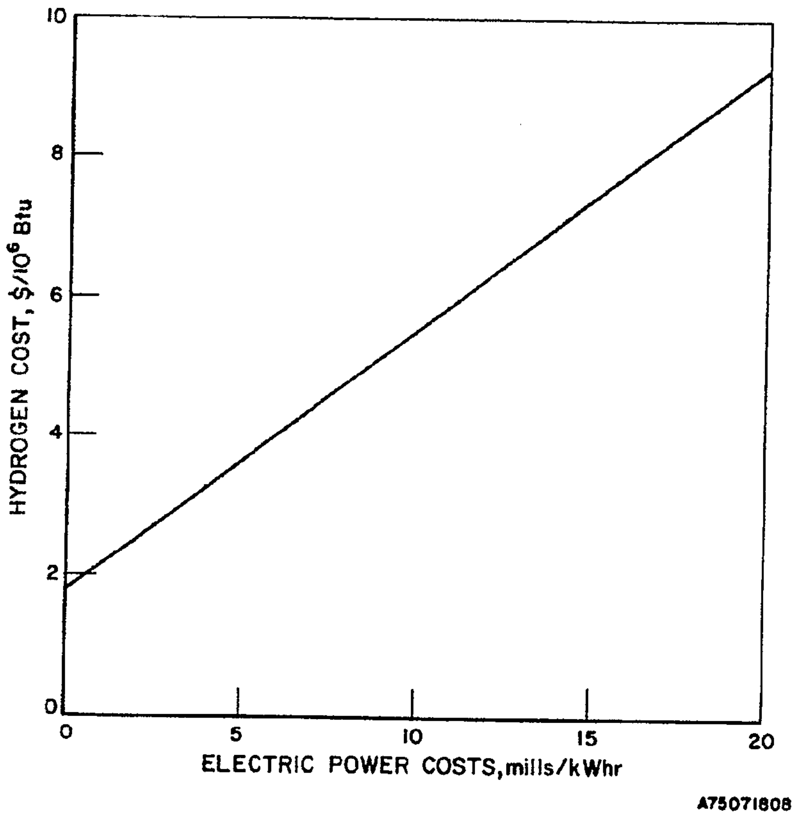

Figure 6-3. COST OF HYDROGEN PRODUCED BY AN ADVANCED ELECTROLYZER

The efficiency of a cycle can be defined as the heat available in the hydrogen produced (usually considered to be the high heating value, HHV, of the hydrogen, or 68.3 kcal/g-mol) divided by the quantity of heat required to produce one gram-mole of hydrogen; this quotient is multiplied by 100.

$$\text{Efficiency} = \frac{\text{HHV}_{H_2}}{\text{Heat Input}} \times 100 \qquad (6\text{-}13)$$

The HHV of hydrogen is recommended as the measure of product energy for three reasons:

1. The HHV is consistent with the overall thermodynamic requirements of water splitting. Liquid water is the primary raw material, and gaseous hydrogen and oxygen are the products. The enthalpy of this decomposition process (at 1 atm and 25° C) is equal to the negative of the HHV of hydrogen.

2. Although most fuel-burning equipment used today does not extract even the low heating value (LHV) of the fuel, energy costs, conservation, and emphasis on efficiency will tend to remedy this waste in the future —

particularly if manufactured hydrogen is the fuel. Laboratory tests of developmental models of hydrogen-burning appliances have already demonstrated that it is possible to extract more than the LHV of hydrogen fuel. Further, it would make little sense to deal with utilization efficiencies exceeding 100% (basis LHV) in the future.

3. The Gas Utility Industry uses the HHV by convention and by statute. This is not arbitrary, but is partly because comparable calorimetry determinations can most easily and accurately be made by condensing the condensable products of combustion (H_2O) and cooling to near room temperature.

Techniques for Estimating Cycle Efficiency

A form of Equation 6-13 is used by almost all research organizations that attempt to estimate cycle efficiencies. However, distinctions between techniques for efficiency estimation (explained below) lie in determining the denominator of the equation. Only a few organizations have not developed efficiency calculation procedures. Usually, these organizations have done valuable survey work and have not been concerned with deriving and evaluating cycles. Examples of such organizations are Atomic Energy of Canada, Ltd., Pechiney Ugine Kuhlmann (Paris), and the Stevens Institute of Technology. Other organizations, such as Lawrence Livermore Laboratory (LLL) and Iowa State University, have been more concerned with cycle chemistry and have not concentrated on efficiency estimates.

The researchers at LLL do, however, employ a simple estimate of "efficiency" in order to measure the quality of one cycle against another. They calculate a heat input that is equal to the sum of the enthalpy changes of all endothermic reactions calculated at 25° C. This is by no means an estimate of process efficiency. Indeed, it is nothing more than a "yardstick" by which to measure the expected energy inputs of cycles.

There are certain reasons for taking this approach. First, it is a quick, simple way to compare cycles. Second, there is extensive thermodynamic data (e.g., enthalpy of formation) for chemical compounds at 25° C, but measured or extrapolated data at higher temperatures is often incomplete. There are also many disadvantages to this simple estimation or comparison procedure. First, it makes no distinction between free-energy (work) requirements and entropy (heat) requirements; and, of course, it does not account for the relative change between the two as a function of temperature for a chemical reaction. Second, work requirements for reaction product separation are ignored, and these requirements may be significantly different for cycles of "similar" chemistry. Additionally, this procedure does not account for internal heat utilization and rejection (waste) that occurs from heat exchange between steps within the cycle.

Los Alamos Scientific Laboratories (LASL) makes a small addition to the LLL method. Researchers there sum the enthalpy changes of the endothermic reactions calculated at 25° C and add to that the sum of the positive free-energy changes of reactions calculated at 25 ° C. This total is assumed to be the heat input, and an efficiency is calculated via Equation 6-13.

Again, this efficiency is only used as a measure of quality and should not be confused with process-type efficiencies. However, even as a comparative technique it suffers from some of the deficiencies enumerated above for the LLL procedure. It should be noted that free energy is not equivalent to heat; it generally takes about 3 units of heat to generate one unit of work. Cycles of similar chemistry may require significantly different work inputs, and the LASL procedure partially accounts for this (on a comparative basis) by accounting for reaction free-energy changes – but only at 25 ° C.

Researchers at Argonne National Laboratories, who have published articles on cycle analysis,[1] have developed a thermodynamic scheme for estimating cycle efficiency or "figure of merit." They prefer to analyze cycles with respect to the operation of a heat engine, and they define a "figure of merit" that is equal to the free-energy change of water splitting at 25° C divided by the heat requirement, as shown in Equation 6-14.

$$\text{Figure of Merit} = \eta = \frac{\Delta G^\circ_f(H_2O)}{2\ (\text{Heat Required})} \qquad (6\text{-}14)$$

To determine the figure of merit for a multistep cycle, a temperature-entropy diagram is constructed. On such a diagram, the reaction steps are isothermal lines at the reaction temperature, and the lines connecting the isotherms represent the heating and cooling of materials streams. A material phase change would also be represented by an isotherm. The enclosed area of the temperature-entropy diagram must be the work accomplished by operating the thermochemical cycle, $\Delta G^\circ_f(H_2O)$. A simplifying assumption is that the heat absorbed and the heat rejected during the heating and cooling of the reactants and products are equal, so that the reactants are heated to the reaction temperature through perfect heat interchange with the products. The heat required for the cycle is determined mathematically by multiplying the algebraic sum of the entropy changes by the associated temperatures.

The procedure is elegant from the standpoint of thermodynamics; however, it assumes that thermochemical cycles require only heat inputs for operation and that, for comparative analysis, cycles can be evaluated by entropy input only. The idealizations about heat capacity and heat exchange are acknowledged, and the associated errors would be relatively small. However, the work requirements (and the attendant heat energy) to drive reactions, separate products, compress gases, etc., would have to be accounted for separately. These quantities can be large and dissimilar, even for cycles of similar-appearing chemistry.

Researchers at General Electric Co. have published thermochemical cycles and have calculated efficiencies for three of their cycles.[9,10] They calculate the enthalpy changes for reactions at the postulated temperatures and assume that the process heat requirements are equal to the sum of the enthalpy changes for the endothermic reactions. To this value they add between 10% and 15% of that heat as energy needed for pumping and to compensate for miscellaneous losses. (This value was assumed based on similar input requirements of oil refineries.) This total heat requirement is then divided into the low heating value of hydrogen (57.6 kcal/g-mol) to obtain an efficiency. (As previously stated, it is our opinion that the high heating value of hydrogen would be preferable and more consistent.)

The University of Kentucky, EURATOM, and the Institute of Gas Technology have gone a step further with cycle efficiency estimates. They calculate a process heat requirement in the following manner: All heat requirements for endothermic reactions and for heating compounds from one reaction temperature to a higher one are determined. This requires heat-capacity and phase-change data or estimates. Likewise, those process steps in which heat is liberated are determined – that is, those involving exothermic reactions and heat release from cooling a component from some temperature to a lower temperature. Calculations are then performed to determine where, according to temperature levels in the cycle, the available heat can be used to supply endothermic requirements. As much usable heat as possible is transferred internally between endothermic and exothermic steps. A net heat input is required to satisfy all remaining endothermic reactions and component streams. This is the process heat requirement. (This procedure assumes heat exchange efficiencies of 100%.)

In addition to the process heat requirement, there are work requirements for gas separations, for inputs to drive reactions (mechanical or electrical inputs), and sometimes for compression for elevated-pressure operation. The work term for gas separations is assumed to be equal to the free energy, ΔG, of separation calculated by Equation 6-15:

$$\Delta G_{SEP} = RT\Sigma\, a_i \ln x_i \qquad (6\text{-}15)$$

where —

a_i = moles of gas component i at equilibrium

x_i = mole fraction of gas component i at equilibrium.

Before separation, attainment of either equilibrium concentration at the reaction temperatures or some stated extent of reaction (percent of equilibrium) may be assumed for the mixture of gases.

This manipulation is done for all reactions involving gas separations. When possible and advantageous, IGT uses an additional procedure to cool the gas mixture (to a lower step temperature) before the (mathematical) separation is accounted for. In a case in which work is required to achieve reasonable yields from a chemical reaction, the quantity of work is assumed to be at least the positive free-energy change of the reaction. For example, an electrochemical or electrolysis step is presumed 80% efficient, requiring 125% of the reaction free-energy requirement.

The sum of the work terms is the total work input required for the cycle. At this point, the two research groups manipulate the numbers differently.

The University of Kentucky[7] assumes a heat-to-work efficiency of 30% (constant). They determine the heat required to generate this work, add it to the process heat requirements, assume this to be the total heat input, and calculate an efficiency like Equation 6-13 — or more explicitly, according to Equation 6-16:

$$\text{Efficiency or Figure of Merit} = \frac{HHV_{H_2}}{(\text{Process Heat Input}) + \frac{\text{Work Input}}{0.30}} \times 100 \qquad (6\text{-}16)$$

where HHV_{H_2} is the high heating value of hydrogen.

IGT first examines the waste heat from the enthalpy balance — that is, the exothermic heat not available for exchange within the cycle. If heat of a temperature high enough (above 325 °C) to be practically useful in generating work is available, it is converted to work via a power plant with an arbitrarily assumed efficiency. This quantity of work is then subtracted from the cycle work requirement. If more work is required, the heat needed for this work is determined via a power-plant efficiency formula in which the maximum temperature is arbitrarily assumed to be the highest (endothermic) reaction temperature of the cycle and the lowest temperature (for waste heat) is 125 °C. In attempting to calculate a realistic maximum efficiency attainable for a working thermochemical process, IGT uses a limited Carnot factor to determine the work value of heat with respect to temperature. The following equation is used when mathematically converting heat into work:

$$W = \eta Q \left(\frac{T_{MAX} - 400}{T_{MAX}}\right) \qquad (6\text{-}17)$$

where —

W = work, kcal

η = fraction efficiency (of Carnot)

Q = heat, kcal

T_{MAX} = maximum temperature of heat from which work can be generated, °K

IGT uses a fractional efficiency, η, equal to 0.5 when calculating efficiencies based on current technology. However, because thermochemical hydrogen production will not be implemented immediately, such work-generating cycles should account for future technological and efficiency advances. Based on projections for an optimized, staged Rankine cycle with mercury topping, IGT uses the values of η according to Table 6-3.

Table 6-3. FRACTIONAL EFFICIENCY OF CARNOT FOR FUTURE-TECHNOLOGY WORK GENERATION CYCLES

Temperature, °K	η
700	0.65
800	0.67
900	0.68
1000	0.69
1100	0.68
1200	0.68
1300	0.67
1400	0.66

To calculate an efficiency, IGT divides the high heating value of hydrogen by the sum of the process heat and the heat required to generate work:

$$\text{Efficiency} = \frac{HHV_{H_2}}{(\text{Process Heat Input}) + \dfrac{\text{Work Input}}{\eta}} \times 100 \qquad (6\text{-}18)$$

Calculating efficiencies, if done manually, is time-consuming. Therefore, researchers at IGT, the University of Kentucky, and EURATOM (Ispra) have computerized programs for this procedure. (The EURATOM computer program was formulated by the University of Aachen; it is similar to the program at the University of Kentucky.) A computer program makes the task more workable if sufficient property data are available.

Other research organizations have narrowed or isolated their investigations to only a few cycles. Westinghouse Electric Corp., General Atomic Co., and (in some cases) EURATOM have done, or are in the process of doing, engineering flowsheeting. By doing a complete heat and material balance (including pumping and compression requirements) and product separations and recycles and by estimating heat exchanger losses and material makeup, a more exact process efficiency can be generated. This, however, is very time-consuming and costly. In most cases, kinetic data necessary for designing reactors, heat exchangers, and other equipment are not available. Assumptions must be made as to whether steps are heat- or mass-transfer limited. Construction materials or equipment specifications must be decided on; and, though difficult, heat-transfer coefficients must be estimated for the exotic materials and environments. This work is premature for many cycles due to the lack of experimental data. Also, many research organizations have neither the facilities nor a financial budget capable of handling such work. This type of program necessitates selection of one or two cycles that are assumed to be the most promising.

It should be reiterated that there is a certain Carnot-type limitation for thermochemical cycles. Therefore, other factors being equal, cycles that accept heat at high temperatures should inherently have higher efficiencies than those that accept heat at lower temperatures. For example: A cycle that utilizes heat at 900° C may have a maximum attainable efficiency of 45% and a cycle that operates with a maximum-temperature heat requirement of 750 °C may have a 40% efficiency. In this case (by comparison to a Carnot cycle), the second cycle utilizes the lower quality heat (750 °C and below) more "efficiently" than does the first cycle, even though the first has a 5%-higher overall efficiency. Therefore, energy efficiencies should be normalized with respect to the temperature levels of heat acceptance. The Institute of Gas Technology does this by comparing calculated efficiencies for thermochemical cycles with an ideal efficiency for electrolytic hydrogen production where like quantities of heat are available, at the same temperature as that used within the thermochemical cycle, for generating electricity. Dividing these two efficiencies results in a "water-splitting ratio" that takes into account the quality of the heat utilized.

In summary, there is no accepted standard technique for calculating efficiencies. The term "efficiency" or "figure of merit" is used by all researchers, but the numbers generated by the different groups are not comparable. Even the terms themselves are often misleading. To date, none of the numbers generated could be considered as practical process efficiencies. Rather, they are more correctly construed as maximum attainable efficiencies or figures of merit for various levels of ideality assumed for the cycle in question.

Evaluating Cycles

Thus far, the most generally accepted method of evaluating cycles, energy efficiency, has been discussed. Efficiency (when calculated on a consistent basis) is probably the most important parameter and the best for comparison of different cycles. There are, though, a number of other parameters that should be closely examined when evaluating cycles. The following is a list of the key parameters used by researchers for such evaluations:

- Energy efficiency (figure of merit)
- Heat transfer and reaction rates (kinetics)
- Number of reaction steps
- Corrosive properties of chemical intermediates
- Availability and costs of raw materials (makeup material for the cycle)
- Temperature schedule of heat requirements (heat-source interface).

The extent of consideration of these parameters was determined through personal and phone interviews with a majority of the research organizations listed in Appendix B. Efficient cycles generally have steps that are staged in temperature to accommodate internal heat exchange between exothermic and endothermic steps. Maximizing this internal exchange of heat helps to minimize waste heat. Kinetics have an indirect effect on efficiency, and thermodynamics alone cannot be used to predict the magnitude of this effect. If the kinetics are slow, more heat loss to the environment per unit of hydrogen produced will occur. Rapid kinetics are particularly advantageous for the high-temperature, endothermic steps of a cycle.

One general trend a number of researchers have observed is that the fewer the chemical reactions within the cycle, the higher the predicted efficiency.

This makes sense because there will be fewer heat-transfer steps, fewer gas separations, fewer material-handling steps, and less overall system pressure drop. Hence, the number of chemical process steps is drastically reduced.

Some researchers believe that a 2-step, pure thermochemical cycle can be proved to be thermodynamically impossible when practical temperature conditions are imposed.[1,8] To date, there are no known pure thermochemical cycles – i.e., those that require only heat inputs; and there are no known workable 2-step cycles that are essentially thermochemical.

Some research organizations have presented cycles that are not purely thermochemical; these are termed "hybrids" or "heat-plus-work"[4] cycles. They have one or more reactions that are performed essentially with electrochemical or mechanical work inputs. This scheme is often used when a reaction within a cycle cannot be thermally driven. For example, if the free-energy change of a reaction is slightly positive, the reaction might be made to proceed if a configuration that allows the imposition of a small electrical potential is feasible. This situation is sometimes observed in mildly endothermic or exothermic liquid-phase reactions in which low-temperature operation is desired. Reactions enhanced by work inputs are characteristically, but not exclusively, those that have increasing free-energy changes with increasing temperature and that have a free-energy change between -5 and +15 kcal at 25° C. A voltage of about 0.3 volts or less theoretically would be required to drive this type of reaction. (The electrolysis of water theoretically requires 1.23 volts.)

The general consensus is that cycles of from 3 to 5 reaction steps look most advantageous from the standpoint of efficiency, practicality, and workability.

Another key parameter considered when evaluating cycles is the corrosivity of the compounds in the cycle. Many of the proposed cycles have compounds that are extremely corrosive to common construction materials, and it is questionable whether there are economically available materials that can contain the compounds and not contaminate them. Therefore, materials that can withstand high temperatures and chemical attack are of utmost importance to thermochemical hydrogen production. Such materials for process equipment for thermochemical cycles have been of moderate concern in a few research programs, notably the EURATOM program. In general, detailed studies of this type are probably premature in view of the state of cycle selection. Corrosivity seems a characteristic of workable cycles; but efforts to develop cycles involving less corrosive, but sufficiently reactive intermediates might be rewarding. A large number of different compounds in a cycle complicates the problem of materials compatibility.

Cycles involving relatively noncorrosive materials are of great interest and are a prime objective of many research programs. One of the problems with thermochemical hydrogen production is that a low-temperature reaction step is often required to close a cycle. Although high-temperature steps usually proceed readily (with good kinetics), the compounds in the cycle must also be sufficiently reactive (corrosive) to proceed at low temperatures. One potential way to decrease corrosivity and still have a workable cycle is by employing a low-temperature electrolytic step — i.e., by using a hybrid cycle.

During our telephone survey, discussions sometimes arose concerning the availability of compounds that appear as chemical species in many cycles. There are usually two questions regarding them. First, is there enough material available to supply numerous plants with initial raw-material and makeup requirements? Secondly, will the cost of the raw-material charge be prohibitive?

These questions are difficult to answer. It is difficult to estimate the quantity of material necessary to initially charge the process because reaction kinetics are unknown. The faster the cycle kinetics, the higher the hydrogen production rate, or the lower the required materials inventory for a given hydrogen production rate. The makeup requirements are likewise unknown. Again, it should be remembered that the process should be totally contained so that the makeup of intermediate compounds is minimal. Even the smallest "leak" will cause large makeup requirements that could prove too costly for continued economical plant operation.[12]

What will the new demand for some of the less plentiful compounds do to their market prices? It is easy to see the advantages of low cost, plentiful materials, but limiting the number of elements that can be used in thermochemical cycles also limits the number of potential cycles. This question also remains unanswered, but it is agreed that these parameters are of importance when evaluating cycles.

The temperature of the heat required from a heat source is another key parameter that should be considered when evaluating a cycle. An HTGR, for example, might, in the future, deliver helium from its nuclear core at about 1000° C and require that the helium stream be reduced to perhaps 500 °C or below before reinjection to the core. On the other hand, a thermochemical cycle may require a considerable portion of its heat above an isothermal condition for a reaction at, say, 800 °C. Therefore, there must be modifications to the process or a bottoming energy-conversion cycle included so that the heat available from the nuclear reactor matches the load of the combined processes. There are alternatives for thermochemical cycles with problems in this area. First is a need for some electric power to operate pumps, compressors, and other utilities for the process. An electric generating plant could be the bottoming cycle, utilizing, per the example, the unused portion of the 500° to 800° C heat. Second is the possibility of "stacking" thermochemical cycles, but this may involve difficult process control and heat balancing. This possibility will generally have drawbacks such as extremely complex plant operations and a diversity of chemical process equipment.

To utilize heat from a nuclear source, a compatible thermochemical cycle must accept the heat from the nuclear coolant stream so that the temperature of the stream is reduced to acceptable core reinjection levels.

Summarized here are the attributes of a "good" thermochemical cycle for hydrogen production as derived from the criteria used by the research organizations surveyed in this study:

- A cycle should have a higher efficiency, or at least a more practically attained efficiency, than a proposed electrolysis process using the same temperature energy source.
- The cycle kinetics should not be strongly limited by slow heat-transfer or reaction rates. Fast rates are generally desirable.
- The cycle should have as few reaction and heat-exchange steps, gas separations, and material-transport steps as possible.
- It is desirable that chemical intermediates within the cycle be noncorrosive to construction materials commonly used in the chemical process industry and that exotic construction materials not be required.
- It would be advantageous to use several chemical intermediates that are abundant and inexpensive. A cycle that involves a rare or expensive element is generally undesirable.
- If a thermochemical cycle is driven by heat from a nuclear source, the heat demand should match the heat available from the nuclear coolant stream as it cools. (The inherent isothermal aspect of thermochemical cycles appears to make them adaptable to high-temperature solar applications.)

These criteria are of value when comparing one cycle with another or with the electrolytic splitting of water. Eliminating a cycle because it violates a criterion is not good practice, but selecting one cycle as more promising than another, based on all criteria, is a practical and necessary approach.

Heat Source Specifications and Availability

We have outlined the chemical and thermodynamic bases for thermochemical hydrogen production. Cycles that work in the laboratory and that have promising efficiencies and/or that meet other evaluation criteria are extremely important. At this juncture, however, the future of thermochemical hydrogen production is largely dependent on the development of high-temperature thermal sources. We have shown that, because of the second-law limitation on the splitting of water into hydrogen and oxygen through the application of heat, the highest temperature at which heat can be used may produce the most efficient cycle. By having the largest temperature envelope for selection of reaction operating temperatures, we allow the greatest latitude in chemical-species selection. The question that really should be addressed is: In the foreseeable future, what thermal sources will be available and what temperatures will they attain?

In the last two decades, considerable work has been done in the area of nuclear-reactor development for electric power generation. Recently, however, modest investigations have been directed toward the possibility of using nuclear reactors as sources of process heat. Table 6-4 presents coolant temperature ranges for various types of nuclear reactors that are in operation or are under development.[16]

Most research organizations have chosen a temperature envelope that ranges from a minimum of 25°C to a maximum of between 600° and 1000°C. With this information, from examination of Table 4, and by allowing a 50° to 100°C temperature drop for the heat exchanger between the reactor coolant stream and the high-temperature, endothermic step of the cycle, it is clear that HTGR's will be desired for thermochemical hydrogen production. GCFBR's would be marginal in temperature capability. Other reactor types would serve as well, or better, for electrolysis.

If a hydrogen-energy system is contemplated for the future and if nuclear water splitting is the hydrogen source, then we must plan reactor development to match the production method. At this time, BWR's, PWR's, LTGR's, and even LMFBR's do not appear to be particularly useful for thermochemical hydrogen production. It is disturbing to note that the U.S. breeder reactor program, the success of which is vital for the provision of enough nuclear energy to meet our post-1990 demands, is based upon the

Table 6-4. NUCLEAR REACTOR COOLANT TEMPERATURES

Reactor Type	Coolant	Reactor Core Coolant Exit Temp., °C
BWR (boiling-water reactor, 1957 technology, Vallecitos)	Water	250-325
PWR (pressurized-water reactors, 1957 technology, Shippingport, submarines)	Water	275-350
LTGR (low-temperature, gas-cooled reactor; 1963 technology, Windscale, Great Britain)	Carbon dioxide	350-575
BWR/SH (boiling-water reactor with superheat, current technology)	Water	450-575
LMFBR (liquid-metal, fast-breeder reactor; experimental)	Liquid sodium	450-625
GCFBR (gas-cooled, fast-breeder reactor; experimental)	Helium	500-700
HTGR (high-temperature, gas-cooled reactor; 1967 technology, Peach Bottom)	Helium	780-900
HTGR-Otto (same as above with "Otto" fueling scheme, experimental, Germany)	Helium	900-1000
UHTGR (same as above, 1969 experiments, LASL)	Helium	1000-1300
Rover (nuclear rocket power plant, 1970 to 1972, LASL or Aerojet-Westinghouse NERVA project)	Hydrogen	2000-2500

LMFBR, which is probably not acceptable as a heat source for a thermochemical hydrogen process.

The nuclear-electric industry has made various estimates of the demands for nuclear-electricity generation capacity through the years 1990 and 2000. We have considered, for the purposes of illustration, the extra amount of nuclear capacity that will have to be developed to meet the deficit in natural gas supplies that are projected to exist in the year 2000. Estimates of the demand for natural gas in the year 2000 are on the order of 65 trillion SCF/yr, and it is generally accepted that only about half of this demand will be met with domestic, imported, and substitute natural gas sources. Thus, a deficit of about 33 trillion SCF/yr (or 33 quadrillion Btu/yr) is expected.

This deficit can be compensated for in three ways. One way is to altogether deprive the U.S. energy market of this energy, requiring enormous conservation measures and probably resulting in a lowering of economic standards throughout the country. Another way is to meet this energy demand with nuclear-generated electricity, thus requiring major installations of new transmission, distribution, and utilization equipment. The third way is to supply synthetic hydrogen, made through use of a nuclear energy source to a part of the U.S. gas market. The nuclear capacity that would then be required is within the currently anticipated capability of the nuclear industry.

Assuming that reactor materials technology allows for HTGR process-heat production at 925° to 1000 °C in the time frame with which we are concerned, we can reasonably anticipate a practical thermochemical hydrogen production efficiency of about 50%. To produce 33 quadrillion Btu/yr of hydrogen (to meet the gas deficit for the year 2000), we will need a nuclear plant capacity of 66 quadrillion Btu/yr, or 2250 GW (thermal). Because nuclear plant capacities today are conventionally expressed in electrical generating units, it is convenient for purposes of comparison to correct 2250 GW (thermal) to an equivalent 700 GW (electric), assuming a typical 31% nuclear generating efficiency (40%, or 900 GW, for all new-technology HTGR's).

Can an extra 700 GW (electric) of nuclear generation be provided by the nuclear industry? Allowing a 20% downtime for maintenance, refueling, etc., we are really asking for about 850 GW (electric) of plant capacity. Figure 6-4 shows two projections by the Atomic Energy Commission (AEC)[21] and one by the Atomic Industrial Forum (AIF)[2] of the growth of nuclear-electric capacity. The lower two lines are the "most likely" case and the "high" projected case by the AEC. The top line is the AIF's indication[9] that a growth rate somewhat greater than the AEC's "high" projection can be maintained by the nuclear industry if necessary. Much of the need behind the AEC's accelerated case is due to an anticipation of a take-over of part of today's fossil-fuel markets by nuclear electricity. It seems reasonable to assume that if, for the sake of this example, nuclear hydrogen is to fill the natural gas deficit, the electric demand will be amply satisfied by the "most likely" case, 1200 GW (electric).

In Figure 6-5, we have superimposed a demand point that corresponds to meeting both the 1200-GW (electric), nuclear-electric demand and the 850-GW (electric) needed to meet the gas deficit projected for the year 2000. In terms of nuclear capacity, we assume that the capability for thermal capacity would be the same, per the AEC and AIF projections, whether the "additional" 2250-GW (thermal) be a mix of reactor types or predominantly HTGR's. Of course, for thermochemical hydrogen production the crucial question is whether or not this projected capability can include a significant HTGR contribution.

It can be seen from Figure 6-5 that achievement of this total nuclear generating capacity is probably within the AIF's projected nuclear-industry capability. However, it is important to realize that this point can only be achieved by the year 2000 if the nuclear industry begins its accelerated growth pattern very soon – say by 1980 – and cannot be met if such a decision to expand is delayed until say, 1995. Thus, an early commitment to nuclear thermochemical hydrogen production seems mandatory if we are to develop the necessary quantity of the type of reactors needed to meet our demands of 25 years hence.

To date, no experimental work has been done on applying solar furnace technology to thermochemical hydrogen production. There are, today, solar furnaces that can attain temperatures above 1000°C.[6] They have the apparent advantage of being able to supply heat at somewhat more isothermal conditions than do nuclear reactors. There are, however, problems with

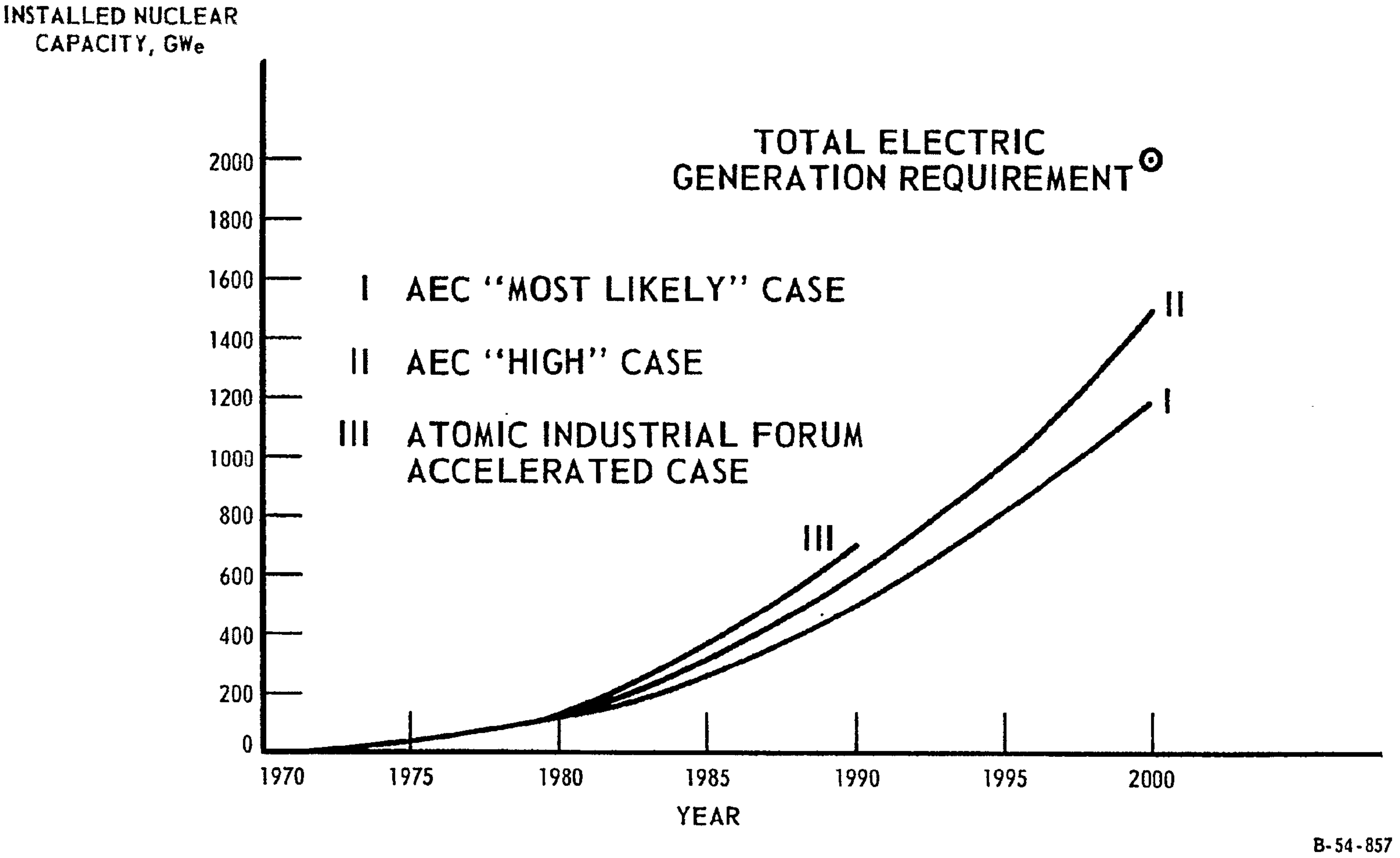

Figure 6-4. PROJECTED GROWTH OF U.S. NUCLEAR CAPACITY
(Source: AEC WASH-1139 and Atomic Industrial Forum)

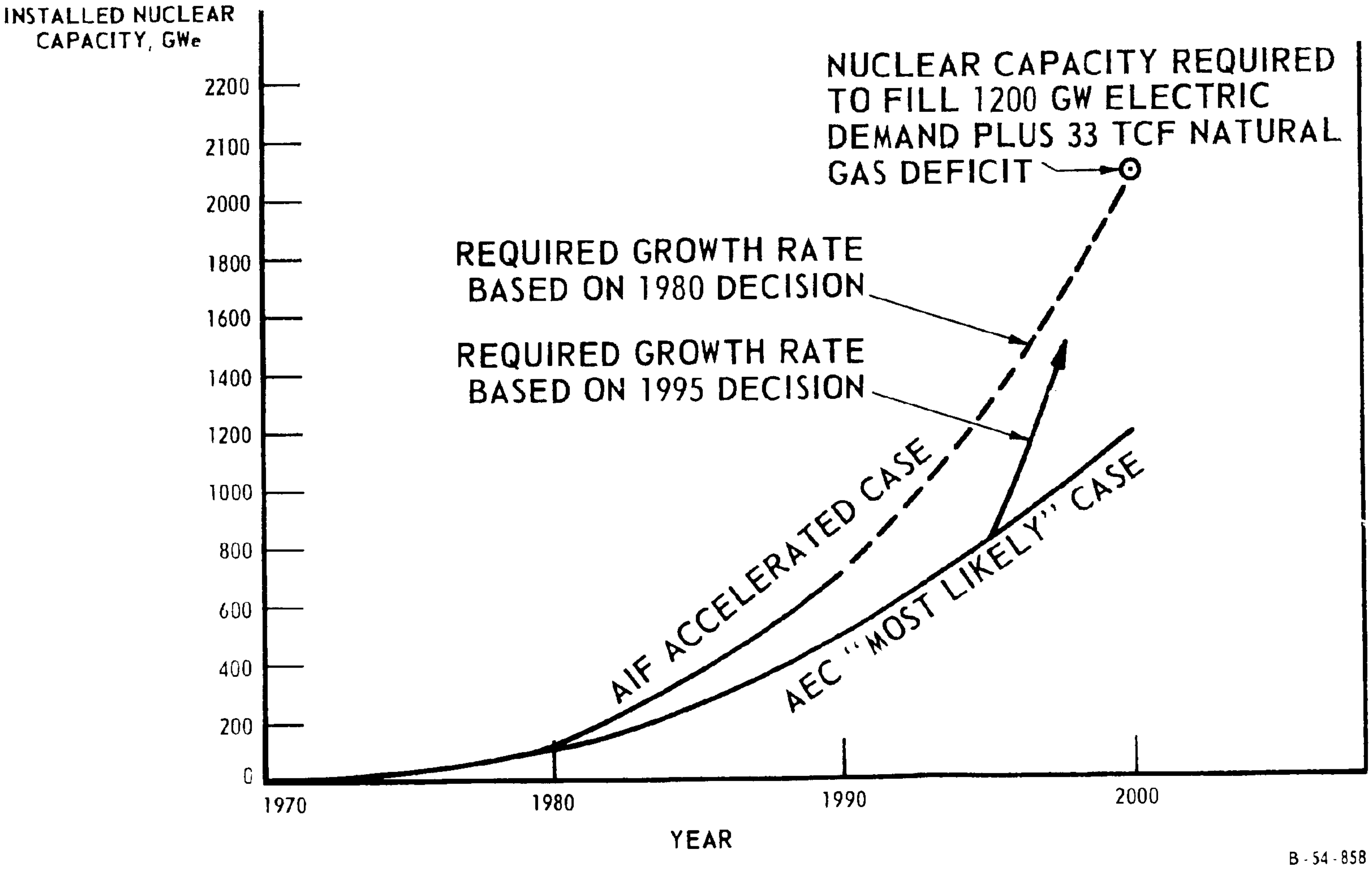

Figure 6-5. GROWTH RATE OF NUCLEAR CAPACITY REQUIRED TO MEET GAS AND ELECTRICITY NEEDS

transient operating conditions for chemical process equipment and/or difficulties in high temperature heat storage during overcast periods and nighttime. These problems might be overcome by use of relatively uncomplicated, high-temperature thermochemical cycles of not more than 3 reaction steps that could be operated efficiently and intermittently.

Technology Development and Identifiable Gaps

The development of technology for thermochemical hydrogen production, as an approximate consensus constructed after our interviews, is depicted in Figure 6-6. The series of stages is intended to portray an orderly development of the technology. The series was developed after interviews with over 20 groups recently and/or currently involved in research on thermochemical hydrogen production. On the average, the state of technology for the various programs surveyed is at stage 3 or 4. A few groups are still working at stage 1. A few others have progressed to stage 8; but this rapid progression has not included most of stages 4 and 6, and it has not included any of stage 7. (Depending on its facilities and philosophy, it may be expeditious for an organization to delay stage 7 until stage 8 is completed.) Most of the research groups interviewed placed attainment of stage 10 in 1985 or later; and most groups at stage 3 or 4 placed attainment of stage 7 in from 1978 to 1980 with annual funding requirements of from $500,000 to $1 million and on condition that, at this point, one cycle be selected for further development.

It should also be stressed that it is difficult to determine the state-of-the-art for thermochemical hydrogen production. Every research organization has a unique approach with independent objectives and direction. Many organizations have taken a proprietary stand, and their "best" work is unavailable. Some research that is sponsored by private industry is protected from public disclosure at this time.

The overall objective of several research programs is, however, demonstration of a cycle in the laboratory. It is hoped that within five years, a bench-scale demonstration will be in continuous or semicontinuous operation. Researchers at some organizations, such as at LASL, IGT, GE, EURATOM, and LLL, have proved the feasibility of individual reactions. Some (those at LASL, IGT, and EURATOM) have demonstrated cycles by recycling materials through each reaction step in a batch-type operation;

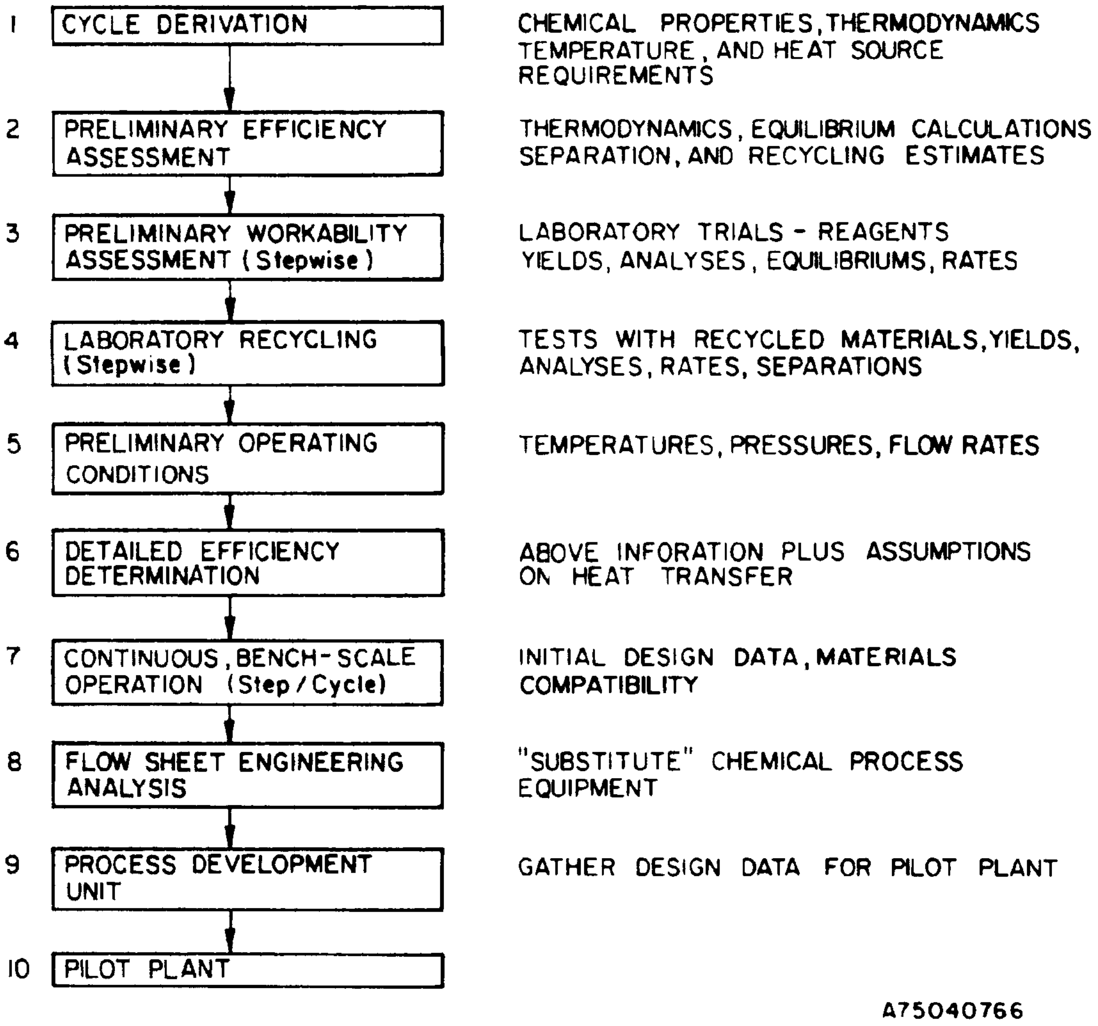

Figure 6-6. REQUIREMENTS FOR TECHNOLOGY DEVELOPMENT IN THERMOCHEMICAL HYDROGEN PRODUCTION

but to date, none has set up a continuously operative cycle in the laboratory. To do this, a research group must first select one cycle. At this stage, it may be difficult for most groups to make such a selection with any degree of confidence. If this were done, it would imply that the organization either believed that this cycle would prove to be one of the best or that they had sufficient funding to allow them to make additional searches for better cycles in parallel efforts.

To build a continuous bench-scale operation, kinetic data on all reactions are required so that reactor design and sizing will allow compatible and balanced material flows throughout the demonstration system.

The objective of other programs is to eventually do engineering designs of proved cycles. These could be used to generate flowsheet-based costs for thermochemical hydrogen production — something that has not yet been achieved; but, for at least one program, will soon be. When asked about capital and operating cost requirements for thermochemical processes, most organizations would not comment; and none had "hard data" to present. Considerable work will be required to generate the cost figures, but the eventual implementation of thermochemical hydrogen will depend on economics.

One important factor brought out by ongoing research is that currently identified technology gaps would limit the practicality of thermochemical hydrogen production. The areas in which research is required can be isolated, and appropriate research programs can be initiated now to find solutions before the world's energy demands include large-scale utilization of hydrogen fuel.

One main area that requires further development is the high-temperature heat exchanger for transferring heat from the nuclear reactor to the endothermic steps of the thermochemical process. Because highly efficient utilization of heat is of utmost importance, heat exchangers will play a prime role in thermochemical plant designs. High surface area, high-efficiency heat exchangers must be developed that will withstand 800° to 1000° C temperatures, with ultrapure helium on one side and, possibly, corrosive atmospheres on the other side. They must be of reasonable size, cost, and expected lifetime.

The availability of materials that can handle the chemical environments is an area that will require extensive testing and development work. Needs for materials for particular functions in thermochemical cycles have not yet been extensively identified. Before commercialization, some of the cycles will require new materials to ensure adequate life for reactor vessels and piping exposed to corrosive atmospheres at high temperatures. Construction materials are evidently a limiting factor in determining the practicality of many of the proposed cycles.

As discussed previously, high temperature heat sources are currently under development. In Germany (KFA) and in Japan, extensive work is under way on the development of HTGR's with coolant stream temperatures in excess of 950° C. Because efficient thermochemical hydrogen production methods require such temperatures, the future of these methods is dependent on the successful completion of this work. The possibility of other high-temperature sources, such as solar furnaces, has not been fully explored.

One other area of concern with nuclear reactors involves the containment of helium in the coolant loop. It has been observed that in some test loops, operating in temperature ranges of 500° to 1000 °C, a complete recharge of helium is required each year. With increased usage of HTGR's, this practice could become cost- or supply-limited.

Work on solutions to the problems anticipated in connection with the gaps in hydrogen production technology should be incorporated into an overall program of hydrogen research. The future of thermochemical hydrogen production is dependent on finding these answers; the merits of the hydrogen production method are clear and warrant such investigations.

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7. PRODUCTION OF HYDROGEN BY PHOTOSYNTHETIC PROCESSES — R. H. Elkins

Introduction and Problem Definition

Practically all of the energy required for the growth of our technological civilization up to this time has been ultimately supplied by the photosynthetic conversion of solar energy to cellulose and cell material that has been stored through the ages as fossil fuels. Faced with the rapid depletion of this source of energy, considerable attention is now being given to determining whether or not (and if so, to what extent) the photosynthetic process can be accelerated to meet current and future energy needs. The most fundamental problem is the inefficiency of solar energy conversion to chemical energy. With conventional plant growth, the efficiencies are generally quite low — only 0.5% to 2.0% of the total flux is converted to fixed carbon. As will be shown, there is no thermodynamic factor preventing attainment of efficiencies as high as 10% for hydrogen-producing photosynthetic processes.

Of course, most research activity in this area has centered on the more conventional approaches for accelerating the growth of plants and algae or on converting residues (particularly wastes such as human and animal sewage) to methane.[6,9,12,45,46,61] However, because the concept of a future hydrogen economy has received much attention, a number of proposals have been addressed specifically to the production of hydrogen by photosynthetic processes.[4,5,8,10,24,34,36,42,43] These ideas include not only the more conventional approach of converting carbonaceous photosynthetic residues to hydrogen by the action of nonphotosynthetic organisms or photosynthetic processes, but also (and more importantly) the direct photochemical splitting of water into hydrogen and oxygen. At this time, the proposals for direct water splitting are generally only research suggestions, so objective engineering evaluations are not possible at this time. Nevertheless, a brief analysis of the energetics of the photosynthetic process indicates that the process is, in fact, thermodynamically capable of producing hydrogen and oxygen from water.

In evaluating such proposals, it must be kept in mind that a number of methods already exist or can be developed by which the carbonaceous products of photosynthesis can be converted to hydrogen. Furthermore, the most fundamental problem remains the improvement of the efficiency at which solar energy can be converted to chemical energy, in whatever form. In this light, the problem becomes primarily one of evaluating —

- Whether or not photosynthesis has the potential to produce energy in amounts significantly in excess of our food requirements; and, if so, what research and development would be required to achieve that potential
- Whether hydrogen can be produced more efficiently directly by photosynthesis or indirectly from other photosynthetic products.

However, the evaluation of these points is still largely subjective and will differ even among the acknowledged "experts" in the field. Many in the field express considerable (but not universal) optimism that photosynthesis can be used as an efficient converter of solar energy, but only on a long-range basis. All acknowledge that breakthroughs will be required; but most agree that the effort is worthwhile, even if unsuccessful, because of the fundamental importance of a complete understanding of photosynthesis for possible application in increasing food production.

Historical Review of Photosynthesis Research[14,15,52]

Historically, the development of our understanding of photosynthesis has paralleled the development of chemistry as a science. By 1800, shortly after the discovery of oxygen by Priestley, the essential material balance for the process had been identified as –

$$CO_2 + H_2O \xrightarrow[\text{green plant}]{\text{light}} O_2 + \text{organic matter}$$

By 1845, coincident with his formulation of the law of conservation of energy, Mayer understood the essential energy balance, as well as the material balance of the process:

$$CO_2 + H_2O + \text{light energy} \rightarrow O_2 + \text{organic matter} + \text{chemical energy}$$

At this point, he realized the tremendous importance of photosynthesis as nature's primary means for storing solar energy.

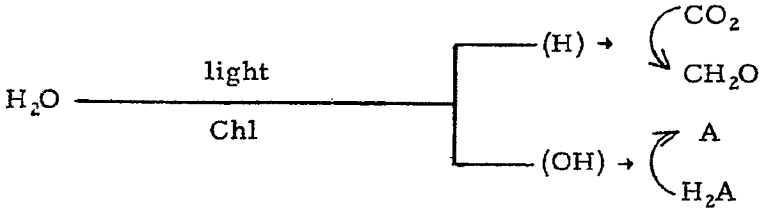
Little progress was made toward understanding the mechanisms of this reaction until the 1930's, after Van Niel's comparative studies of photosynthesis in green plants and in photosynthetic bacteria. These bacteria, like green plants, utilize light energy for growth and contain an essential pigment, bacteriochlorophyll, which differs only slightly from green-plant chlorophyll (Chl). However, the bacteria do not evolve molecular oxygen, and their photosynthetic growth depends on the presence of an oxidizable substrate such as hydrogen, hydrogen sulfide, or a variety of organic compounds (particularly the simpler alcohols and organic acids). To include these organisms, Van Neil formulated the photosynthesis reaction as an oxidation-reduction process:

$$CO_2 + 2H_2A \xrightarrow[Chl]{light} CH_2O + H_2O + 2A$$

in which H_2A represents a general class of oxidizable compounds and A is the product of its oxidation. Soon after this formulation it was realized that green-plant photosynthesis might be a special case in which the oxidizable substrate, H_2A, is water, which is oxidized to oxygen. If so, the overall reaction of green-plant photosynthesis would be written —

$$CO_2 + 2H_2O \rightarrow CH_2O + H_2O + O_2$$

On this basis, Van Niel postulated that the primary photochemical event is the splitting of water to produce an oxidant, denoted (OH), and a reductant, denoted (H). In turn, the primary reductant would bring about the reduction of carbon dioxide to a carbohydrate, denoted as CH_2O, and the primary oxidant would react with H_2A:



(The primary oxidant and reductant were not regarded literally as hydrogen atoms and hydroxyl radicals, but rather as unspecified oxidizing and reducing species.)

Thus, the Van Niel hypothesis suggested that the unique event of photosynthesis was an oxidation-reduction reaction driven by chlorophyll in a photoactivated state. Since then, the oxidation-reduction nature of the process has been established beyond question.

The Energetics of Solar Radiation and the Thermodynamics of Photosynthesis[14,15,38,52]

The energetics of photosynthesis in nature are constrained by the nature of living matter and by the spectrum of sunlight reaching the earth's surface.

Most of the ultraviolet (UV) light below about 300 nm is absorbed by ozone in the upper atmosphere and never reaches the earth. Infrared radiation (IR) is absorbed by the water that universally surrounds living matter and by atmospheric water vapor, thus having no chemical effect. As a consequence, the range of wavelengths available for photosynthesis is from about 300 to 1300 nm.

In nature, every part of the spectrum from 300 to 950 nm is absorbed (and is thus available for utilization) by one organism or another. Green plants, in which photosynthesis involves the splitting of water, primarily absorb radiation in the visible range (from 400 to 700 nm). This represents about half of the total solar radiation that reaches the earth's surface: The other half is in the infrared range.

The energy content of light is inversely proportional to its wavelength, and the energy content of photons in the visible spectrum ranges from about 70 kcal/Einstein[*] at 400 nm to about 40 kcal/Einstein at 700 nm. Thus, the energy of the solar radiation available for photosynthesis is limited to the range of from 40 to 70 kcal/Einstein, far less than the energy required to break the oxygen-hydrogen bond (about 111 kcal/mole). Furthermore, efficient conversion of the absorbed solar energy requires its utilization in increments as small as 40 kcal/mole.

Series Model for Photosynthesis[14,15,23,38,52,63]

The series model, which came into vogue in the early 1960's, is shown in Figure 7-1. Essentially, this figure is a flow diagram of the electron transport during the photosynthetic process in the context of the electrochemical potential at which the electron exists (a measure of the energy of the electron, or its reducing power) at various stages of the process. Thus the ordinate denotes the chemical reducing power of the negative ion in which the electron resides, and the horizontal progression denotes the chronological or chemical sequence of the transport. The arrows show the direction of electron flow.

The photochemical reaction in photosystem II (PS II) generates a strong oxidant, Z^+, which is capable of liberating oxygen from water, and a weak reductant, Q^-. A second photochemical reaction, in photosystem I (PS I),

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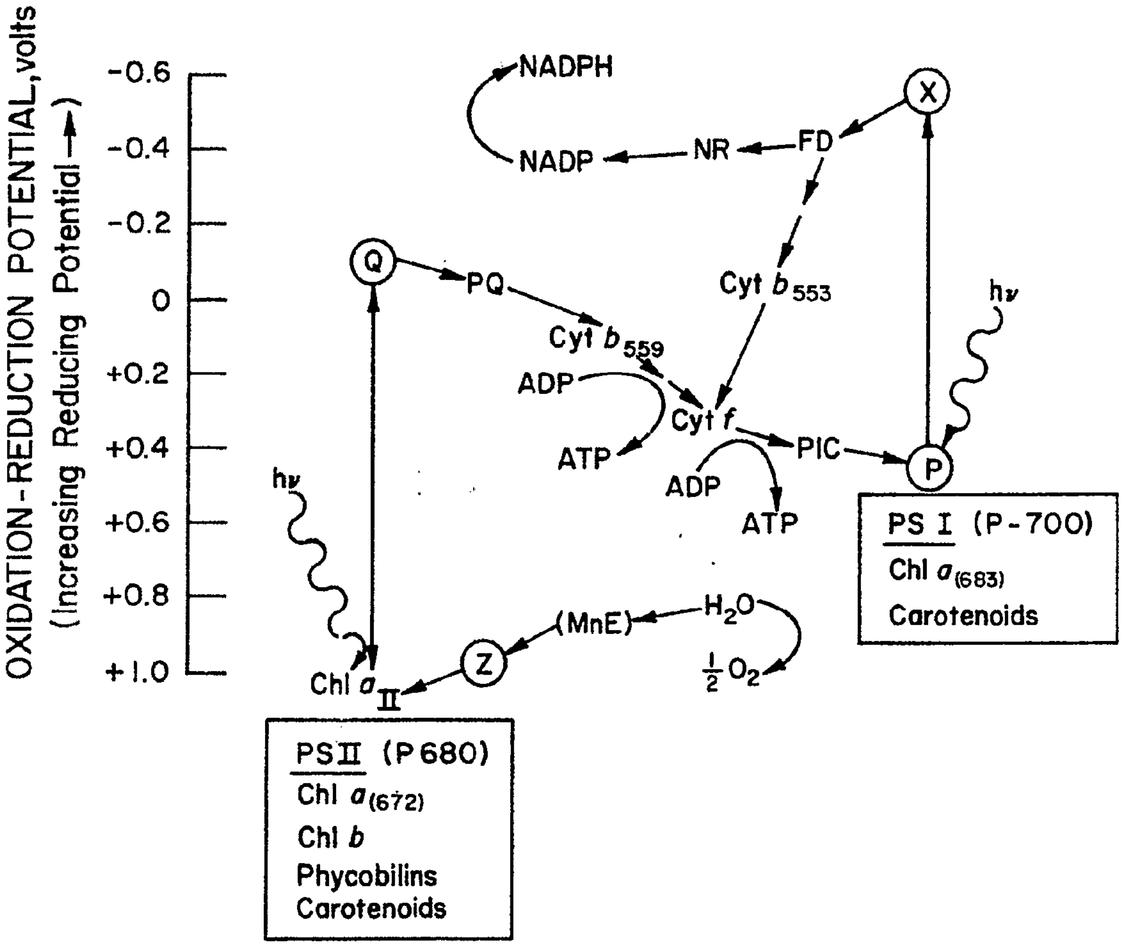
[*] 1 Einstein = 1 mole of photons.



MnE = hypothetical enzyme containing manganese
Z = hypothetical donor of electrons to oxidized Chl a (672)
Q = primary electron acceptor in the photochemistry of system II; may be a quinone
PQ = plastoquinone
PIC = plastocyanin
NR = NADP reductase
FD = ferredoxin
P = hypothetical donor to oxidized Chl a (683) if any

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Figure 7-1. TWO-QUANTUM-SERIES MODEL OF ELECTRON FLOW IN PHOTOSYNTHESIS generates a weak oxidant, P^+, and a strong reductant, X^-, which has a potential more negative than that of the hydrogen electrode. The two systems are connected in series by the reaction of Q^- with P^+ through an elaborate electron-transport system. Together, the two systems generate an oxidant strong enough to oxidize water and a reductant strong enough to reduce hydrogen ions to molecular hydrogen.

This, then, is the basic photochemical process associated with photosynthesis in green plants. In addition, however, some of the exothermic energy released by the "down-hill" electron transfer between the two halves of the process, $Q^- \longrightarrow P^+$, is converted by unknown mechanisms to adenosine triphosphate (ATP), the universal medium of energy exchange in biological processes of all kinds.

The thermodynamic requirement for the photosynthesis reaction (or for the splitting of water) is about 114 kcal/2 moles:

$$2H_2O + CO_2 \rightarrow CH_2O + H_2O + O_2 \quad \Delta F_{298} = +114 \text{ kcal/mole}$$

$$2H_2O \rightarrow O_2 + 2H_2 \quad \Delta F_{298} = +113.4 \text{ kcal/mole}$$

The fundamental problem with photosynthesis or with solar photolysis of water is supplying the large endothermic energy requirement from the relatively small increments available in sunlight.

To put this in proper perspective, it is necessary to remember that photochemical energy acts upon matter through the electrons on a one-to-one basis — i.e., the energy of one quantum of light is transferred (at varying efficiency) to one electron. In this sense then, the energy of a photon is analogous to electrochemical potential in that it represents the available free energy per electron rather than per mole of product. On this basis, 40 kcal/Einstein corresponds to an electrochemical potential of 1.74 volts,* which is more than sufficient to split water. (The theoretical voltage requirement for splitting water is 1.23 volts.)

The reduction of carbon dioxide to CH_2O and the evolution of oxygen from water are processes that involve the transfer of four electrons per molecule — i.e., the primary photochemical process must occur at least four times to

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* 1 volt = 23.053 kcal.

reduce one carbon dioxide molecule and to evolve one oxygen molecule. On this basis, the quantum requirement for photosynthesis would be at least 4 quanta per molecule, if the primary reaction is driven by a single quantum as originally assumed. If this is the case, the thermodynamic efficiency would be about 71%.

In the early 1920's, experimental determinations by O. Warburg, using manometric techniques for the measurement of the oxygen and carbon dioxide, appeared to confirm that the quantum requirement for photosynthesis is four. However, more realistic estimates of the energy requirement, which include the probable thermodynamic losses in the process, suggested that the actual requirement must be in excess of 4 quanta per molecule. On this basis, the primary photochemical process would require at least 2 quanta of light for each electron — an overall minimum requirement of 8 quanta per molecule. This initiated a controversy that lasted 30 years. It was finally established that each electron transfer does, in fact, require two photochemical reactions for each electron — a total quantum requirement of eight per oxygen molecule evolved, thus indicating a thermodynamic efficiency limit of about 35%.

However, the problem was not then resolved by direct experimental measurement of the quantum requirements for oxygen and carbon dioxide exchange. Instead, the initial evidence for a two-quantum primary photochemical process came from a fascinating series of studies on the effect of monochromatic light of varying wavelength on the efficiency of photosynthesis. The results of these studies led to the Z scheme (or series model) of photosynthesis, which postulates that the primary photosynthetic process actually involves two separate photochemical systems that act cooperatively in series and that are connected by an electron-transport system that utilizes cytochromes. Furthermore, photosynthesis can occur only when both systems are operative, either simultaneously or consecutively. The overall photosynthesis reaction is then completed by coupling the photochemical reactions to the "dark" enzymatic reactions (i.e., those that occur in the dark) required to allow Z^+ to oxidize water to oxygen and X^- to reduce carbon dioxide to glucose.

Possible Approaches to Hydrogen Production

The above analysis indicates that it is theoretically possible to split water into hydrogen and oxygen if alternative processes can be found for the enzymatic reaction of X^-. Although it appears to be universally true that the reducing power, X^-, generated by green-plant photosynthesis is always used to reduce carbon dioxide to cell material, biological hydrogen production by photochemical processes, as well as dark processes, has been observed. The study of these processes has resulted in the suggestion of a number of approaches to photosynthetic hydrogen production.

Hydrogen Production by Natural Biological Processes[25]

Certain bacteria and algae contain enzymes, such as hydrogenase, and are capable of catalyzing the reduction of hydrogen ions to molecular hydrogen.[7,19,25,33,59] Such organisms do, in fact, product hydrogen under certain conditions by photochemical reactions, as well as by the dark reactions.

Hydrogen is produced by a number of anaerobic microorganisms, notably the Clostridium types, during the anaerobic metabolism (fermentation) of carbohydrate. The hydrogen donor in these systems is organic and is usually formic or pyruvic acid, intermediates in fermentation.[25] Thus hydrogen is actually produced as a by-product.

Hydrogen can also be produced by a number of photosynthetic bacteria that contain nitrogenase, an enzyme for fixing nitrogen.[25] However, hydrogen is only produced by growing cells in the absence of nitrogen and by certain nitrogen metabolites on a substrate such as glutamic acid, which contains both the nitrogen and carbon required for growth. Cells in the resting stage, however, can produce hydrogen almost quantitatively from substrates such as acetic, succinic, and malic acid:

$$C_2H_4O_2 + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Thus in the case of photosynthetic bacteria, the hydrogen donor for hydrogen production is also primarily organic, and no species has been found in which water is the ultimate source of the hydrogen produced. This is consistent with the fact that photosynthetic bacteria do not incorporate photosystem II.

Until recently, no case had been found in which water was the substrate or in which PS II participated[7,59]; but certain algae, containing hydrogenase or nitrogenase, have been found that, after anaerobic adaptation, do produce hydrogen photochemically.[19] Because the algae show photosystem-II activity, the possibility exists that water could be the source of the hydrogen produced. In all cases, however, the rates of photohydrogen production have been very slow compared with the rates of photosynthesis.[7, 33, 59]

Still, the biochemical mechanisms involved in biological hydrogen production are not well understood. The process appears to be primarily associated with anaerobic conditions and processes. (Hydrogenase is oxygen sensitive.) Its function appears to be regulatory in nature. Gray and Gest state[25]:

> "In heterotrophic organisms, the anaerobic mode of growth poses special problems for the cell with respect to the disposition of electrons from energy-yielding oxidation reactions. This is particularly so when the overall adenosine triphosphate (ATP) requirement for biosynthetic activity can be satisfied only by degradation of a relatively large quantity of an organic compound that serves as the energy source. Accordingly, various kinds of specific controls are necessary to regulate electron flow in the metabolism of strict and facultative anaerobes. One of these is reflected by the ability of many such organisms to dispose of excess electrons in the form of such molecular hydrogen (H_2) through the activity of hydrogenases, which, in effect, catalyze the reaction:
>
> $$2e^- + 2H^+ \rightarrow H_2$$
>
> From a general standpoint, the formation of molecular hydrogen can be considered a device for disposal of electrons released in metabolic oxidations."

Kok also suggests[33] that the function of hydrogen formation in algae is to "prime the photochemical pump under anaerobic conditions." He further suggests that algae frequently encounter anaerobic conditions under which the photosynthetic electron-transport chain is reduced, thus effectively blocking flow. However, utilization of the electrons to reduce hydrogen ions effectively primes the pump by converting the electron-transport system back to the oxidized state, thus allowing photosynthesis to proceed. Land plants, on the other hand, never encounter anaerobic conditions and thus contain no hydrogenase.

Thus the hydrogen-production mechanism does exist in photosynthetic bacteria and in algae, but its function is regulatory rather than primary in nature. Indeed, an organism in which the photosynthetic apparatus has been subverted to produce hydrogen rather than cell material can no longer be considered a viable, self-reproducing system. Furthermore, the aerobic water-splitting and anaerobic hydrogen-production functions are not compatible because hydrogenase is highly oxygen sensitive. Thus it would appear that the direct production of hydrogen and oxygen from water by living organisms has a very low probability of success.

Recently, however, a nitrogen-fixing algae species, *Anabaena cylindrica*, has been found that under certain conditions does, in fact, evolve oxygen and hydrogen simultaneously under the influence of light while in a growth stage.[5] This discovery could be important, if not as the basis for solar conversion, at least as a guide to how it might be accomplished *in vitro*.

Anabaena cylindrica is a heterocystic filamentous nitrogen-fixing alga in which the nitrogenase activity apparently exists in distinctly differentiated cells located at intervals among the vegetative cells of the filament. In the vegetative cells, photosynthesis occurs as usual, splitting water to produce oxygen and, with carbon dioxide, cell material. However, some of the carbohydrate so produced is supplied to the nitrogenase containing cells (heterocysts) as feedstock for photosynthetic nitrogen fixing. Thus the two types of cells have a symbiotic relationship.

Typical of nitrogen-fixing species is that hydrogen, rather than fixed nitrogen (ammonia) is produced when nitrogen is excluded.[5,25,26] Because nitrogenase is oxygen sensitive, nature apparently developed heterocysts to separate the aerobic photosynthetic process from the anaerobic nitrogen fixing. Thus both oxygen evolution and hydrogen (ammonia) production can coexist in the same organism, although in different cells.[5]

Usually oxygen production is several times greater than nitrogen production. However, after several days of nitrogen starvation, oxygen production decreases, and hydrogen production increases. Thus it may be possible to control the stoichiometry — unfortunately, however, at the expense of solar-conversion efficiency.[5] It is presumed also that a nitrogen nutrient would have to be supplied. On the other hand, it may be possible to find or to develop genetically improved strains.

Similar possibilities exist for certain plant-nitrogen fixing algae systems that normally live in symbiotic relationship. One such system consists of *Anabaena azollae*, a blue-green algae, and *Azolla*, a genus of water ferns. This system has been used in Asia as a fertilizer and as animal food, and nitrogen-fixing rates of up to 125 lbs/yr-acre have been reported. Recently G. A. Peters (of Kettering Research Laboratory) has shown that the algae, when separated from the fern, continues to fix nitrogen for up to 12 hours at a somewhat reduced rate and without further growth.[51] Thus it appears that the algae depends upon the fern for at least some of its nutrients (presumably carbohydrate) and supplies its partner with nitrogen. It might be possible, with such systems, to control the hydrogen-oxygen stoichiomery under nitrogen-starvation conditions by controlling the relative algae/fern ratio. Again it would be necessary to provide nutrient nitrogen.

The Nature and Efficiency of Nitrogenase Reductions

There has been considerable research on biological nitrogen fixing for the production of ammonia, as well as of hydrogen, since 1960 (when nitrogenase was first isolated).[26,40] However, the nature of nitrogenase and the reaction mechanisms involved are not well understood.[26,65] Both ATP and an energy-rich substrate, such as pyruvate or possibly reduced nicotinamide-adenine dinucleotide phosphate (NADPH), are required. The reductive input to the system appears to involve an iron-containing enzyme similar to the ferredoxins that mediate the reduction of nicotinamide-adenine dinucleotide phosphate (NADP) to NADPH in photosynthesis. Nitrogenase is also a complex enzyme, containing both iron and molybdenum. The system is remarkably versatile in that it can bring about the reduction not only of nitrogen and hydrogen ions, but also of a variety of unsaturated compounds, such as that of acetylene to ethylene.[26] The acetylene reduction is used as a quantitative monitor of nitrogen-fixing rates.

Unfortunately, the nitrogen-fixing reaction is extremely inefficient. Hardy and Havelk estimate[26] that a minimum of 24 moles of ATP are required for the reduction of one molecule of nitrogen. As a result, it has been estimated that almost 20% of the photosynthate produced by ligumes is used by the associated nitrogen-fixing species to fix nitrogen. Thus ammonia or hydrogen production is apparently accomplished at a high cost to the efficiency of photosynthesis, at least in natural symbiotic systems. (No efficiency data were given by Beneman[5] for the heterocystic-algae case.)

Genetic Engineering

A number of suggestions have been put forth concerning the use of "genetic engineering" for developing strains of organisms or plants to solve many of these problems. Certainly, the genetic approach has had some spectacular successes in bringing about the "green revolution" in conventional agriculture. Until recently, however, these techniques had been aimed primarily at increasing food and lumber production.[11,64] Broadening of the genetic approach to include energy production is obviously justified.

Proposals to develop mutant, or "engineered," organisms to produce stored energy in a form other than cell material are much more difficult to evaluate.[7,34,44,58,60,62] First, the science of molecular genetic manipulation is in its infancy, and evaluating the chances of success is difficult. Second, such organisms, if developed, would not be growing, self-repairing, self-reproducing systems and therefore would require maintenance and stabilization.

The possibility does exist, however, that such systems may be amenable to stabilization for long "catalyst" life. Furthermore, the "spinoff" results from such studies may contribute to the development of high-efficiency converters of solar energy to more conventional cell-material energy.

In Vitro Processes

The feasibility of coupling the hydrogenase (and nitrogenase) activity to the photosynthetic process PS I in green-plant chloroplasts was demonstrated in the laboratory as early as 1961.[1] However, in these experiments, PS II activity, and therefore oxygen evolution, was effectively blocked; and an artificial electron donor was substituted.

By 1973, however, Benemann *et al.*[4] actually demonstrated that hydrogenase activity can, in fact, be coupled to the photosynthetic apparatus of green plants to produce hydrogen and oxygen in the laboratory. Inhibition of the hydrogenase activity by the oxygen produced was minimized by continuous flushing with argon. However, the rates of hydrogen evolution were relatively slow compared with those in experiments in which oxygen evolution was blocked (by inhibition of PS II and substitution of an artifical electron donor) or scavenged by glucose oxidase. The results indicated that the oxygen inhibition of both hydrogenase and ferredoxin is a problem that must be solved before further development can proceed.

Since 1973, Kaplan has been able to purify *Clostridium* hydrogenase and immobilize it on glass surfaces.[29] In the immobilized form, the hydrogenase appears to be stable in the presence of oxygen. Similar suggestions have been made by various workers in the field.

Another approach to coupling hydrogenase to photosynthesis has been suggested by L. O. Krampitz at Case Western Reserve University.[34,36] Instead of direct coupling, he suggests that the photosynthetic apparatus of green plants be used to produce a stable reduced species (in the absence of carbon dioxide) that can be converted to hydrogen by hydrogenase in a second step, without the inhibiting effect of oxygen. Again, the feasibility of this approach has been demonstrated in the laboratory with triphosphopyridine nucleotide (TPN) as the electron acceptor. TPN is an alternative term for NADP — the natural hydrogen acceptor in photosynthesis that, in the reduced form, mediates the reduction of carbon dioxide. It is a fairly complex, but stable, chemical species.

In the first-stage reaction, TPN was added to a suspension of spinach chloroplasts and ferredoxin, which was then illuminated. The reaction produced oxygen and reduced triphosphopyridine nucleotide (TPNH). The TPNH was then subjected to Clostridium hydrogenase and ferredoxin, in a second-stage reaction, to evolve hydrogen. Thus the feasibility of a two-stage process was demonstrated in terms of a fairly complex biological chemical:

$$H_2O + TPN \xrightarrow[Chl]{h\nu} 1/2O_2 + TPNH_2$$

$$TPNH_2 \xrightarrow{\text{hydrogenase}} TPN + H_2$$

Obviously, a simpler, more stable first-stage electron acceptor is desirable and is being sought.[34]

It is apparent that hydrogen can be thermochemically produced from any stable, reduced product of photosynthesis. The most obvious thermochemical process would involve the use of natural photosynthetic products (such as carbohydrate) to reduce water. However, other possibilities exist. For example, it has been known since 1937 that slurries of chloroplasts (isolated from green leaves) with a suitable electron acceptor, such as benzoquinone, will evolve oxygen and yield hydroquinone when illuminated with visible light (the Hill reaction).[15,52] Thus, the following two-stage, water-splitting cycle can be visualized:

$$2H_2O + 2Q \xrightarrow{h\nu} 2QH_2 + O_2$$

$$2QH_2 \xrightarrow[\text{catalyst}]{} 2Q + 2H_2$$

Unfortunately, only a portion of the total reducing power of the photosynthetic apparatus (that is, only PS II) is utilized in the Hill reaction. However, the reducing power of the whole photosystem is available, as shown in the studies by Krampitz[4] and Benemann *et al.*[34] Thus it may be possible to find a terminal oxidant for photosynthesis that yields a stable reduced species from which hydrogen can be produced by a thermochemical second stage.

Cell-Free Reconstituted Systems[42,43,59]

Understanding of the photosynthesis process and biological hydrogen formation is sufficient to have stimulated proposals for *in vitro* systems reconstituted from the various components of the natural systems. In this way it might be possible to physically separate the aerobic and anaerobic functions. However, because membrane structures and coupling mechanisms are two large unknowns at this time, the potential for this approach lies in the future. Also, because these then are no longer living, growing species, maintenance or stabilization of the very complex, delicately balanced system becomes of paramount importance.

As we have seen, the stabilization of hydrogenase appears to have been accomplished.[29] However, stabilization of the photosynthetic system will presumably present a much more difficult problem. Unfortunately, the photosynthetic systems in chloroplasts are, for reasons unknown, highly degradable, so the Hill reaction lasts only a few minutes. Similar photolytic catalysts with improved stability can be prepared simply by lyophilization of whole photosynthetic bacteria or algae. These preparations have shelf stabilities of up to 1 year, and their catalyst life is increased from a few minutes to a few hours.[35]

Stabilization of the photocatalytic system is now recognized, in the field, as a high-priority goal.[46] However, this recognition has come only recently, with the realization of the energy crisis. Thus, work toward this goal is just beginning.

Two-Stage Photochemical and Fermentation Processes

Fermentation of Photosynthetic Residues

Obviously, it is possible to produce hydrogen and oxygen from water by a conventional two-stage process with living and growing organisms — that is, by the secondary conversion of photosynthetic marine or agricultural residues to hydrogen by anaerobic fermentation or by the action of photosynthetic bacteria. Such processes have been proposed,[34,36] and hydrogen production by fermentation with clostridial species actually has been performed commercially.[3] However, hydrogen is produced in such processes only as a by-product of the primary production of alcohols, ketones, or fatty acids. Presumably, better strains could be developed to maximize hydrogen production. Also by-product alcohols and fatty acids might be converted to hydrogen in separate reactions by other bacteria. However, such processes would merely represent alternative methods for converting primary photosynthetic products to useful fuels such as methane or cellulose. Furthermore, methane processes are much closer to commercial feasibility. Wolfe believes[20] that a relatively modest investment (~ $1 million) in basic research on methane fermentation would result in substantial technical and economic improvement.

We do not discount the potential for hydrogen or methane production from carbonaceous photosynthetic residues, particularly those that would otherwise be waste materials (e.g., sewage or garbage). However, this potential is ultimately subject to the basic limitations on the efficiency at which solar energy can be converted in marine and agricultural residues to feedstock for hydrogen or methane production.

Nonbiological Photolysis

It seems likely that nonbiological water photolysis that utilizes a substantial portion of the available solar flux will require the coupling of two or more photocatalytic (or stoichiometric) reactions in a closed cycle in order to bridge the energy gap. In photosynthesis, two photochemical processes are coupled "in series" via an elaborate electron-transport chain so that a net electrochemical potential of about 1.2 to 1.4 volts is imparted to each electron involved, and the reaction is accomplished in one integrated step. It may be possible to accomplish this in the laboratory, but at present it appears difficult.

There are, however, other ways to accomplish the same objectives. For example, it should be possible to electrochemically couple certain photochemical reactions. In particular, the overall potential needed for splitting water might be provided in smaller increments by coupling two or more electrochemical cells in series.

Fujishima and Honda have demonstrated[18] an effective means for coupling the photochemical sensitization of n-type semiconductors to the production of hydrogen and oxygen from water. This was accomplished simply by using the irradiated titanium dioxide (TiO_2) semiconductor as the anode of an electrochemical cell in series with a platinum-block cathode. The photochemical and electrode reactions are presumed to be as follows:

$$4h\nu \xrightarrow[TiO_2]{} 4p^{+} + 4e^{-}$$

$$\begin{array}{lr} 4p^{+} + 2H_2O \rightarrow O_2 + 4H^{+} & -1.23\ V \\ 4e^{-} + 4H^{+} \rightarrow 2\,H_2 & 0.0\ V \\ \hline 4h\nu + 2H_2O \rightarrow O_2 + 2H_2 & +0.5\ V \end{array}$$

The anode was irradiated with 415 nm light (~3.0 volts), corresponding to the band gap of TiO_2. The electromotive force (EMF) of the completed cell was 0.5 volt. Thus, the photochemical reaction must have generated an electrochemical potential of 1.73 volts (1.23 + 0.5). This corresponds to a quantum-energy-conversion efficiency of about 58% (about the same as in photosynthesis). Unfortunately, the quantum efficiency was only about 10%, and the process can utilize less than 10% of the solar spectrum. However, the experiment is important because it illustrates a practical method of utilizing photochemically generated electrochemical potential.

This approach is also being studied in a NASA-sponsored program at M.I.T. under the direction of M. S. Wrighton.[47] Their work, in general, confirms the work of Fujishima and Honda, although the electrolysis actually requires a 0.2-volt assist. This program will explore TiO_2 and other semiconductor systems, as well as other variables in the system.

Similarly, other photocatalyzed reactions could be used as half-cell components of an electrochemical cell. Unfortunately, however, the potential generated by photocatalytic reactions that utilize significantly longer wavelengths of light will not be sufficient to split water. Such reactions do, however, result in the storage of energy or in the generation of electrochemical potential. The problem then becomes one of coupling the incremental energies generated by the partial reactions into a multistage process that will result in the splitting of water.

Ohta and Kamiya have suggested[48] that electrochemical potentials of less than 1.23 volts can be used to assist the electrolysis of water by conventionally generated electricity. For example methylene blue (MB) and ferrous ions generate an electrochemical potential of about 0.2 volt when irradiated:

$$2Fe^{++} + H^{+} + MB^{+} \xrightarrow{h\nu} 2Fe^{+++} + MBH$$

If such a cell were placed in series with a water-electrolysis cell, the potential required for electrolysis would be reduced by about 0.2 volt — a rather small assist. Alternatively, it might be possible to use a stack of eight such cells in series to generate a potential of 1.6 volts (ignoring overvoltage), which would be sufficient for the electrolysis of water. However, the solar-energy-conversion efficiency would be reduced to a maximum of about 7% of the absorbed energy.

Ohta and Kamiya have also demonstrated that three complex dye systems in series can generate significantly greater EMF values ($\sim$0.6 volt) and a negative potential at the anode close to that of the hydrogen electrode. Thus they have a prototype for an anode that is almost capable of reducing hydrogen ions to molecular hydrogen. Their paper, however, did not give detail sufficient for evaluation of whether this series utilizes one or two photons per electron. If it is a two-photon event, the solar-energy-conversion efficiency is probably no greater than that for each individual cell. In any case, only the anode portion of the cell was studied. Thus coupling into a complete electrochemical cell has not been achieved.

On the other hand, to our knowledge, none of the photochemical reactions discovered thus far appear to be able to generate an oxidant strong enough to liberate oxygen at the cathode (utilizing the longer wavelengths of light). However, the approach is valid, although on the basis of current knowledge, such processes will probably be very complex, as illustrated by the proposal by Graves and Stramonde[24] that utilizes three half-cell reactions based on organic dyes (one with a cyctochrome redox system), hydrogenase to evolve hydrogen, and a six-stage thermochemical cycle to evolve oxygen. Obviously, photochemical half-cell reactions that are capable of bridging a much larger portion of the 1.23-volt energy gap are needed. This would increase efficiency, as well as simplify the coupling problem.

Efficiency of Solar Utilization[32,33]

The Basic Photosynthetic Process

Ideally, the above formulation indicates that photosynthesis utilizes 8 Einsteins of light at an energy of 40.8 kcal/Einstein to produce the free-energy equivalent of 2 moles of hydrogen plus 1 mole of oxygen. Thus the maximum internal thermodynamic efficiency of the process is about 35% [114 kcal/(40.8 X 8)] of the energy received by the reaction center. In actuality, however, the reduction of carbon dioxide to carbohydrate requires about 4 molecules of ATP, in addition to the light-generated reducing function (NADPH).[15] About half of the ATP requirement is generated by the exergonic electron-transport system at no cost in light energy. The other half, however, is generated by photophosphorylation and apparently requires two extra quanta of light. The maximum thermodynamic efficiency for producing carbohydrate, therefore, is actually closer to 28% of the energy received.

These calculations are in agreement with similar estimates made on the basis of charge separation produced by 700-nm light (~ 1.77 volt). Thus, at an efficiency of 56%, 700-nm light produces a charge separation of about 1 volt. A total of two quanta, at 1.77 volts each, produces a net charge separation of about 1.23 volts – an overall efficiency of about 35%. Thus the thermodynamic efficiency at which the process utilizes the energy delivered to the reaction center is relatively high.

To convert the above efficiencies to solar-utilization efficiency, we must allow for two other factors:

- In order to utilize light energy at a constant 1.77 volts, higher energy photons have been degraded to that level. The average wavelength of the light absorbed is about 550 nm, which corresponds to an energy of 2.25 volts (or 52 kcal/Einstein).
- Only about 45% of the solar spectrum is in the 400 to 700-nm range.

Taking these two factors into account, the actual maximum utilization efficiency should be 22% [114/(10 X 52)] of the light absorbed, or about 10% of the total solar flux. There appears to be a considerable amount of experimental confirmation of the order of magnitude of this value. Kok states[33] that "algae and higher plants have been grown (in weak light) with efficiencies approaching this value – converting 20% of the absorbed solar radiation (~ 550 nm)." Of course, this is under ideal laboratory conditions. However, solar-utilization efficiencies as high as from 5% to 6% have been measured on a daily basis, under field conditions, for crops such as corn and sugar cane.[39, 56] Thus a maximum practical efficiency of 10% does seem reasonable.

Marine and Agricultural Photosynthesis [39] [56]

The solar utilization efficiencies found in nature, on the other hand, are substantially lower that 10%. Kok states[33] that "net production in the field seldom exceeds 2%; typical values are 0.5% to 1.5% (3 to 10 kW/acre)." However, he indicates that annual efficiencies of from 4% to 5% have been observed and cites efficiencies of ~3% for sugar cane and ~2% for forestry on the south coastal plains. Loomis et al.,[39] as well as Schneider,[56] generally confirm the order of magnitude of the above-quoted efficiencies, on an annual basis, for a number of crops. However, both show data indicating that daily efficiencies that approach 6% can be achieved with certain crops, such as corn, sugar cane, and tropical grasses. It is significant that, although the highest daily efficiencies for corn and sugar cane are about the same, the annual efficiency for sugar cane is about twice that for corn because of the length of the growing season. Thus annual efficiencies tend to be higher nearer the equator. It seems probable that annual efficiencies might actually approach the average daily efficiencies if cropping could be carried out on a continuous basis rather than in batches. Examples would include mixed natural ecosystems, such as the tropical rain forests, and a continuous algae-growth process.

The loss mechanisms have been summarized by Schneider [56] and by Loomis.[11] Many losses (e.g., those due to the density of the ground coverage, grazing and insects, or lack of nutrients) can be controlled by agricultural practice. Other losses, however, are more intrinsic to the photosynthetic process itself or to the overall plant physiology. These include—

- In strong light, limitation of the velocity by the dark enzymatic reaction (most plants attaining saturation of photosynthesis at intensities below that of noon sunlight)[52]
- In weak light, a decrease in net efficiency brought about by respiration and other factors[33]
- Further limitation of the maximum rates by the availability of water; organic nutrients (such as nitrate ions, NO_3^-); and, in particular, carbon dioxide
- Consumption by plants of a significant fraction of their gross production (< 50%) for their own maintenance (respiration)[64]

Each of these factors, particularly photorespiration and light-saturation intensity, varies considerably among different plants. Thus plant breeding and genetic manipulation could lead to significant improvements in the efficiency of photosynthesis in practice.[64]

Potential Efficiencies of Artifical In-Vitro Processes

Reconstituted in vitro photosynthesis, if it could be developed, could eliminate the need for respiration, as well as ATP formation. This would reduce the quantum requirement from 10 to 8 Einsteins per mole of oxygen evolved and would increase the theoretical maximum efficiency to 13.7% of the solar flux. Furthermore, because such processes could be carried out on a continuous (rather than batch) basis, the annual efficiencies would approach maximum. On the other hand, the energy required for control and maintenance of such systems would certainly reduce the overall efficiency.

Current Status and Future Prospects of Photosynthesis Research

The photosynthesis model presented in Figure 7-1 is consistent with the known experimental data, although other models can probably be devised to explain the same data. Clayton suggests[19] that the figure is a reasonable consensus as of 1970. However, the model, as it stands, is still incomplete. The general state-of-the-art and the problems yet unsolved are discussed below.

Electron-Transport System[14,15,52]

The electron-transport system connecting the two photochemical half-cell reactions has been fairly well elucidated.[14,15,52] The detail presented in Figure 7-1 primarily serves to illustrate the complexity of the transport chain. Each of the electron carriers shown (and there are probably more) is a complex chemical entity attached to or in the form of a protein. Furthermore, the relative amounts of the carriers vary. For example, there are 10 equivalent of PQ for every Q, two equivalent of cyt b_{559} for every cyt f, and one of PIC for every P_{700}. Thus the difficulties that might be anticipated in trying to stabilize such a system for use in vitro or in trying to construct a synthetic electron-transport system become evident.

Carbon Dioxide Reduction[21,22]

The ultimate electron acceptor in the photosynthesis process is actually NADP, a complex biological chemical. As indicated in Figure 7-1, NADP is reduced by the photochemical reductant, X^-, through a second electron-transport chain involving several more complex enzyme species, including an iron-containing ferredoxin. Although the sequence of these carriers has been reasonably well established, the nature of the photochemically produced reductant itself is unknown. Furthermore, the manner in which the electron-transport chain is coupled to the primary reductant is still a mystery.

NADPH (the reduced form of NADP) and ATP reduce carbon dioxide to carbohydrate. This process has been named the Calvin-Benson cycle: Elucidation of the mechanisms involved in the reduction earned Calvin and his associates at Berkeley a Nobel Prize.

Oxygen Evolution and PS II[13,16,52]

The electron donors and acceptors immediately surrounding chlorophyll a in PS II remain unidentified. The electron acceptor, Q, is presumed to be a quinone. Even less is known about the nature of Z (the oxidizing agent) and the reactions and reactants mediating the oxidation of water to oxygen. (It is known that manganese and chloride ions are somehow involved because extraction thereof effectively stops oxygen evolution.)

The generation of oxygen is one of the more critical steps in the whole process because it involves the molecular mechanism by which a chemical process is coupled to a photoactive membrane system (which, incidentally, can be synthesized in the laboratory[30]). Thus, if we knew how to couple such a membrane to a chemical or voltaic process, photosynthesis might be reproducible in the laboratory. In any case, the lack of analytical success suggests that a greater emphasis should be placed on the synthetic approach.

Stoichiometric Pathways[15,32]

The model, as currently formulated, accounts for a single-electron process. However, the release of one oxygen molecule requires the accumulation of four electrons at a specific energy level. How this is accomplished is not well understood. Again this emphasizes the complexities, as well as the lack of understanding, of the mechanism by which a chemical reaction is coupled to the primary photochemical species.

Photophosphorylation [15,38,41,49,52]

In addition to the production of reducing power (NADPH), photosynthesis also results in the storage of enetgy in the form of ATP, which is the universal medium of energy exchange in biological processes. Although we are primarily interested in the reducing power generated by the photosynthetic process, consideration of the mechanism by which the phosphorylation process is coupled to the electron-transport system may lead to a better understanding of the process as a whole.

Phosphorylation appears to be of vital importance to many or all membrane processes in which active ion-transport occurs. In 1970, A. L. Lehninger stated [55]:

> "There can be no doubt that the most central and overriding problem we face today in the study of photosynthesis and respiration is the nature of the chemical and physical events involved in the conversion of electron-transport energy into phosphate bond energy. In both processes we have chains of electron-carrying proteins which are fixed in membranes, the structure of which is vital for their function. In both cases electron transport can lead not only to ATP formation, but also to transport of ions as H^+ across the membrane..."

Until recently, it was assumed that the coupling is chemical in nature, although the required chemical intermediates have never been identified. Furthermore, the chemical coupling hypothesis does not explain the necessity of a membrane structure for functionality.

More recently, P. Mitchell proposed [41] that the coupling occurs not through chemical intermediates, but rather occurs because of the electrochemical state of the membrane in which the electron-transport system is arrayed. This view, called the chemiosmotic hypothesis, postulates that electron transport occurs in a chain of geometrically oriented carriers within the membrane and is stoichiometrically related to the transport of hydroxyl ions across the membrane, which separates the inner and outer phases. Thus, an electrochemical potential, estimated to be on the order of 0.3 volt (quite sufficient to drive the ATP formation), is generated. [15,54]

Experiments show that illumination of chloroplasts is associated with a difference in pH across the membrane, as well as with ATP formation. Furthermore, Racker and Stoeckenius [53] (at Cornell) have reconstituted membranes from the photosynthetic pigment of purple bacteria with an ATP enzyme from heart mitochondria that, when illuminated, generate a hydrogen ion gradient and ATP.

Whether the Mitchell hypothesis is basically correct in its present form or not remains unresolved.[38,49,57] However, it has served to focus attention on the importance of the membrane structure and dynamics and on biological membranes as energy transducers. In particular, the Mitchell hypothesis emphasizes our lack of understanding of the relationships between biological-membrane structure and function.

Nature of the Photosynthetic Unit[14,15,52]

The most fundamental, as well as the most important, unknown in the current understanding of photosynthesis is the nature of the photosynthetic unit itself in terms of structure and function. The primary photoacceptors in photosynthetic organisms belong to a small family of closely related pigments known as the chlorophylls. The principal members of this family are chlorophyll a and b (Chl a and Chl b) in green plants and algae and bacteriochlorophyll (BChl) in photosynthetic bacteria. Without exception, Chl a is present in all organisms that carry out photosynthesis with the evolution of oxygen. Although the chlorophylls appear to be the primary and essential components of the system, they are in nature associated with a number of other pigments, including the carotenoids and the phycobilins (phycoerythrin and phycocyanin). Together, these pigments absorb most of the visible spectrum of solar radiation. (See Figure 7-2.)

According to current views, the basic photosynthetic unit consists of about 300 to 400 molecules of Chl a, together with the associated pigments (most of which function only to "harvest" light and to transfer energy to a reaction center within the unit). The efficiency of the energy-transfer process is in excess of 90%.

The brief survey of nonbiological photolysis serves to highlight the unique properties of the chlorophyll photosensitizer in photosynthesis, in particular —

- Its ability to harvest light over the whole solar spectrum and to transfer the energy efficiently to the reaction center
- The photocatalytic nature of the reaction centers and the efficiency with which they convert photoenergy to electrochemical potential.

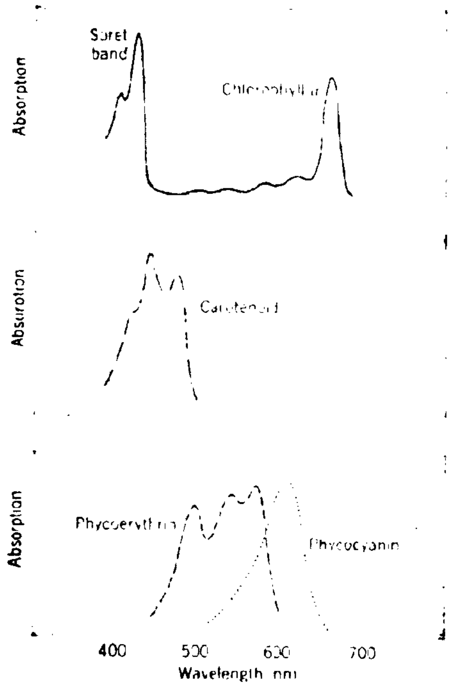

Figure 7-2. ABSORPTION SPECTRA OF THE THREE TYPES OF PLANT PIGMENTS

These properties appear to exist in nature only in photosynthesis, and both are derived from the nature of the chlorophyll molecule.

Of particular interest is the contrast between the photochemical reactions of chlorophyll in solution with those occurring in photosynthesis. For example, Chl a in methanol is photooxidized by suitable electron acceptors – such as Fe^{+++}, quinone, and a variety of dyes – in reactions reminiscent of the Hill reaction[52]:

$$\mathrm{Chl}\ \underline{a} + \mathrm{Fe}^{+++} \underset{\mathrm{dark}}{\overset{h\nu}{\rightleftarrows}} \mathrm{Chl}\ \underline{a}^{+} + \mathrm{Fe}^{++}$$

or

$$2\mathrm{Chl}\ \underline{a} + \mathrm{Q} \underset{\mathrm{dark}}{\overset{h\nu}{\rightleftarrows}} 2\mathrm{Chl}\ \underline{a}^{+} + \mathrm{QH}_2$$

However, the reactions are stoichiometric, and the oxidized chlorophyll species does not appear to be reactive with water. Furthermore, the overall electrochemical potential bridged appears to be on the order of only 0.1 to 0.2 volt.

Similary, Chl a can be photoreduced by certain electron donors, such as ascorbic acid ($E_0 \approx 0.0$), in a reaction analogous to the Krasnovsky reaction[37 52]:

$$\text{Chl } \underline{a} + \text{ascorbic acid} \underset{\text{dark}}{\xrightarrow{h\nu}} \text{ChlH}_2 + \text{dehydroascorbic acid}$$

Again the reaction tends to be stoichiometric, although $ChlH_2$ can be reoxidized by various electron acceptors with electrochemical potentials of up to 0.02 volt. Thus the maximum energy stored is only 0.2 volt.

In contrast, each chlorophyll reaction center in photosynthesis generates a charge separation of about 1.0 volt at an efficiency of about 56% (1/1.77), and the process is photocatalytic. This accomplishment has only been partially explained, but considerable progress toward understanding the process has been made during the last 5 years.

Structure and Function of Chlorophyll

Chlorophyll a is a fascinating member of the porphyrin family. It consists of a cyclic tetrapyrrole chelated with magnesium. (See Figure 7-3.) In addition, the structure includes the following important features:

- An alicyclic ketone structure fused to one of the pyrrole rings, which appears to be conjugated to the unsaturated double-bond structures throughout the molecules
- An aliphatic acid group esterified with a 20-carbon-atom aliphatic alcohol.

The overall molecule is polar and hydrophilic at one end and nonpolar and hydrophobic at the other end. This strongly affects its colloidal behavior, particularly in nonpolar solvents and at polar-nonpolar interfaces. However, the most important and distinctive feature of the chlorophylls is that they contain both an electron-donor and an electron-acceptor function within the same molecule.

The central magnesium atom is constrained by the cyclic tetrahydropyrrole structure to a coordination number of 4 and is therefore coordinatively

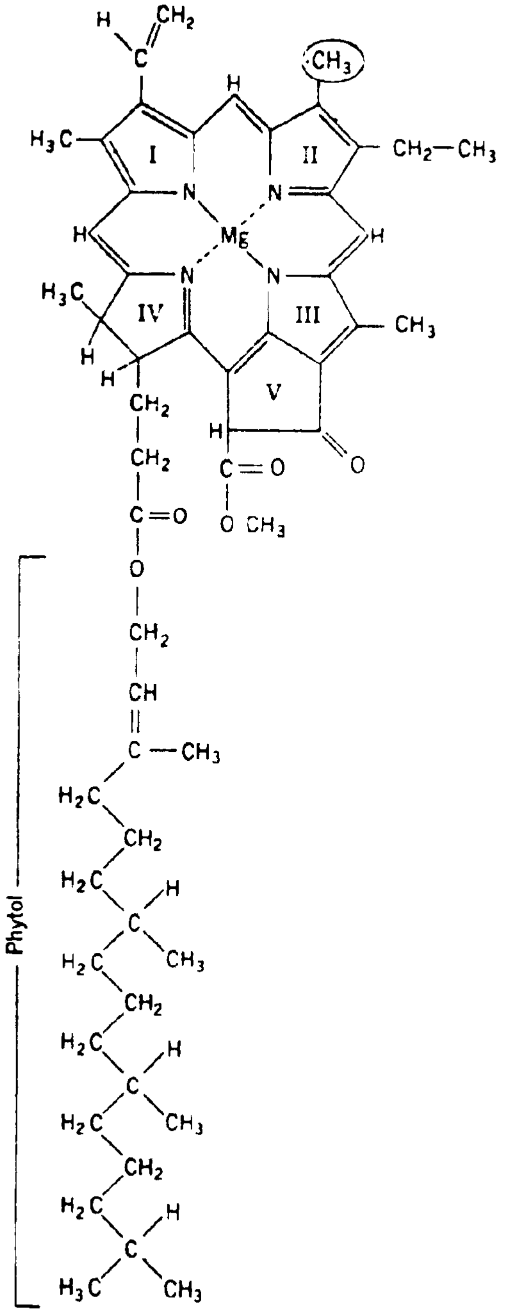

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Figure 7-3. CHLOROPHYLL $\underline{a}$

unsaturated and tends to behave as a Lewis acid (i.e., it accepts electrons from an electron donor). This is quite analogous to the strong acid catalyst properties of silica-magnesia gel in which magnesium ions are constrained by the silicate matrix to a coordination number of 4, thus generating Lewis-acid function. The electron-donor function is provided by the alicyclic ketone group ($>\text{C} = \text{O}$) as a result of the fact that the energy change associated with the loss of an electron from the ketone can be delocalized and distributed over the whole porphyrin structure by resonance of the conjugated double-bond system.

As a result of its electron donor-acceptor properties, chlorophyll tends to form coordination complexes with itself and with other nucleophilic agents such as water.[30] In nonpolar solvents it exists as dimers or oligomers, the molecular weight of which is dependent on the concentration. In polar solvents, chlorophyll forms coordination adducts. Bifunctional liquids, such as dioxane and water, interact with chlorophyll to produce cross-linked coordination adducts of colloidal dimensions. Thus the structure, and therefore the properties, of Chl *a* will depend strongly on the chemical environment in which it exists.

On this basis, J. J. Katz and associates[30] (at Argonne National Laboratories) took a synthetic approach to delineating the nature of the antenna chlorophyll and of the reaction center. Thus the properties indicative of light harvesting and photoactivity of different synthetic chlorophyll preparations in various colloidal states and adducted with various nucleophilic agents were determined and compared with *in vitro* reaction-center preparations. These studies have been quite informative.

Comparative studies of the absorption spectra of the oligomers of chlorophyll in nonpolar solvents with those of *in vivo* reactive-center preparations provide good experimental support for the hypothesis that the bulk of the Chl *a* *in vivo* (i.e., the antenna chlorophyll) exists as high-molecular-weight oligomer (Chl *a*). The oligomers, however, show no indication of photoactivity, such as the photoreversible electron spin resonance signal (ESR) or the characteristic shift in absorption toward the far red (P_{700}), both characteristic of the reaction center in photosynthesis.

On the other hand, adducts with bifunctional ligands (complexing agents), such as dioxane and water, show a remarkable red shift. However, of all of the bifunctional adducts, the 1:1 chlorophyll/water adduct $(\text{Chl } \underline{a}\cdot H_2O)_n$ is the only one that shows a photoreversible ESR signal when illuminated by red light with a wavelength greater than 650 nm. These results suggest that the chlorophyll reaction center in vivo involves a nucleophilic interaction similar to the water adduct, even though the red shift in the 1:1 $(\text{Chl}\cdot H_2O)_n$ adduct is much too large and the ESR signal much too narrow for specifically P_{700}. However, these discrepancies can be rationalized in terms of a theory that suggests the red shift and ESR signal of an isolated $(\text{Chl}\cdot H_2O\cdot \text{Chl})$ entity would be completely consistent with the in vivo P_{700}.

Thus Katz postulates a model in which one water molecule inserted into a high-molecular-weight oligomer, composed of about 300 chlorophyll molecules, is the photosynthetic unit. Mechanisms exist for a plausible explanation of the photochemical charge separation in such a model. Furthermore ESR data on P_{865} in purple photosynthetic bacteria are completely compatible with the special chlorophyll pair hypothesis.[30]

The Katz chlorophyll-pair model is also consistent with the empirical results of parallel analytical studies of the reaction center of photosynthetic bacteria. Parson and Cogdell have recently reviewed[50] the current status (as of March 1975) of understanding of the primary reactions in bacterial photosynthesis. Considerable progress has been made possible since the development of techniques (in 1968) for physically separating and purifying the reaction centers for the organism R. spheroides of light-harvesting and other components of the photosynthetic unit. These techniques led to an intensive analytical study of the nature and photochemical reactions of the reaction-center preparations.

The basic chlorophyll component of the reaction center in the bacteria R. spheroides has been shown to consist of a complex of four BChl molecules plus two molecules of BChl in which the magnesium atom has been replaced with two hydrogen atoms. ESR studies of the reaction-center preparations indicate that when the complex loses an electron, the remaining unpaired electron is shared by two of the BChl molecules, and the energy transfer with the other two BChl molecules is broken. These observations are compatible with a dual-function model such as that by Katz.[50] Furthermore, it has been shown that dehydration (over phosphorous pentoxide) reversibly blocks the photochemical activity of bacterial chromatophores, thus implicating the water molecule as an integral part of the reaction center.

These results suggest to us that photocatalytic activity, as well as the large charge separation produced by the reaction centers, is associated with dual functionality of the reaction center. Dual functionality is inherent in the special chlorophyll pair model by Katz:

$$\text{Chl } \underline{a}\cdot H_2O\cdot\text{Chl } \underline{a} \xrightarrow{h\nu} \text{Chl } \underline{a}^{+}\cdot H_2O\cdot\text{Chl } \underline{a}^{-}$$

Such a dual-function catalyst provides for not only the generation of both an oxidant and a reductant for photocatalytic activity; but also, perhaps, double the charge separation that either half-stoichiometric, half-cell process alone could achieve.

Whether the Katz or similar models are valid remains to be demonstrated. However, the fact remains that it has been possible to synthetically prepare chlorophyll films in the laboratory that exhibit, qualitatively at least, the light harvesting and photoactive properties of the photosynthetic organisms. This accomplishment represents a large step toward synthetic photosynthesis. On the other hand, it has not yet been possible to couple the measurable photoactivity (that is, charge separation) of such chlorophyll aggregates with a suitable elelctron-transport system to achieve either chemical reaction or voltaic activity.

Primary Electron Donor and Acceptor

It is curious that the Chl^+ generated in a methanol solution appears to be incapable of interacting with water directly. As a matter of fact, the redox potential of Chl a in methanol has been measured to be 0.62 volt,[63] clearly too weak to oxidize water (which requires 0.82 volt). Perhaps this is because the Chl^+ ion is stabilized by forming a complex with the solvent.

The ligand effect on the stability, and therefore on the redox potential of metallic ions is a well known phenomenon. Thus the oxidation potential for the iron couple —

$$Fe^{+++} + e^{-} \rightarrow Fe^{++}$$

varies from as high as 1.14 volts (with electron-withdrawing ligands such as

1, 10 phenanthroline) to 0.36 volt (with anionic electron-donor ligands such as cyanide ion, CN^-). The standard oxidation potential for Fe^{+++} in which the ligand is water is 0.77 volt.[2] It is also very interesting that the oxidation potential of Fe^{+++} is reduced even further in the electron-transport enzymes – for example, to a range of from –0.3 to -0.3 volt in cytochromes and to only –0.42 volt in ferredoxin.

Thus the ligand environment of the oxidant and reductant produced by the photocatalyzed reaction may be critical in determining the charge separation attained and the reactivity of the species. On this basis, the function of the electron-donor and -acceptor molecules immediately associated with the photocatalyst may be to provide the ideal ligand field for the terminal oxidant and reductant, thus facilitating electron transport and reaction with water.

Support for such an effect is cited in the Parson and Cogdell review[50]:

> "The E_m values that have been reported for P_{870} are significantly below that of bacteriochlorophyll in solution, which is +0.52 volt in methanol and +0.64 volt in CH_2Cl_2.... The E_m of chlorophyll in alcoholic solution varied by 0.23 volt, in the series methanol < ethanol < i-propanol. Although the effect awaits rationalization, it could reflect the complexing of the alcohol with the chlorophyll Mg atom or with the ring keto oxygen."

On the other hand, an equally important property of the primary electron acceptor is to quench the fluorescence of the excited chlorophyll (i.e., to trap the electronic energy). Parson and Cogdell cite[50] literature indicating that the quenching ability of electron acceptors decreases with decreasing redox potential (i.e., the better the oxidant, the greater the quenching ability). On the other hand, the quench rates increase with increasing concentration, up to the point at which diffusion becomes controlling. Such factors probably, in part, account for the fact that photochemical reactions in solution do not seem to bridge a large energy gap.

Recent studies of reaction-center preparations from bacteria (as interpreted by Parson and Cogdell) also indicate that the primary electron acceptor of the photochemical process is an integral component of the reaction center. Its composition is still unknown; but both a quinone and an iron-containing complex (probably similar to ferredoxin) are involved in series, in parallel, or as an integral complex. The intimate relationship (analogous to infinite concentration with no diffusion control) probably permits use of the acceptor with the lowest oxidation potential (i. e., with the highest reduction potential) without a reduction in the trapping efficiency.

In addition to four BChl molecules and the iron and quinone species, the reaction-center complex contains three protein components of differing molecular weight in a mole ratio of 1:1:1. These proteins undoubtedly have an important function in binding the components together and in providing the ideal ligand environment. For example, denaturation of the protein results in a drastic shift of the adsorption spectrum from that characteristic of the reaction center (with the major peak at 870 nm) to that of monomeric BChl in solution (with the major peak at 760 nm).[14,15,52] Because the heavier unpigmented fraction can be physically removed (by detergent treatment) without affecting the photoactivity, the photochemical activity apparently resides in the two lower molecular weight fractions.[23,38,63]

Considerable information has also been gathered on the kinetics of the photochemical events occurring in the reaction center in terms of rates of absorption, fluorescence, and charge separation (ESR). In this way, the structural and functional relationships are gradually being elucidated, although no quantitative mechanism has yet emerged. The reaction center is apparently a dual function photosensitizer (e. g., $Chl{\cdot}H_2O{\cdot}Chl$), the photocatalytic activity of which depends on an intimate relationship or complexing with an electron acceptor to trap the photonic energy that would otherwise be reemitted as fluorescence. The primary electron donor appears to be less strongly bound to the reaction center, but in reality it is probably also an integral component of this reaction center. Its role in quenching fluorescence has not been identified, but it is nevertheless required to transmit the positive charge to a reactant. The redox potentials of the donor and acceptor species are dependent on the nature of the ligands provided and seem to be tailored to achieve maximum charge separation, as well as the specific potential levels required to oxidize water in PS II and to reduce NADP in PS I.

This understanding of the reaction center and the empirical observations of the complex structure involved suggest that the laboratory synthesis of photocatalytic membranes, complete with electron transport, will require a major breakthrough. However, the knowledge gained thus far does indicate the direction for further research.

Nonbiological Photolysis

The energy of the carbon-oxygen single bond is about 111 kcal/mole, equivalent to the energy of UV light that has a wavelength of about 260 nm. Furthermore, water does not absorb UV light at wavelengths greater than 185 nm (equivalent to an energy of 155 kcal/Einstein). Obviously, direct photolysis is not possible with sunlight, which does not contain UV light below about 300 nm.

On the other hand, we have learned from photosynthesis that photolysis of water can be carried out by red light that has an energy content of only 40 kcal/Einstein if the energy is applied incrementally to one electron at a time. This is analogous to the electrolysis of water, which can be driven by energy units as small as 28.4 kcal/Einstein (1.23 volts). Thus the low energy content of the available solar radiation does not preclude the possibility of developing a relatively efficient photolysis process. It does, however, impose rather severe constraints on how such a process can be accomplished.

It has been estimated that the theoretical maximum free energy (ΔG_{max}) made available by absorption of light is limited by the second law of thermodynamics to about 70% of the energy of the light absorbed.[31] Thus red light at 700 nm, which has an energy content of 1.8 volts, theoretically can provide a net free energy of 1.26 volts (1.8×0.7), which is sufficient to drive the splitting of water. However, in photosynthesis, 700-nm light yields a charge separation of only about 1 volt (an overall efficiency of 55%). On the basis of a 55% efficiency, the photogeneration of 1.23 volts would require quantum energy of 2.24 volts (~543-nm light). If 1.47 volts (corresponding to the reaction enthalpy) is actually required to electrolyze water, a quantum energy of 2.7 volts (~450-nm light) would be required. Thus it seems improbable that direct, one-step photolysis or electrolysis of water can be accomplished, except at short wavelengths.

Requirements for Efficient Photolysis by Sunlight

Because water does not absorb visible light, attainment of efficient photochemical reaction will require special considerations:

- For efficient utilization of the solar flux, a sensitizer must be used that is capable of utilizing all or a substantial part of the visible spectrum. Most pure chemicals absorb over a fairly narrow portion of the visible spectrum. Thus it may be necessary to employ one or more accessory pigments for harvesting light. This, in turn, would require a mechanism for efficient transfer of harvested energy to the sensitizer. These requirements suggest that perhaps a black pigment (e.g., a carbon or graphite) should be considered. However, the best possibility seems to be the oligomeric Chl a membranes described by Katz.[30]

- The photochemical reaction must be photocatalytic or capable of coupling to other reactions to close the cycle. Generally, photochemical reactions are stoichiometric and result in the oxidation or reduction of the sensitizer. Such reactions comprise only one half-cell reaction of a photocatalytic reaction. Therefore, the sensitizer in its altered oxidation state must be capable of driving a second half-cell reaction, either in situ or in a separate stage, to regenerate the original sensitizer and to complete the desired reaction.

- Electron-transport mechanisms will be required to couple the sensitizer to the reaction system or to couple one half-cell reaction to the other. Thermodynamic considerations suggest that at least two photocatalytic reactions will be required analogous to the requirement of 2 quanta per electron for photosynthesis. Therefore, means must also be provided for coupling two or more reactions into a complete system that produces hydrogen and oxygen from water. Conversely, thermodynamic considerations limit the number of photocatalytic reactions that can be used in series efficiently. For example, if photosynthesis required 4 quanta per electron instead of two, the maximum efficiency would be halved.

These criteria obviously have been set up by analogy with photosynthesis, which is the only model we have to work from at present. From this point of view, it might also be useful to set up an idealized process analog of photosynthetic hydrogen production as a working model. Such a model would consist of three discrete reaction stages that operated in sequence (in series) to split water as follows:

$$2H_2O + 2Q \xrightarrow[\text{PS II}]{h\nu} O_2 + 2QH_2 \qquad (1)\ E_1 \approx 1$$

$$2QH_2 + 2P \longrightarrow 2Q + 2PH_2 \qquad (2)\ E_2 \approx -0.8$$

$$2PH_2 \xrightarrow[\text{PS I}]{h\nu} 2P + 2H_2 \qquad (3)\ E_3 \approx 1$$

$$2H_2O \xrightarrow[\text{PS I + II}]{h\nu} O_2 + 2H_2 \qquad E \approx 1.23$$

The light-driven reactions, 1 and 3, require quantum energies equivalent to about 1 volt and are coupled through Reaction 2, which occurs spontaneously with the release of energy. Thus the photosynthetic model suggests that to accomplish the overall reaction in three stages with only light-driven reactions, it is necessary for each photochemical event to involve water directly – one producing oxygen, and the other producing hydrogen. Futhermore, each light-driven reaction must achieve a net energy input equivalent to more than 0.6 volt so that Reaction 2 occurs spontaneously. Otherwise a portion of the hydrogen produced must be used to drive Reaction 2. However, it is possible to achieve a completely light-driven cycle with only two photochemical steps without direct involvement of water if the energy gap bridged is sufficient to generate products from which hydrogen and oxygen can be recovered by spontaneous reactions. This would, however, require additional reaction stages.

Photochemical Sensitizers

It is not surprising that natural evolutionary processes resulted in as complex a photocatalyst as chlorophyll: It is difficult to find simple photosensitizers that can utilize visible light and that are capable of interacting with water. Most inorganic materials that can photooxidize or reduce water do so only in the UV-light range and can therefore utilize only a small fraction of the light in the visible range. Such materials, therefore, are not suitable for efficient solar photolysis. Examples of such reactions with inorganic materials include –

$$2Ce^{++++} + H_2O \rightarrow 2Ce^{+++} + 1/2O_2$$ [27]

$$Fe^{++} + H^+ \rightarrow Fe^{+++} + 1/2H_2$$ [28]

$$Cr^{++} + H^+ \rightarrow Cr^{+++} + 1/2H_2$$ [17]

The first of these reactions (i.e., the ceric-ion oxidation of water) does not even represent a storage of solar energy because the ΔG_{298} for the reaction is negative.

The basic problem appears to be that most inorganic materials are weakly absorptive of light in the visible range, and those that are colored yield excited states (or ions) that are not capable of reacting with water. Most colored ions are ions of the transition metals. According to Basolo and Pearson,[2] most ionic complexes of the transition metals exhibit two distinct types of light absorption. Absorption of visible light is of low intensity and produces electronic transitions that lead not to charge transfer, but only to weakening of the ligand bonding. Such effects can promote reactions such as ligand substitution and racemization, but not oxidation-reduction reactions. The intense absorption in the ultraviolet region is of the "charge-transfer" type and is "characteristic of associated pairs of molecules, where we can identify a charge donating group and a charge accepting group, or alternatively, a Lewis base and a Lewis acid, or a reductant and an oxidant." Absorption of light in the visible range involves primarily d-orbital electrons, and "The intensity is low because the transitions are parity forbidden and sometimes spin forbidden."[2]

On the other hand, a number of highly colored organic materials are known, many of which do undergo photochemical oxidation-reduction reactions under the influence of visible light[52]:

$$\text{dye} + 2\text{Fe}^{++} \underset{\text{dark}}{\overset{h\nu}{\rightleftarrows}} \text{leucodye} + 2\text{Fe}^{++}$$

However, the reactions thus far discovered result in the generation of relatively small EMF's (from 0.2 to 0.3 volt), and none generate an oxidant or reductant strong enought to react with water. Such reactions are stoichiometric. However, if the reaction is carried out in an emulsion of ether in water, the product leucodye can be continuously extracted, thus resulting in the storage of solar energy in the form of a leucodye.[52]

Thus far, our experience suggests that the probability of finding a simple inorganic or organic photosensitizer is not great. However, it should be emphasized that investigation of the photochemical properties of materials absorbing light in the visible range has not been extensive. Thus the field is wide open for research, particularly because we know photochemical water splitting can be done (i.e., as in photosynthesis). At present, the Katz approach[30] seems to have the greatest potential.

Summary and Conclusions

Photosynthesis in green plants is a process that results ultimately in the splitting of water into molecular oxygen and a strong reducing species with an electrochemical potential below that of hydrogen. Thus the photosynthetic process is thermodynamically capable of producing hydrogen and oxygen from water. However, it appears to be universally true that, in green plants, the reducing power so generated is always used for the reduction of carbon dioxide to carbohydrate and other cell material.

Certain bacteria and algae do contain enzymes, such as hydrogenase and nitrogenase, that are capable of catalyzing the reduction of hydrogen ions to molecular hydrogen. Such organisms do in fact produce hydrogen under certain conditions by photochemical and dark reactions. However, this hydrogen is not produced from water, but is produced at the expense of an energy-rich nutrient substrate supplied by a separate photosynthetic process (performed by either itself or other organisms). Thus the two biological mechanisms required for producing hydrogen and oxygen from water exist in nature in separate organisms. The questions then become whether and how efficiently the two functions can be coupled to split water directly.

Obviously, it is possible to produce hydrogen and oxygen from water by a conventional two-stage process with living and growing organisms – that is, by the conversion of photosynthetic marine or agricultural residues to hydrogen by anaerobic fermentation or by the action of photosynthetic bacteria. Such processes have been proposed, and hydrogen production by fermentation with clostridial species actually has been performed commercially. However, hydrogen is produced in such processes only as a by-product of the primary production of alcohols, ketones, or fatty acids. Presumably, better strains could be developed to maximize hydrogen production. However, there may be a basic limitation in the efficiency (or kinetics) because biological hydrogen production appears to have a regulatory function, rather than a metabolic function by which organisms can live and grow. Such processes would merely represent alternative methods for converting primary photosynthetic products to useful fuels, such as methane and alcohol, which are much closer to commercial feasibility.

We do not discount the potential for hydrogen or methane production from carbonaceous photosynthetic residues, particularly those that would otherwise be waste materials (i.e., sewage or garbage). However, they are ultimately subject to the basic limitation in the efficiency at which solar energy can be converted in marine and agricultural residues to feedstock for hydrogen or methane production.

A number of other biological approaches have been suggested for the production of hydrogen:

a. Genetic improvement of certain nitrogen-fixing algae species in which the biological functions for both water splitting and ammonia or hydrogen production do coexist, but in separate cells. In the absence of nitrogen gas and with the proper nitrogenous nutrients supplied, such species do, in fact, produce hydrogen and oxygen from water. However, the solar-utilization efficiencies are significantly lower than in normal photosynthesis.

b. Direct coupling of bacterial hydrogenase with the intact photosynthetic apparatus extracted from algae or green plants. The scientific feasibility of this approach has been demonstrated (in μmole quantities) in the laboratory. However, two substantial problems remain: The hydrogenase activity is destroyed by oxygen, and the catalyst life of the intact photosynthetic apparatus in vitro is very short (lasting only minutes).

c. Two-stage coupling in which the aerobic and anaerobic functions are separated processwise. In the first stage, water splitting is performed, producing a stable reductant other than carbohydrate, by the intact photosynthetic apparatus extracted from algae. The stable reductant is then separated and reacted with hydrogenase in a second stage. The scientific feasibility has been demonstrated (in μmole quantities) in the laboratory with a fairly complex biological chemical. Obviously, a simpler stable reductant is needed; and the brevity of the catalyst life remains the primary problem.

The above approaches are all based on utilization of the intact photosynthetic apparatus of natural organisms. However, when removed from the self-repairing environment of the living organism, the photocatalytic life of these complex systems tends to be very short. Although some progress has been made toward stabilization or protection of these systems, a major research effort will be required before successful application can be expected.

Significant progress toward synthetic photosynthesis has been made by development of synthetic chlorophyll membranes that exhibit, at least qualitatively, the light-harvesting capability and photoactivity of photosynthetic membranes. However, it has not been possible to couple such membranes to the electron-transport mechanism required to achieve photochemical or photovoltaic action. Furthermore, a major breakthrough may be required before this coupling can be achieved.

The major barrier to understanding how the primary photosensitizing entity is coupled to electron transport has been the lack of effective analytical tools. It is our impression that the barrier is beginning to yield to a combination of analytical, synthetic, and theoretical approaches; however, the breakthrough may still be a few years hence.

There can be little doubt that photosynthesis has vast potential for converting solar energy to chemical energy for use as fuel, as well as food:

- Theoretically, the photosynthesis process is capable of converting up to 10% of the solar flux to chemical energy.
- Under laboratory conditions, efficiencies approaching 10% have been observed with algae.
- Maximum daily efficiencies as high as from 5% to 6% have been achieved in agriculture.
- If the theoretical maximum efficiency of 10% based on total solar flux could be achieved, production from about 1% of the total area of the United States would be sufficient to meet all of our energy needs.

The maximum annual marine or agricultural efficiency achieved is about 3%, but efficiencies are usually much lower – in the range of from 0.5% to 1.5% conversion of the total solar flux. It becomes evident, therefore, that the primary goal should be to increase the efficiency of oxygen generation by the basic process; and whether the reducing is utilized to produce hydrogen directly or to produce other reduced materials, such as carbohydrate, methane, or ammonia, should be of secondary import.

On the basis of current knowledge, nonbiological photolysis does not appear promising. However, investigation of the potential of this approach has not been extensive, and the field is wide open for research. It is our feeling that exploratory synthetic work in this area, guided by parallel research on the mechanisms of photosynthesis, will prove worthwhile.

In conclusion, there is no doubt that photosynthesis offers a vast potential for the production of energy, as well as of food and organic materials. It is also clear that the great challenge to research in this area is increasing the rate of transduction of solar energy to chemical energy, whether as food or as fuel. Although first priorities are, and should be, directed toward food production, in the long run it makes little difference because food and energy are, to a major extent, interconvertible. Furthermore, it is conceivable that higher efficiencies of solar-energy conversion can be achieved by engineered "*in vitro*" photosynthetic processes than by conventional marine or agricultural processes, particularly on an annual basis.

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8. HYDROGEN PRODUCTION BY OTHER PROCESSES — J. B. Pangborn and D. P. Gregory

In addition to the hydrogen production processes that have been described in earlier sections, there are three more processes that, although not mentioned as often as the others in connection with the large-scale use of hydrogen, deserve some attention. One of these is the production of hydrogen from waste materials, such as sewage, garbage, and agricultural wastes. Another is the splitting of water through use of neutron or ultraviolet radiation in a chemical sequence resembling a thermochemical process. The last process, the direct thermal dissociation of water, deserves special attention because it could make use of solar energy.

Hydrogen Production From Waste Materials

There is a possibility that hydrogen can be produced from waste materials such as sewage, garbage, and agricultural wastes. These materials, largely cellulosic, represent a considerable reserve of "energy" and are currently being considered as feedstocks for a variety of synthetic fuel production processes. Hydrogen production must be considered as a possible option.

Cellulosic wastes can be converted to a variety of fuels by four primary routes: 1) partial oxidation, 2) high-temperature reaction with steam, 3) pyrolysis, and 4) fermentation. In the first three cases, the initial process is one of gasification, converting the cellulosic material to a raw gas that consists primarily of hydrogen, carbon monoxide, carbon dioxide, and hydrocarbons, together with many other components. This gas stream can then be processed in a variety of ways to yield methane, methanol, synthetic "gasoline," or hydrogen, or it can be used directly as a boiler fuel. In the fourth case, depending on the selected fermentation agent and fermentation conditions, a variety of products can be derived, including alcohols, methane, or hydrogen.

Considerable research is already under way for the development of commercially viable processes, employing each of the methods described above, for the production of SNG (primarily methane), liquid hydrocarbons, and alcohols from sewage, garbage, and agricultural wastes. There seems to be little or no effort directed toward the production of hydrogen. However, the problems being addressed are primarily concerned with the initial conversion of the raw waste to "raw gas" and are those that result from the considerable variation in feedstock "quality," which in turn results in much variation in the raw-gas composition. For this reason, most processes entering the commercial-application stage are those in which the raw gas is simply used as a boiler fuel, often added to a conventional fuel supply such as coal, oil, or natural gas.

Once consistent raw-gas production has been achieved there seems to be little doubt that a fairly conventional gas "clean-up" process could be designed to produce hydrogen-rich gas rather than SNG or a liquid fuel, should the need exist. Therefore, there seems to be little justification at this stage for setting up a special research program aimed at producing pure hydrogen from these waste-material feedstocks. In the case of fermentation processes, the problems are similar to those already described in the section on photosynthetic hydrogen production.

A word of caution is appropriate at this point. There will be continuing demand for hydrocarbons and carbon-based organic materials long after conventional sources of fossil fuels have been depleted. Because the waste materials considered here are all carbonaceous, they must be regarded as an important source of organic carbon for such applications as lubricants, plastics, and pharmaceuticals. In the long run, it may be quite wrong to consider using them as a source of hydrogen and to develop processes that break down the organic carbon molecules.

Hydrogen Production by Radiation

Researchers at KMS Fusion, Inc., a private company in Ann Arbor, Michigan, have been carrying out research on the production of fusion energy through use of a laser beam. They have achieved significant success in producing fusion reactions by irradiating deuterium-tritium targets with laser energy, and the resulting fusion reaction produces a burst of radiation that consists primarily of neutrons with an energy of 14 MeV. They are still trying to demonstrate the "break-even point," at which their equipment will produce as much energy as it consumes. In parallel with this work is a project, funded by Texas Gas Transmission Corp., for the development of a process that splits water into hydrogen and oxygen under the influence of 14-MeV neutron irradiation. Thus, the successful development of such a process would enable hydrogen to be produced from a nuclear fusion reactor without the intermediate production of electricity and heat.

Details of the hydrogen-generation process have not been released, and staff at both KMS Fusion and Texas Gas Transmission Corp. regard this work as highly proprietary. However, representatives of KMS have announced[2] that they are actually producing hydrogen in the laboratory through a process that is driven by 14-MeV neutrons, that are obtained from a cyclotron. They describe the process as being similar to a thermochemical reaction sequence, in which a number of chemical processes are carried out in a cyclic fashion, but the energy supply to this sequence comes from one or more steps that absorb neutron energy rather than absorbing heat.[7] They point out that such a process offers considerable advantage over thermochemical processes because it is not necessary to include a high-temperature step; thus corrosion of process equipment is less likely to occur. Because no experimental results have been released, it is impossible to assess the status of this research; but it was recently announced that Texas Gas Transmission Corp. has renewed its funding of KMS's program for a second year at a very substantial level, which gives credence to the belief that significant progress is being made. To our knowledge, no other company is investigating similar processes.

Chemonuclear Water Splitting

In fusion reactions, deuterium nuclei are combined to form helium nuclei (alphas). In fission reactions, U^{235}, U^{233}, Pu^{239}, etc., are split into fission fragments whose kinetic energy represents about 85% of the energy released by the fission process. Use of the high-energy radiation from nuclear fusion or use of the kinetic-energy fission products to excite or ionize molecules and to break chemical bonds has been suggested by Juppe[9] and by Harteck and Dondes[8] as a means for the production of hydrogen from water. Experiments have shown that water can be split with fission fragments and that steam can be split with alpha irradiation.

IGT has been granted a patent on a multistep thermochemical process in which the chemonuclear decomposition of carbon dioxide to carbon monoxide and oxygen is used.[14] In this process, invented by C. G. von Fredersdorff, hydrogen is produced thermochemically by the action of steam on iron, and the iron oxide so produced is reduced with carbon monoxide to carbon dioxide. Fissiochemical decomposition of the carbon dioxide, by exposure to high-velocity fission fragments, reproduces the carbon monoxide and liberates oxygen. In principle, fissiochemical reactions are different from thermochemical or direct (single-step) thermal water-splitting steps, which could use the heat generated by a nuclear reactor. (In conventional nuclear reactors, the fission products are slowed by collisions to yield their energy as heat.)

For hydrogen and oxygen production from water via chemonuclear splitting, efficiency is measured in terms of the number of water molecules split per dose of radiation (100 eV by convention). The enthalpy required to split liquid water, 68,300 cal/g-mol, corresponds ideally to 33.8 molecules of hydrogen produced/100 eV; and the enthalpy required to split steam, 57,900 cal/g-mol, corresponds ideally to 39.9 molecules of hydrogen produced/100 eV. For fission-fragment bombardment of water, an experimental chemonuclear yield of 1.75 splits/100 eV has been reported; this corresponds to an efficiency of 5%. For alpha irradiation of steam, a yield of 6 splits/100 eV has been observed; this corresponds to an efficiency of 15%.[9] The use of fusion reactors to produce hydrogen from steam is a technology that may be developed in 30 to 50 years. The experimental verification of a self-sustaining fusion reaction is yet to be demonstrated, and a commercial fusion technology must be considered speculative at this date.

Although fission reactors are in commercial use today, a configuration for chemonuclear reactions is not practical because of the requirements for containment of radioactive material. That is, fission products must be contained by the fuel particles in the reactor core. A fission reactor for chemonuclear-reaction use would then need a thin, high-surface-area nuclear fuel structure through which the chemical reactants could pass to be exposed to fission-fragment tracks. In gaseous systems, this track is about 2 centimeters long; and in condensed systems, it is on the order of 20 microns long. Honeycomb fuel foil structures have been fabricated to make about 38% of the fission-fragment energy available for chemonuclear reactions. The main technical problem with this configuration is that the chemical reactant streams become contaminated with all manner of fission-product radioactivity.

Nuclear-Photochemical Water Splitting

Water can be split into hydrogen and oxygen by exposure to ultraviolet (UV) light of the correct wavelength; however, a spectrum of UV light will produce many excited states and radicals that are not desired. Water is transparent to visible light, but wavelengths of less than 2000 Å are absorbed. A continuum from about 1850 to about 1450 Å results in –

$$H_2O \rightarrow H + OH \qquad (8\text{-}1)$$

With UV light at 1849 Å, Ung and Back[13] observed the production of hydrogen and hydrogen peroxide from steam at 200° to 350°C. In the vicinity of 1236 Å, another decomposition mechanism has been observed:

$$H_2O \rightarrow H_2 + O \qquad (8\text{-}2)$$

For this mechanism, nearly monochromatic or quite-intense, narrow-spectrum UV light would be required for significant yields of hydrogen, and the light would have to be produced artificially. Only insignificant intensities of sunlight at these wavelengths reach the earth's surface.

Eastlund and Gough[4] have proposed the use of a "fusion torch" for producing UV light for water splitting. They conclude that because water molecules, under bombardment by the ultraviolet rays of sunlight, are split apart (producing hydrogen and oxygen) in the upper atmosphere, the same process might be achieved on the earth's surface by using radiation from controlled fusion. They have calculated the requirements for a photolysis system, including a fusion reactor that generates plasma energy and a plasma-leakage stream that produces the correct UV light for transmission through a window (of unspecified character) and into water vapor. By using an optimistic plasma energy-to-photon conversion, a hydrogen production efficiency of about 20% is achieved. Waste energy is converted to electricity and then to hydrogen by electrolysis for an overall system efficiency (UV light to hydrogen) of 36%. Based on the reactor plasma energy, the system efficiency is about 29%.

Photolysis can be combined with other mechanisms to split water and produce hydrogen. For example, in an aqueous solution (or vapor) of mercury atoms, the photosensitized decomposition of water by excited mercury atoms occurs; mercuric oxide is produced, and hydrogen is evolved. The quantum yield (water molecules split per photon) is about 0.02 at

1849 Å.[11] Temperatures of 500° to 700° C are adequate for decomposing the mercuric oxide to mercury and oxygen, thus closing the cycle.

Direct Thermal Decomposition of Water to Produce Hydrogen

Description of the Direct Decomposition Reaction

At sufficiently high temperatures, water (steam) will undergo appreciable dissociation into its elements, hydrogen and oxygen. This is a direct decomposition via one reaction step: $H_2O(g) \rightarrow H_2(g) + {}_1/{}_2O_2(g)$. At equilibrium, the extent of this thermal decomposition depends primarily upon the temperature, but also upon the pressure of the steam-hydrogen-oxygen system. An inverse pressure dependence for the decomposition is evident from the fact that one mole of steam produces one and a half moles of gaseous products. The procedure of supplying high-temperature heat to steam to cause this decomposition has been suggested as a method for splitting water to produce hydrogen.[1,5]

The enthalpy required to convert water at 25°C and 1 atm to hydrogen and oxygen at 25°C and 1 atm, is 68.3 kcal/g-mol of hydrogen produced. In a process involving internal heat exchange, heat is needed to vaporize the water and to raise the temperature of the steam to the desired reaction temperature. Dissociation will occur continuously during this heating, and heat must be supplied for this reaction as well. Upon achieving satisfactory decomposition and having prevented recombination (by product separation), the latent heat of the product streams can be transferred to the cooler incoming reactant stream (water).

Temperature Dependence of Hydrogen Production

The temperature dependence of the dissociation may be related to the free-energy change of the dissociation reaction, ΔG_{Rx}, according to the conventional equation for the equilibrium constant, (for pressure) K_p:

$$\Delta G_{Rx} = -RT\ln K_p \qquad (8\text{-}3)$$

The equilibrium constant in Equation 8-3 is defined as –

$$K_p = \frac{(\text{Hydrogen Partial Pressure})(\text{Oxygen Partial Pressure})^{1/2}}{(\text{Water Partial Pressure})} \qquad (8\text{-}4)$$

The dissociation reaction may be expressed as —

$$H_2O(g) \rightarrow (1-x)H_2O(g) + xH_2(g) + 1/2xO_2(g)$$

where x is the number of moles of hydrogen present at equilibrium. Assuming that the partial pressures are equal to the mole fractions for the components simplifies the calculation determining the mole fraction of hydrogen present, y, as a function of temperature, provided the ΔG_{Rx} is known. Algebraically, $y = \frac{x}{1 + x/2}$. We have made this calculation to illustrate that relatively high temperatures are required for appreciable hydrogen production. The equation relating the equilibrium constant to the reaction stoichiometry is —

$$K_p = \left(\frac{x}{1-x}\right)\left(\frac{x}{2+x}\right)^{1/2} \qquad (8\text{-}5)$$

Table 8-1 is based on the tabulated enthalpy and free-energy data for water.[12] In Table 8-1, ΔH_{Rx}^{T} is the enthalpy required for the dissociation of one gram-mole of steam, and ΔG_{Rx}^{T} is the free energy of this dissociation. The hydrogen produced at equilibrium (at temperature T) is that amount resulting from the dissociation of one mole of steam at one atmosphere total pressure. (At lower absolute total pressures, the extent of dissociation is higher.)

Thermodynamic Considerations and Energy Requirements

The reaction enthalpy is often considered to be the ideal amount of energy, heat (entropy) plus work (free energy, G), that must be supplied to drive a chemical reaction. By analogy to electrolysis, entropy is usually supplied by resistive dissipation of electricty as heat, and free energy is supplied through ion and electron movement across an electrical potential, splitting water into hydrogen and oxygen. This is a case in which practical methods are approaching ideal limits.

In the case of thermal dissociation of steam, however, supplying the energy equivalent of the standard enthalpy, H, of formation (for water) does not accomplish the decomposition reaction or the required gas separations (to pure hydrogen and pure oxygen) at the reaction conditions. To illustrate this point, consider the dissociation of steam at 4310 °K, where ΔG_F^O of water is zero and ΔH_F^O is 61.06 kcal (heat)/g-mol. At this point, the equilibrium K_p is 1.0, and the product of the hydrogen partial pressure and the square

Table 8-1. THERMODYNAMIC DATA AND HYDROGEN YIELD FOR THE THERMAL DECOMPOSITION OF STEAM

Reaction Temp., T		Reaction Enthalpy, ΔG_{Rx}^{T}	Reaction Free-Energy Change, ΔG_{Rx}^{T}	Equilibrium Constant, K_p	Mole Fraction of Hydrogen Present, y (vol % ÷ 100)	Moles of Hydrogen Produced, x, Per Mole of Water Reactant
°K	°F	kcal/g-mol				
500	440	58.28	53.52	1.30×10^{-23}	7×10^{-16}	7×10^{-16}
1000	1340	59.25	46.04	8.67×10^{-11}	2.5×10^{-7}	2.5×10^{-7}
1500	2240	59.82	39.30	1.88×10^{-6}	1.92×10^{-4}	1.92×10^{-4}
2000	3140	60.15	32.40	2.88×10^{-4}	5.48×10^{-3}	5.50×10^{-3}
2500	4040	60.36	25.44	5.97×10^{-3}	3.76×10^{-2}	3.83×10^{-2}
3000	4940	60.53	18.44	4.54×10^{-2}	1.40×10^{-1}	1.51×10^{-1}
3500	5840	60.70	11.41	1.94×10^{-1}	2.90×10^{-1}	3.39×10^{-1}
4000	6740	60.91	4.35	5.78×10^{-1}	4.35×10^{-1}	5.56×10^{-1}
4500	7640	61.16	−2.73	1.36×10^{0}	5.30×10^{-1}	7.22×10^{-1}

root of the oxygen partial pressure equals the partial pressure of the undissociated water. Work (about 20 kcal/g-mol of hydrogen), must still be supplied to separate these components. If a hydrogen separation is not performed, rapid reaction kinetics will cause recombination (burning) as the gas mixture is cooled.

The free-energy change associated with separating gas mixtures at some temperature, T, or the ideal separatory work requirements may be calculated by Equation 8-6:

$$\Delta G_{sep} = -RT\Sigma X_i \ln y_i \qquad (8\text{-}6)$$

In this equation, X_i is the number of moles of component i present at mole fraction y_i. Calculations of ΔG_{sep} (required to produce one mole of pure hydrogen by thermal dissociation of water) show that ΔG_{sep}^{T} equals or exceeds ΔG_{Rx}^{T}. At 3500°K, for example, $\Delta G_{sep} = 22.7$ kcal/g-mol of hydrogen and $\Delta G_{Rx} = 11.4$ kcal/g-mol of hydrogen.

Estimates of Theoretical and Ideal Energy Efficiencies

We have not considered, in detail, the thermodynamic efficiencies that have been or might be applied as limiting cases for the direct thermal decomposition of water. However, some discussion of this is in order because "ideal" efficiencies can appear particularly deceiving or overly optimistic when applied to direct thermal decomposition. The maximum theoretical, ideal water-splitting efficiency is[6,10]—

$$E_{ideal} = \frac{\Delta H}{\Delta G}\left(\frac{T_1 - T_2}{T_1}\right) \qquad (8\text{-}7)$$

where T_1 is the "high" temperature of heat supply and T_2 is the "low" temperature of heat rejection. This relation has been used in the context of thermal dissociation of water.[1] Its use here is not incorrect, but the relation is highly optimistic and requires restrictions. Obviously, if T_2 is held at 25°C and T_1 is high enough, E_{ideal} will approach $\Delta H/\Delta G = 1.2$. However, from the first law of thermodynamics it can be shown that negative heat rejection would occur to $T_1 > 1650$°C and under all conditions of $E \leq 1.0$. (See Section 6.) Hence, it is advised that Equation 8-7, unaltered, not be used in setting an upper bound (ideal efficiency limit) for direct thermal water splitting.

To properly estimate the maximum attainable efficiency of direct thermal decomposition, and if heat is the primary energy source, all work-generating steps must be accounted for. One arbitrary way to postulate an energy efficiency limit for thermal decomposition (used by IGT in its hydrogen-production program) is to divide the high heating value (HHV) of the product hydrogen by the sum of the reaction entropy, the heat required to generate the reaction free-energy change, and the heat required to perform the extra separatory work (not satisfied by the supplied free energy). Separatory work is calculated for the composition and temperature of the decomposition. Table 8-2 presents these quantities based on an arbitrary 35% efficiency for work generation from heat (probably not appropriate for the 500 °K case). In our opinion, irreversibilities and heat losses would result in practical efficiencies of about 50% to 65% of those listed for $T > 2000°$ K, assuming that process equipment and plant materials could be used with performance similar to that attained with modern technology. For $T < 2000$ °K, the separatory equipment for recovering the very small concentrations of hydrogen produced would be excessive in complexity and in energy consumption. Thus, practical efficiencies would be very low for temperatures below 2000 °K.

In 1972, The Futures Group prepared a hydrogen technology assessment for the Northeast Utilities Service Co.[5] In that report, they summarized their analysis of a water dissociation system operating at 5000 °F (3033 °K) and at 1 atm. Steam was forced through a vortex tube at high velocity, and the hydrogen was separated from the steam and oxygen. The hydrogen stream and the water plus oxygen stream were cooled to condense the steam and separate the gases; the condensation was taken through 10 stages for 90% heat recovery. The efficiency of this system, based on heat and mass balance, "was computed to be only 35%."

The recent study by Bilgen[1] considers solar energy as a heat source for direct thermal dissociation of water. However, no particular process or flow diagram was analyzed. The author does conclude that 3000 °K heat is required "for a substantial yield in hydrogen production." A general description of solar concentrators, with cost estimates, is presented for components capable of high temperatures. Bilgen is optimistic about being able to achieve suitably high temperatures with a combination of a mirror field and concentrating units and states that 3500 °K should be achievable.

Table 8-2. ESTIMATED UPPER EFFICIENCY LIMITS FOR DIRECT THERMAL DECOMPOSITION OF WATER

Reaction Temp., T		Reaction Entropy	Heat for Free Energy	Heat for "Extra" Work	Efficiency Limit Based on HHV of Hydrogen, %
°K	°F	kcal/g-mol	kcal/g-mol	kcal/g-mol	
500	440	5.92	152.9	0.0	43
1000	1340	13.21	131.5	0.5	47
1500	2240	20.54	112.3	3.5	50
2000	3140	28.11	92.6	11.1	52
2500	4040	34.92	72.7	17.4	55
3000	4940	42.09	52.7	24.6	57
3500	5840	49.29	32.6	32.3	59
4000	6740	56.56	12.4	43.7	61
4500	7640	58.43	0.0	49.1	63

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9. COMMERCIAL TECHNOLOGY FOR HYDROGEN PRODUCTION –

T. D. Donakowski

Catalytic Steam Reforming of Natural Gas

Steam reforming of natural gas is the most widely used hydrogen manufacturing process in the United States.[3] Commercial operations began in 1930 after a 15-year development period. A typical process for a large, modern hydrogen-production facility is discussed below and is illustrated in Figure 9-1.

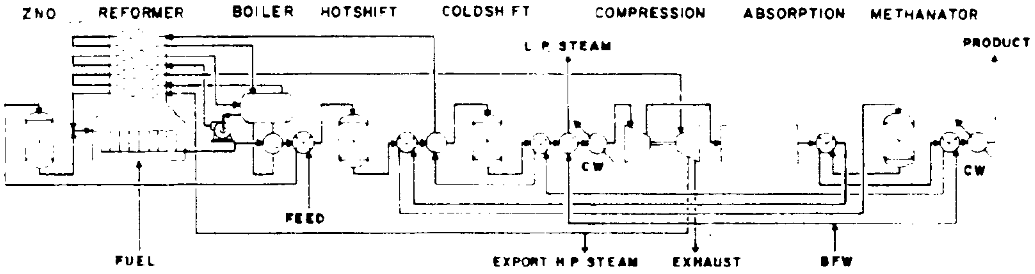

Figure 9-1. FLOW DIAGRAM OF A STEAM-REFORMING PROCESS[1]

The primary step in the production of hydrogen from natural gas is the endothermic steam-methane reaction:

$$CH_4 + H_20 \rightarrow CO + 3H_2$$

To reduce any catalyst-poisoning sulfur compounds to a level of less than 5 ppm,[1] the natural gas is passed through a sulfur guard drum that contains zinc oxide. The sulfur-free natural gas is combined with superheated steam, thus forming the feed for the reforming furnace. (Steam-to-methane ratios are usually 3:1 or 4:1, by volume.) The steam is then passed through a vertical array of type 25-20 chrome-nickel steel tubes that contain a catalyst. A typical commercial catalyst is composed of nickel oxide on a refractory substrate. The catalyst may be shaped into pellets 1/2 to 3/4 inch in diameter and length or into Raschig rings of similar size.

Reforming has been performed at pressures of up to 600 psi, but 300 psi is typical. If a high-pressure hydrogen product is desired, it is preferable to reform the natural gas at a high pressure. The reforming reaction increases the volume of the gas, so less compression is required if the feed is initially at high pressure. However, high pressures require high temperatures to ensure a favorable equilibrium. A more efficient recovery of heat from the product gas is attained at the higher temperatures. Gas typically exits the reforming furnace at temperatures of from 1500° to 1650°F. The equilibrium constant for the steam-methane reforming reaction increases by a factor of 3 as the temperature is increased from 1470° to 1560°F, so temperature is an important process operating parameter.[3] Heat is transferred to the reformer furnace tubes from the radiant section of the furnace, and large amounts of heat are available for steam generation in the convection section.

The reformed gas is composed of hydrogen, water, carbon monoxide, carbon dioxide, and residual methane. It is cooled to about 700°F and is passed through a shift reactor in which excess steam reacts with carbon monoxide to form carbon dioxide and more hydrogen via the exothermic reaction –

$$CO + H_2O \rightarrow CO_2 + H_2$$

An iron oxide-chromium oxide catalyst is used. The equilibrium constant for this reaction increases with a decrease in temperature, and at 700° F, a satisfactory conversion of carbon monoxide to hydrogen cannot be achieved. A second shift reactor is used that operates at temperatures of from 350° to 450°F and that utilizes a low-temperature catalyst containing copper, chromium, and zinc oxides. This low-temperature catalyst is permanently damaged if it is used at temperatures higher than design.[3]

The shifted gas stream is then compressed, typically with steam-turbine-driven centrifugal compressors, and enters a carbon-dioxide-removal system. In choosing a carbon-dioxide-removal system for the process, the desired purity of the product and the inlet pressure of the absorber feed-gas must be considered. Several absorption processes are commercially available (e.g., monoethanolamine and hot-potassium-carbonate systems).

Finally, if desired, traces of carbon oxides can be removed by reacting the gas with hydrogen to form methane via the exothermic reactions –

$$CO + 3H_2 \rightarrow CH_4 + H_2O$$

and

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$$

The reactions occur in the presence of a nickel catalyst at from 750° to 840°F and at pressures of up to 600 atmospheres. Water is removed, thus leaving the hydrogen product (typically 97% pure).[1] A process and utility summary for the steam reforming of natural gas is presented in Table 9-1.

Table 9-1. EFFICIENCY, PROCESS, AND UTILITY REQUIREMENTS OF STEAM REFORMING NATURAL GAS FOR THE PRODUCTION OF 97%-PURE HYDROGEN
(Per 1000 SCF of Hydrogen)[3]

	Amount
Process Feed, lb of methane	11.9
Fuel, lb of methane	7.9
Electric Power, kWhr	0.4
Cooling Water, gal	400
Boiler Feedwater, gal	10
Condensate Returned, gal	6

Input 19.8 lb of methane X 23,880 Btu/lb = 472,800 Btu
0.4 kWhr Electricity X 3414 Btu/kWhr = 1,400 Btu
Total 474,200 Btu
Output = 1000 SCF of Hydrogen X 325 Btu/SCF = 325,000 Btu

$$\text{Efficiency} = \frac{\text{Output}}{\text{Input}} = \frac{325{,}000}{474{,}200} \times 100$$
$$= 68.5\%$$

Partial Oxidation of Hydrocarbons

There are two partial-oxidation processes that have been extensively commercialized: the Texaco Process (since 1954) and the Shell Gasification Process (since 1956). Gas consisting primarily of hydrogen and carbon monoxide is produced by burning hydrocarbons with high-purity oxygen or an oxygen-rich stream. The main processing features of the Texaco Process are shown in Figure 9-2 and are discussed below.

High-purity oxygen (95% to 99%) is injected into the gas generator, along with preheated steam and heavy oil (10° API gravity). Proper metering of the feed into the specially designed mixing burners is essential. A typical steam-to-oil weight ratio would be 0.5:1. It should be noted that oxygen and oil are not premixed; therefore flashbacks and limits to preheat are not encountered. A high degree of steam and oil preheat is desirable because it significantly reduces the oxygen requirement.[3] The use of less oxygen results in the presence of less diluent nitrogen in the final hydrogen product stream.[2] Any percentage of sulfur in the oil feed is permissable, although the efficiency

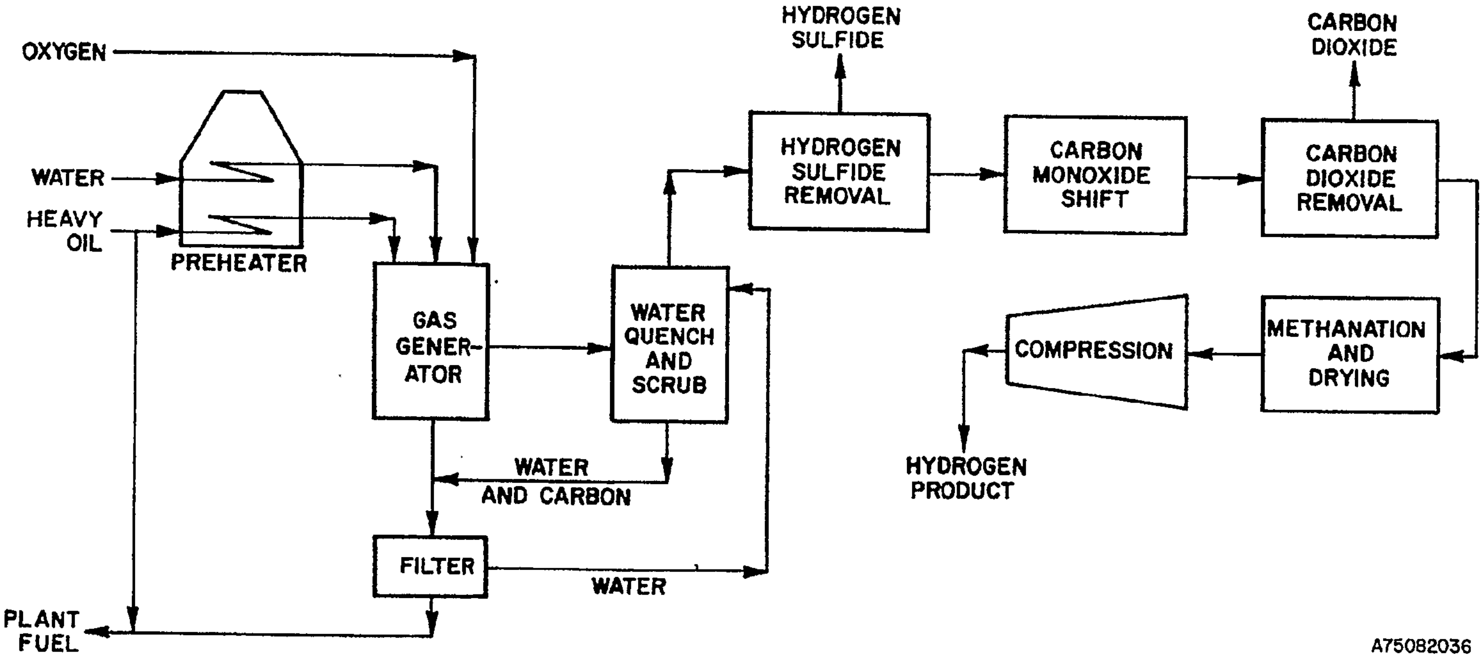

Figure 9-2. TEXACO PARTIAL-OXIDATION PROCESS (Heavy Oil to Hydrogen)[2]

of hydrogen production is lower for a higher sulfur-content oil than for a sulfur-free oil because hydrogen is consumed in the removal of sulfur as hydrogen sulfide. A refractory-lined reactor is used to withstand the 2500 °F final gas-generation temperature. The Texaco gas-generating reactor can be run at pressures of between 200 and 600 psi. Better compression economics can be obtained if the gasifier is operated at high pressure because the gaseous volume of the feed materials is less than the volume of the hydrogen generated. Heat from the reactor is used for internal generation of steam via a water-quenching step. The steam is subsequently reacted in a carbon monoxide-water shift step. The water quench also removes particles of unreacted carbon, which are recovered by filtration and can be mixed with oil for plant fuel requirements.[3]

The synthesis gas then undergoes aftertreatment steps, similar to the steps undergone downstream in a steam-natural gas reforming process, to increase the amount and the purity of the hydrogen. Hydrogen sulfide is removed; and the stream is shifted, in a carbon monoxide conversion step, to produce more hydrogen. Carbon dioxide is removed from the hydrogen by an absorption process. If desired, final traces of the carbon oxides can be removed by reaction to methane; and finally water is removed from the system. The hydrogen can then be compressed to the required pressure.

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10. SURVEY OF PATENTED HYDROGEN-PRODUCTION PROCESSES – H. C. Maru

In order to complete this survey of hydrogen-production processes, we examined the literature with the hope of finding novel processes that had been suggested, but that had never been fully developed. We anticipated that, in the past, the ease of making hydrogen by steam reforming relatively cheap natural gas would have made the development of other hydrogen processes unattractive; but that now, with the supply of natural gas rapidly dwindling, these processes might be worthy of attention.

Ideally, search of this type would involve a complete literature review and evaluation. However, the number of literature entries on hydrogen production is immense, and a comprehensive search of all published literature was out of the question. We decided to proceed on the assumption that if a novel hydrogen-production method had not been developed, it would at least have been patented.

We conducted a search through abstracts of patents published in Chemical Abstracts from 1917 to 1974 using the following key words appearing under the heading, "Hydrogen":

- Formation of
- Manufacture of
- Preparation of
- Production of.

We limited our attention to those processes that made either pure hydrogen or significant amounts of hydrogen mixed with nitrogen, carbon monoxide, and/or carbon dioxide because these mixtures could easily be converted to pure hydrogen.

Literature prior to 1917 was scanned through two important monographs dealing with hydrogen production.[5,14] Increased activity of the recent years has been documented in several symposia proceedings[1,17,18] and compilations.[4,7] These documents were also scanned for this survey.

Classification of Processes

The number of relevant patents found was staggering. We had expected that only about 200 or so processes would have been patented in the last 60 years. Instead, we found about 1800 patents.

We sorted the patents into 10 categories, as shown in Table 10-1. Patents relating to purification schemes, storage, safety, or corrosion and those describing hardware or control equipment were rejected. Approximately 56% of the total number of patents related to hydrogen production from hydrocarbons, 22% related to coal, and 7% related to water electrolysis. The patents related to unconventional hydrogen-production processes were assigned to a general category, "Other Sources."

Table 10-1. CLASSIFICATION OF PATENTS FOR HYDROGEN PRODUCTION

Category	Code	Number of Patents	% of Total
Electrolysis of Water	E	128	7
Electrolysis of Impure Water and Other Solutions	I	47	3
Coal and Related Sources	C	394	22
Hydrocarbons and Fossil Fuels	H	985	56
Oil Shale	K	9	0.5
Synthetic Fuels	F	29	2
Thermochemical	T	10	0.5
Solar, Windpower, Geothermal, and Ocean Thermal Gradients	S	2	--
Waste Materials	W	9	0.5
Other Sources	O	157	9
Total		1770	
Patents Rejected (Not Processes)		500	
Total Examined		2270	

The patents in each category were arranged alphabetically by assignee organization (or by author if the patent was not assigned to an organization). The purpose of this arrangement was to assemble all the patents related to a single process, thus allowing us to judge the state of development of each process and to eliminate duplication. The patents, so arranged, are listed in Appendix C.*

Evaluation of Processes

After classification and arrangement, the patents in each category were evaluated by an IGT expert in the particular field in order to find any promising processes. All the patents and literature were further reviewed by the chemical engineer in charge of the patent survey. Figure 10-1 is a schematic flow diagram of the procedure used for this survey.

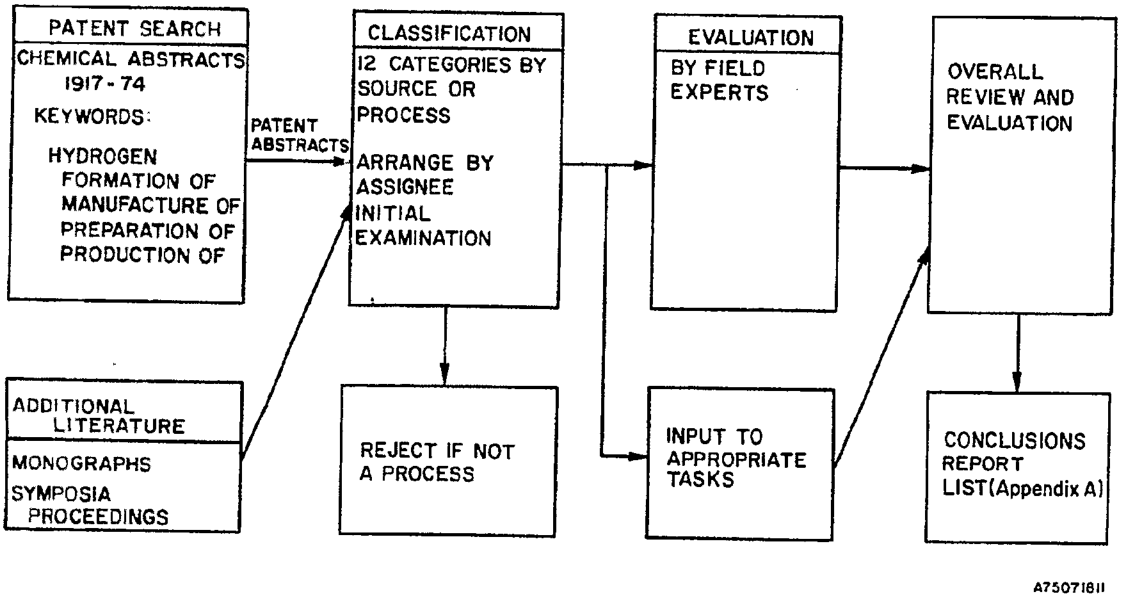

Figure 10-1. FLOW DIAGRAM OF LITERATURE SURVEY OF HYDROGEN-PRODUCTION TECHNIQUES

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*An alphanumeric code has been assigned to each patent, as explained in Appendix C. References to these patents in the text are made using this nomenclature.

Several novel processes and suggestions were identified as being worthy of further consideration. Because of the large number of patents retrieved (approximately 10 times the number originally anticipated), by mutual agreement with NASA only the novel processes and suggestions have been cataloged in detail. Many of the processes currently under development are discussed in other sections of this report.

Electrolysis of Pure Water

Several patents describe means of increasing the current density and efficiency of electrolysis via minimization of electrode overvoltages and ohmic polarizations. Recently, processes that use thermally aided electrolysis have been proposed.[3]

Overvoltage Reduction

Several proposed methods of electrode and electrolyte modification are described in Table 10-2. As can be seen in this table, improvements of as much as several hundred millivolts have been claimed.

A patent by DEMAG Electrometallurgic GmbH (ED3) sugggests additions of wetting agents to facilitate bubble removal, thereby minimizing concentration polarization. A patent by E. G. Clark (EC4) claims that current densities as high as 7200 A/sq ft can be achieved when the electrolyte is forced through a thin layer placed between the electrodes. A somewhat different flow-through electrode system is being tested at Brookhaven National Laboratories.[10] Large drops in pressure and structural difficulties in manifolding are anticipated with this concept. At present no commercially operating system uses such a concept.

Because oxygen polarization is a major factor in many water electrolyzer cells, several depolarization schemes have been suggested.[3, 8] The patents by General Electric Co. (EG3) and H. H. Moebius and B. Rohland (EM10) suggest putting a reducing gas (e.g., producer gas) in a solid-oxide system to depolarize the oxygen electrode. Juda and Moulton[8] suggest adding sulfur dioxide in the form of sulfurous acid in an acid-electrolyte cell. A voltage gain of about 800 mV has been claimed for such a system. Additional corrosion and contamination problems and the added cost of a depolarizing agent are the trade-off considerations. Recently Bockris[2] suggested the use of this concept for simultaneous pollution cleanup, where, for example, nitric

Table 10-2. PROPOSED ELECTRODE AND ELECTROLYTE MODIFICATIONS

Assignee or Author	Reference*	Electrolyte	Electrode† Hydrogen	Electrode† Oxygen	Proposed Method	Claimed Improvements
Clark, E.G.	EC4	NaOH	X	X	Forced electrolyte flow through spaces between the electrodes	Obtain a C.D. of 7200 A/sq ft
Consolidated Mining and Smelting of Canada Ltd.	EC6	Caustic alkali	--	--	Vanadium in sol. form (e.g., V_2O_5) added to electrolyte	Cell voltage reduced
DEMAG Elecktro-metallurgie, GmbH	ED3	Aqueous solutions	X	X	Wetting agents to facilitate bubble removal, silicone oils added to fatty acid to prevent foaming	Lower concentration polarization
East Asia Synthetic Chemical Industries Co.	EE2	18% NaOH	--	--	0.05 g/l $(NH_4)_2SO_4$ added to electrolyte, other S compounds – e.g., $(NH_4)CNS$ or $(NH_2)_2CS$ – can be used.	Lowered total cell volume by 20 mV at 50 mol/sq cm
General Electric Co.	EG3	Solid oxide		X	Reducing gas mixture to depolarize oxygen electrode	Lower oxygen overvoltage
Imperial Chemical Industries of Australia and New Zealand Ltd.	EI3		X		(Mo, W)-(Fe), (Mo)-(Ni, Co) or (Mo)-(Co, Ni, Fe)-(Co, Ni, Fe), and (Ti-Pt) coatings electrodeposited	A W-Fe coated electrode resulted in 80 mV decrease in overpotential; an Mo-Co rated electrode resulted in 150 mV decrease in overpotential
Juda, W. and Moulton, D. M.	Ref. 8	Aqueous acidic		X	Add SO_2 in the form of H_2SO_3	800 mV lowering of polarization
Lonza Elektrizitäts-werke	EL13		X		Electroplating Pt, Rh, Pd, Os, or Ir on Fe cathode; reactivation by OCV operation	Several hundred mV lowering in H overvolt
Maschinenfabrik Oerlikon	EM3		--	--	Compound of sixth group metal of Na_2MoO_4	Overvoltage reduction
Moebius, H.H. and Rohland, B.	EM10	Solid oxide		X	Reducing gas mixture to depolarize oxygen electrode	Lower oxygen overvoltage
Pintsch Bamag AG	EB1	KOH (?)	--	--	Deposit alloy (e.g., Zn-Ni-Cu) from a bath containing a complex-forming reagent such as a cyanide, pyrophosphate on sulfamate; activate by partly dissolving a first component of the alloy (e.g., Zn) in an alkali or cyanide solution.	Surfaces not pyrophoric, greater flexibility in selection of structural and final shape
Siemens and Halske AG	ES17		X		Cathode treated with an electrolyte containing metallic oxygen acids – e.g., chromates, molybdates, tungstates, columbates, titanates; alternatively, add small amounts to cathode chamber.	The compounds dissolve, but do not decompose; lower overvoltage
State Pedagogical Inst., Kharkov, U.S.S.R.	ES21		X		Alloys of Ni-Ru or Co-Ru applied on a metal base consisting of Fe, Ni, Cu, or Ti	Lower hydrogen overvoltage
Tseung, A.C.C. and Vassie, P.R.	Ref. 16	KOH		X	Co_2NiO_4 catalyst	High anode activity, stable performance at room temperature
Werlen, A. *et al.*	EW1		X	X	Hg-Cu-Zn catalyst on anode and an alkali phosphate as depolarizer on Al cathode	

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*Unless otherwise noted, refers to Appendix G.

†Where known, the electrode(s) considered for modification is denoted with an "X."

oxide can be oxidized to nitric acid or sewage can be oxidized to carbon dioxide. The resulting cost reductions in the depolarized-anode systems may be attractive.

Alternatively, to minimize the oxygen overvoltage, Tseung and coworkers[15, 16] have reported the use of a highly active electrode catalyst. A rapid electrode deactivation was observed when operated in the fuel cell mode,[15] but stable performance for several hundred hours was obtained at room temperature when operated in the oxygen-evolution mode.[15]

Electrolyte Systems

Electrical conductivity and electrode kinetics can be improved by the use of suitable electrolytes. An Atlantic Richfield Co. patent (EA6) claims operation of a molten-alkali electrolyte cell at 1.3 volts (an apparent efficiency of 113%) and at current densities of 500 mA/sq cm with use of a 90% calcium hydroxide, 10% sodium hydroxide electrolyte at 480°C. Problems of corrosion, electrode sintering, and performance stability are anticipated. Another patent (EB5) claims use of molten sodium hydroxide or potassium hydroxide containing 5% to 10% water. The cell in this case was operated at 300° to 350°C and iron electrodes were used.

The use of solid-oxide electrolytes at high temperatures has also been proposed[13, 19] (EG3 and EM10) for water-vapor dissociation. Higher efficiencies and rapid electrode kinetics can be obtained at high temperatures; but research shows some major problems: thermal stresses in the ceramic electrolytes, retention of sufficient electrolyte purity to avoid the onset of semiconducting properties, selection of metals for the electrode at the oxygen side in the 800° to 1000°C operating range, and difficulty in finding materials suitable for intercell current collectors. Because of these problems, almost all research on this type of system has been abandoned. Bockris[3] suggests that even if these problems were solved, the cost of high-temperature electrolyzers would be about the same as that of low-temperature electrolyzers currently being developed. Therefore, research on moderate-temperature (80° to 400°C) electrolyzers should be emphasized.

Cell Design

Two patents (EA5 and EU2) claim a cell design suitable for zero-gravity operation. One patent issued to Reynolds Metals Co. (ER1) is for a cell designed to produce gases under hydrostatic pressure with the gases collected outside the vessel. Several high-pressure units that use pressure vessels for pressure containment have been built, for special applications, by Construction John Brown Ltd. of Great Britain.[11, 12] Such designs, however, may not be cost effective for large-scale production because of the high containment-material cost compared with that for diaphragm-type cells.

System Design

A Swedish patent (ES24) claims a modification that purifies a contaminated electrolyte by electrolyzing the impure electrolyte in a mercury cell and subsequently decomposing the amalgam with water to obtain an alkali solution. The modification would, however, involve additional investment for a mercury cell. Therefore adopting such a modification is a question of relative economics.

A vapor-diffusion water feed arrangement has been suggested in a patent by TRW, Inc. (ET1). An in situ purification system that uses a palladium coating on the electrode is suggested in patent ET3. A patent by A. Kilgus (EK3) claims hydrogen yields, upon application of a magnetic field to the electrolyzer, in excess of those determined by Faraday's Law. The validity of this claim is doubtful; but even if this were true, the additional energy used and the complications in maintaining a magnetic field would compensate for the additional yields.

Thermally Assisted Electrolysis

The electrolysis of water at a pressure of 1 atmosphere and at 25°C requires a minimum potential of 1.23 volts. Because electricity cost is a major component in the overall hydrogen cost, electrolysis of an alternative substance that has a lower reversible cell potential than water and subsequent thermal decomposition of the products is tempting. Greater overall efficiencies may be possible in such cases. Bockris[2] has suggested four such systems:

1. Electrolysis of hydriodic acid (HI) –
   a) Electrochemical step $2HI \rightarrow H_2 + I_2$ $\Delta E_{25}{}^{\circ} = 0.535$ volt
   b) Thermal step (endothermic) $I_2 + H_2O\ (1400^{\circ}C) \rightarrow 2HI + 1/2\, O_2$

2. Electrolysis of cuprous chloride (CuCl) in a cell containing hydrochloric acid (HCl) —

   a) Electrochemical step

   $2Cu^+ \rightarrow 2Cu^{2+} + 2e^-$

   $2H^+ + 2e^- \rightarrow H_2$ $\Delta E_{25}^{o} = 0.535$ volt

   b) Thermal steps (endothermic)

   $2CuCl_2 \rightarrow 2CuCl + Cl_2$ $\Delta E_{25}^{o} = 0.77$ volt

   $Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

3. Electrolysis of ferrous chloride ($FeCl_3$) in a cell containing HCl—

   a) Electrochemical step

   $2Fe^{2+} \rightarrow 2Fe^{3+} + 2e^-$

   $2H^+ + 2e^- \rightarrow H_2$ $\Delta E_{25}^{o} = 0.535$ volt

   b) Thermal steps (endothermic)

   $2FeCl_3 \rightarrow 2FeCl_2 + Cl_2$

   $Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

4. Electrolysis of stannous chloride ($SnCl_2$) in a cell containing HCl —

   a) Electrochemical step

   $Sn^{2+} \rightarrow Sn^{4+} + 2e^-$

   $2H^+ + 2e^- \rightarrow H_2$ $\Delta E_{25}^{o} = 0.77$ volt

   b) Thermal steps (endothermic)

   $SnCl_4 \rightarrow SnCl_2 + Cl_2$

   $Cl_2 + H_2O \rightarrow 2HCl + 1/2O_2$

Several practical limitations exist, but because there is the potential of minimizing the electrical energy use, thermally assisted electrolysis systems deserve a closer look. According to Bockris' s estimate, systems 1, 2, and 4 may be more economical than the advanced water electrolyzer systems. It is noted here that the high-temperature, direct water electrolysis processes may also consume heat and in that sense can be considered thermally aided electrolysis processes.

Electrolysis of Impure Water and Other Solutions

Our literature search produced four patents (IM3, IO1, IS6, and IT6) related to the direct electrolysis of seawater. The patents claim various means for minimizing the problem of insoluble deposits. Seawater electrolysis has been used for the in situ generation of hypochlorites for use as sterilants. Countries such as Japan use concentrated seawater brine for chlor-alkali production.[9] Thus some experience has been gained in seawater electrolysis. A more detailed discussion of the problems in direct seawater electrolysis is presented in Section 3.

When electrolyzed, aqueous solutions of many salts (such as sodium chloride), sulfates, or acids (such as hydrochloric acid) yield hydrogen as a byproduct. Because this technology is well developed, some of the advances made in this field, such as membranes and electrode technology, may be beneficial to pure- and impure-water electrolyzer systems.

Among the patents retrieved in the present survey is a patent by Matushita Electric Industries Co. (IM1) that suggests the electrolysis of an aqueous solution of ammonium chloride (NH_4Cl) or ammonium nitrate (NH_4NO_3) in the presence of semiconductor powders for the production of high-purity hydrogen. A patent issued to Asahi Chemical Industry (IA3) proposes the addition of platinum or palladium to the electrolyte. An 0.8-volt polarization decrease resulted.

Coal and Related Sources

Most of the 300 or so patents in this category deal with established coal-gasification processes that produce, as a first step, a mixture of carbon monoxide and hydrogen. Fluidized-bed gasification, such as that used in the Winkler and HYGAS® Processes, is often mentioned. Many of the other patents describe suspension gasification processes similar to those being developed by Texaco and those offered for sale by Koppers-Totzek. Some of the patents are for modifications to the steam-iron process – an improved form of which, described in an earlier section, is currently under development for use in coal gasification. These patents often suggest the use of another metal as the oxidizing-reducing agent.

The production of clean gaseous fuels from coal has been intensely researched in the past few years. Consequently it should not be surprising that all of the promising ideas described in this group of patents are currently under development.

Hydrocarbons

This category, largest among the categories surveyed, includes approximately 1000 patents on hydrogen production from fossil hydrocarbons such as natural gas, naphtha, or other petroleum components. The majority of the patents in this category were issued after 1940. The processes include catalytic steam reforming, catalytic and noncatalytic partial oxidation, and thermal decomposition. Because of the rapidly depleting world supply of petroleum and natural gas, their role in future hydrogen production will be limited. The large number of patents in this field is indicative of the amount of research and development that has been carried out, and it is unlikely that any promising processes have been neglected. For these reasons, these patents were merely summarized and listed without further examination. Patents on hydrogen production from oil shale were classified separately, however, because of the possibly significant role of this source as a future energy supply. Patents applicable to multiple sources, such as hydrocarbons, coal, carbon monoxide, and coke, were included in the category "Coal and Related Sources."

Organizations holding large numbers of patents on the production of hydrogen or hydrogen-rich gas from hydrocarbons include I. G. Farbenidustrie (on thermal decomposition of gaseous hydrocarbons), Standard Oil Co. (on the reforming of light hydrocarbons and thermal decomposition of a variety of hydrocarbon liquids), Texaco, Inc. (on partial oxidation), and Badische Anilin and Soda Fabrick (on partial oxidation). These patents describe variations in process conditions (temperature, pressure, etc.), catalysts, reactor designs, and process steps.

Some exotic suggestions, such as the electrolysis of hydrocarbons and the simultaneous production of mechanical energy, were also encountered. Many of the more recent patents describe hydrogen production on a small scale for local application such as self-propelled vehicles, fuel-cell operation in residences or small industries, for special appliances or equipment, and for laboratory or experimentation purposes.

Oil Shale

Our literature search, using the keywords mentioned previously, yielded only nine patents that deal with hydrogen production from oil shale. The patent issued to Chevron Research Co. (KC1) describes a process that uses steam injection for hydrogen production from kerogen-depleted shale formations. The patent issued to Compagnie Francaise des Essences Synthetiques (DC2) claims the coke-free production of hydrogen-rich gas from oil shale and other solid fuels. The Institute of Gas Technology patents (K11, K26, K23, and K24) deal with hydrogasification steps and reactor designs. Hydrogen is obtained as a coproduct in the process patented by P. H. Gifford (KG1). Two patents issued to Phillips Petroleum Co. (KP1 and KP2) describe their partial-combustion process and the utilization of carbon monoxide from the combustion zone for the production of hydrogen.

Synthetic Fuels

This category includes the production of hydrogen from synthetic organic compounds such as methanol, acetylene, ethanol, cyclohexane, and heptane. Because these compounds are usually synthesized by using petroleum, coal, or other fossil fuels, they will probably not be used for large-scale hydrogen production. Methanol, however, has been recognized as a convenient portable fuel. Because of the low reforming temperatures involved, simple materials of construction, and good catalyst stability, it can be reformed at the point of application to produce hydrogen. Fuel cells and automotive fuel are two examples of such applications. Hydrogen is obtained as a byproduct in the thermal dissociation of acetylene to produce carbon black. Of the patents retrieved, a majority of the patents covered these two sources.

Two patents issued to the U.S. Atomic Energy Commission (FU3, and FU4) claim the cracking of hydrocarbons by using x-rays or neutron bombardment. A patent issued to Varta A.G. (FV1) claims the simultaneous production of oxygen and hydrogen by utilizing heat released by the oxygen-generating compound to catalytically decompose the hydrogen-generating compound. Such an arrangement can be beneficial in generating gases for fuel cell or welding equipment.

Thermochemical Hydrogen Production

Our patent search retrieved only 10 patents for this category. It is likely that many cycles have not been patented, and others may be in the process of being patented. The patents retrieved include EURATOM's mercury-hydrobromic acid (Hg-HBr) cycle, Gaz de France's stannous oxide-stannic oxide (SnO-SnO_2) cycle, and others.

In addition to the purely thermochemical cycles, several hybrid cycles have been suggested. The thermally aided electrochemical processes discussed previously are examples of such hybrid cycles.

Solar, Windpower, Geothermal, and Ocean Thermal Gradients

Only a small fraction of the energy available from solar, wind, and geothermal sources is currently being utilized for energy conversion. Several possibilities for utilizing these important sources exist.

Solar radiation can decompose water through either thermochemical, photochemical, photoelectrochemical, or photobiochemical routes.

Direct generation of hydrogen by the use of wind power is not possible. Windpower is first converted to electricity, which then can be used for electrolysis. Geothermal energy could also be converted to electricity for electrolysis, but there is the additional possibility of matching a low-temperature thermochemical cycle to the heat source.

Because the interest in possible applications of solar, windpower, and geothermal sources to hydrogen production is of recent origin, no patent literature exists in this field. Only two patents that deal with system concepts were retrieved. Patent SK1 proposes high-pressure electrolysis as a means of energy storage for solar, wind, or tide energy. (Hydrogen is subsequently converted to ammonia, which is stored.) Patent SO1 claims utilization of windpower in the electrolysis of seawater for hydrogen production. Escher[6] recently proposed an ocean-based, solar-to-hydrogen energy conversion macrosystem. Researchers in several government-sponsored programs are currently exploring the use of these abundant natural sources in hydrogen generation.

Waste Materials

Nine patents were found that were primarily concerned with the production of hydrogen or hydrogen-rich gases from waste materials. Six of these patents (WC1, WC2, WF1, WR1, WS1, and WT1) deal with some form of gasification. The other three deal with fermentation (bioconversion). A considerable amount of patent and other literature exists on gas-production processes. These processes can be suitably modified to produce hydrogen. However, no special literature search was conducted to explore this aspect.

Other Sources

Patents not falling into any of the categories discussed previously were classified as "Other Sources." Patents in this classification were further subdivided by types of reactions, as shown in Table 10-3. Generally, the

Table 10-3. HYDROGEN-PRODUCTION TECHNIQUES USING "OTHER SOURCES"

Subdivision	Description	Number of Patents	Typical Reactions
1	Hydrides and boranes	23	$LiH + H_2O \rightarrow H_2 + LiOH$
			$BH_3(NH_2)_2\ BH_3 + LiBH_4 \rightarrow H_2$ + borohydrides
2	Caustics (silicon and iron	19	$2NaOH + Si + H_2O \rightarrow 2H_2 + Na_2SiO_3$
3	Metals	15	$H_2O + Al + KOH \rightarrow 3/2\ H_2 + KAlO_2$
4	Nonmetals	41	$2H_2O + S \rightarrow 2H_2 + SO_2$
5	Ammonia	28	$2NH_3 \rightarrow N_2 + 3H_2$
			$NH_3 + O_2 \rightarrow 3/2\ H_2$ + nitrogen oxides
6	Inorganic compounds	6	$H_2O + CaC_2 \rightarrow H_2 + 2C + CaO$
7	Miscellaneous	25	$H_2S + 2CO_2 \rightarrow H_2 + 2CO + SO_2$
			$S + 2H_2O \xrightarrow{e^-} 2H_2 + SO_2$
			$H_2S + O_2 \rightarrow H_2 + SO_2$
	Total	157	

patents in this classification describe methods of hydrogen production for special applications, such as onsite welding-gas generation, balloon inflation, torpedo-propulsion systems, and fireworks displays. The processes are energy-inefficient in hydrogen production, either requiring complex starting materials and catalysts or producing hydrogen only as a byproduct. For the most part, they are convenient for the intended use, but are neither practical nor economical for large-scale production. However, some methods may be beneficial in the development of hydrogen-storage concepts (e.g., metal-hydride containment) and might have possible uses within closed-loop thermochemical reactions. No unconventional processes for large-scale hydrogen production were uncovered in this category.

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