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Thermochemical Hydrogen Generation

Thermochemical hydrogen could play an expanding role in future energy and chemical feedstock needs.

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Hydrogen has been discussed increasingly in recent years (*1*) as a potential, highly flexible energy medium of the future because it is ecologically attractive and broadly usable, it is easily stored and transported, and it can be produced from a virtually inexhaustible feedstock, that is, water. Hydrogen is currently a major industrial chemical serving primarily as a chemical intermediate in the production of hydrogen-containing substances such as ammonia, methanol, and refined petroleum products. The total world consumption of hydrogen presently exceeds 10^{10} kilograms annually (*2*).

The most important single barrier to new large-scale uses of hydrogen during the next several years appears to be cost—the price must be competitive with alternate, clean energy media. Most of the hydrogen produced currently in the United States and Europe is made by the steam reforming of natural gas or by the partial oxidation of oil, but decreasing petroleum reserves in the next decade may make it necessary to adopt alternative methods of generation. The major candidate technologies for this century include electrolysis, new open-cycle thermochemical processes based on fossil fuel feedstocks, and closed-cycle thermochemical generation methods. Longer range possibilities include biological and photolytic methods.

Although electrolysis is the best developed of these technologies at present, cost estimates for hydrogen production by the above approaches indicate that electrolysis will probably not be generally competitive in this century with the better projected thermochemical approaches for large-scale uses unless off-peak electricity costs of under 5 mills per kilowatt-hour are available. For smaller scale industrial uses of hydrogen as a chemical raw material, however, hydrogen generated by on-site electrolysis will tend to become increasingly competitive with liquid or gaseous hydrogen delivered by truck.

Open-cycle thermochemical hydrogen generation processes are ideally based on the use of hydrocarbons, water, and heat, yielding carbon dioxide and degraded heat (lower temperature heat), in addition to hydrogen. Demonstrated and presently used open-cycle methods of producing hydrogen or hydrogen-rich gas include the reforming of natural gas, petroleum naphthas, or related intermediates under moderate pressures and the partial oxidation of various fluid hydrocarbons (*3*).

The abundance and lower long-term costs of coal have spurred interest in its use to generate hydrogen from water. Three major types of approaches include: (i) reforming methods with coal, steam, and catalysts; (ii) the use of intermediate metal–metal oxide methods, such as the steam–iron–iron oxide–coal system (*4*); and (iii) variations of high-temperature O^{2-} membrane systems (*5*).

Oxygen solid electrolyte membrane processes currently under evaluation in our laboratory offer the potential for cheaper production of hydrogen than by conventional electrolysis. In the simplified version shown in Fig. 1, coal char is burned to produce CO, and the heat developed is used to vaporize water. The water and CO are then passed over opposite sides of a hot, mixed-conduction solid electrolyte that conducts equally by electrons and by O^{2-}. This results in the oxidation of the CO to CO_2, which is discarded, and the reduction of the resultant steam to H_2 under pressure. Countercurrent flow designs of the process depicted in Fig. 1 will tend to be preferred. In other versions of this process electrodes can be added and the electrolyte modified to provide partial electrical assistance to the water decomposition process (*5, 6*). Further technical advances of the better open-cycle thermochemical processes should permit overall thermal efficiencies of 60 to 70 percent for large plants producing H_2 from coal and water.

Continuing changes in ecological limitations and in fossil fuel prices, however, will tend to make open-cycle processes less competitive than closed-cycle thermochemical processes in the long term. Closed-cycle processes have been the focus of markedly increased research effort in the past 2 years. Our primary purpose in this article is to describe some tested, new closed-cycle thermochemical processes for hydrogen generation and some of the under-

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lying concepts used in their selection. The economic outlook for such closed-cycle thermochemical processes will be compared with that of open-cycle thermochemical and electrolytic methods.

Closed-Cycle Thermochemical Processes: Criteria for Process Selection

In closed-cycle thermochemical processes for hydrogen generation, ideally water and heat are the input ingredients and only hydrogen, oxygen, and degraded heat are the products. Several intermediate chemical steps and other recycled chemical species are necessary to accomplish this result.

In principle, thousands of combinations of multicomponent closed-cycle chemical systems exist that might yield a workable water-splitting process. In order to select the most promising cycles, it is useful to set up a series of criteria for the screening of potential candidate processes. These criteria include the thermal efficiency based on both thermodynamic and kinetic factors, the required maximum temperature of the process and its compatibility with various nuclear reactor or other heat sources, the compatibility of materials, their availability and cost, the apparent system complexity, and ecological or safety constraints.

A high thermal efficiency is desirable for both ecological and economic reasons: less heat is thrown into the environment, and the overall process cost is reduced because the cost of the input heat is a major item. Closed-cycle thermochemical water-splitting processes are Carnot-limited in a thermodynamic sense. The thermodynamic process efficiency, n^*, can be defined on the basis of the Gibbs free energy, or available work, as:

$$n^* = \frac{T_M - T_m}{T_M} = \beta \frac{\Delta G_f}{Q} \qquad (1)$$

where ΔG_f is the Gibbs free energy change associated with the formation of 1 mole of water under conditions where the hydrogen and oxygen are subsequently used (for example, 298°K and 1 atm); Q is the total heat required by the overall process to split 1 mole of water into hydrogen and oxygen; T_M is the maximum absolute temperature of the process; T_m is the minimum absolute temperature occuring in the process; and β is a factor ($\leqslant 1$) which includes energy and entropy losses due to: (i) fundamental heat imbalances from net exothermic reactions occurring at temperatures below endothermic ones, (ii) the operation of reactions at nonequilibrium conditions, and (iii) operating energy requirements such as those involved in pumping, separation steps, and heat losses from the plant. In potentially useful or competitive multistep cycles, β is expected to lie in the range of 0.6 to 0.9. In order to increase reaction rates and reduce unit capital and operating costs, processes will frequently be operated with a considerable displacement from equilibrium.

Equation 1 tells us that n^* increases with the maximum temperature used in the process. An upper limit of 1200°K appears to be realistic, as this represents the highest commercial nuclear reactor coolant temperature expected in the next one to two decades. Furthermore, corrosion and materials problems are more severe at higher temperatures. When the heat transfer between the nuclear reactor and the chemical process involves no phase change (as by condensing a vapor), the heat is carried as sensible heat (that is, the heat capacity multiplied by the temperature difference), and, in order to extract this heat, the temperature of the medium must fall but naturally not below the required chemical reaction temperature. An additional temperature drop is encountered in a heat exchanger. Furthermore, the temperature of the coolant must not be too high when it reenters the reactor in order to avoid materials problems or high circulation power consumption; if only the high-temperature chemical reactions require heat, then the necessary coolant temperature drop could be usefully realized by producing steam for electrical power. We consider a temperature of about 300°K as a lower limit for practical system operation and reaction rates.

Another useful type of process efficiency which has been used by various workers could be called the thermal yield efficiency, ε. It is based upon heat efficiency rather than work efficiency and is given by:

$$\varepsilon = \frac{\Delta H_f}{Q} \qquad (2)$$

where ΔH_f is the heat of formation (or combustion) of a mole of water from hydrogen and oxygen. The quantity ε will always be slightly larger than n^* since the enthalpy of formation of water is larger than the Gibbs free energy of formation (at 298°K, $\Delta G_f° = -56.69$ kilocalories per mole and $\Delta H_f = -68.32$ kcal per mole of liquid water) (*7, 8*).

The free energy of dissociation of water ranges from about 57 kcal/mole at 273°K to 44 kcal/mole at 1200°K. Thus, the equilibrium constant for thermal dissociation ranges from 10^{-45} at 273°K to about 10^{-8} at 1200°K and can be neglected. It is not feasible to dissociate water thermally in one step. However, the decomposition can be carried out in several chemical steps, each operating at its optimum temperature, with the recycling of all products except hydrogen and oxygen.

One thermodynamic criterion that must be met is that the sum of the standard enthalpies of reaction of the individual steps, $\Sigma \Delta H_i°$, must equal or exceed about 68 kcal/mole for an overall dissociation of 1 mole of liquid water (or 57.8 kcal/mole relative to steam input). This value is nearly independent of temperature over the temperature range of interest for a given standard state (that is, -57.79 kcal/mole at 298°K and -59.52 kcal/mole at 1200°K) (*7*).

A second, less stringent thermodynamic criterion is that the standard free energy changes ($\Delta G°$) for each of the separate steps (at their operating temperatures and pressures) be negative or close enough to zero to provide reasonable concentrations of products. For a reaction $r_1R_1 + r_2R_2 + \ldots \rightarrow p_1P_1 + p_2P_2 + \ldots$, where r_1 moles of R_1 plus r_2 moles of R_2 react to yield p_1 moles of P_1 and p_2 moles of P_2, one can use the well-known equation:

$$\Delta G° = -RT \ln \frac{[P_1]^{p_1} \cdot [P_2]^{p_2} \ldots}{[R_1]^{r_1} \cdot [R_2]^{r_2} \ldots}$$

where R is the gas constant; T is the absolute temperature; and $[P_i]$ and $[R_i]$ are the equilibrium activities of species P_i and R_i, respectively, relative to the standard state for which $\Delta G°$ is calculated. The values of p_i and r_i affect the departure of $\Delta G°$ from zero which will provide reasonable concentrations of products. If the p_i for the desired product is unity, then at about 1000°K $\Delta G°$ should not be greater than about 8 kcal for a 2 percent concentration of desired product; higher values of p_i or continuous extraction of products from the reaction site may permit higher positive values for $\Delta G°$. Large negative values for $\Delta G°$ generally imply excessive product stability which would cause difficulties in other steps of the cycle.

Practical considerations indicate that

the number of reaction steps will be at least three. This can be seen as follows, with the representative set of reactions:

$$A + H_2O \rightarrow AO + H_2 \quad \text{at } T_1$$
$$AO + B \rightarrow AB + \tfrac{1}{2} O_2 \quad \text{at } T_2$$
$$AB \rightarrow A + B \quad \text{at } T_3$$

Let us assume as an approximate limit that $\Delta G°$ for each reaction is zero at the temperatures involved, which range between 300° and 1200°K. If, for example, two of the reactions were to take place at 300°K, the $\Delta G°$ of the other reaction must change by 56.7 kcal upon going from 300° to 1200°K. The standard entropy change for the reaction, $\Delta S°$, is given by:

$$\left[\frac{\partial(\Delta G°)}{\partial T}\right]_p = -\Delta S°$$

(where the subscript p signifies constant pressure) and hence for a temperature difference of 900°K the value of $\Delta S°$ is 56,700/900 = 62.8 cal $°K^{-1}$ $mole^{-1}$ for the reaction per mole of hydrogen in the system. Such a large standard entropy change is rarely found. On the other hand, if the 56.7 kcal of $\Delta G°$ were to be divided equally between two reactions, each operating at 1200°K, the maximum allowed temperature, then the required $\Delta S°$ per reaction is 31.4 cal $°K^{-1}$ $mole^{-1}$, which is not so unusual.

Applying Eq. 1 to the temperature limits described here, one can roughly estimate the minimum heat input to a closed-cycle process. Specifically, $(1200° - 300°)/1200° = 0.75 = (56.7)/Q$, or $Q = 75.5$ kcal is the minimum theoretical heat input to the process; this input ideally occurs at 1200°K to satisfy endothermic reactions. For two idealized and complementary reactions at 1200°K, each having $\Delta G° = 0$ and $\Delta S° = 31.4$ cal $°K^{-1}$ $mole^{-1}$, and a limit of $\beta = 1$, one finds $\Delta H°$ for each to be about 37.7 kcal, endothermic. So when $\Delta S°$ is divided between the two reactions, the required heat input is ideally divided in the same ratio.

Since 75.5 kcal is supplied but the sum of all the $\Delta H°$ is 68.3 kcal, one concludes that the low-temperature reaction is exothermic by 7.2 kcal in this ideal case with no system losses. If the low-temperature reaction is more exothermic, then the extra heat must be supplied at higher temperatures. If all the high-temperature reactions do not occur at the maximum temperature, then the thermal efficiency is reduced; more heat must be supplied and more must be rejected to the environment at 300°K.

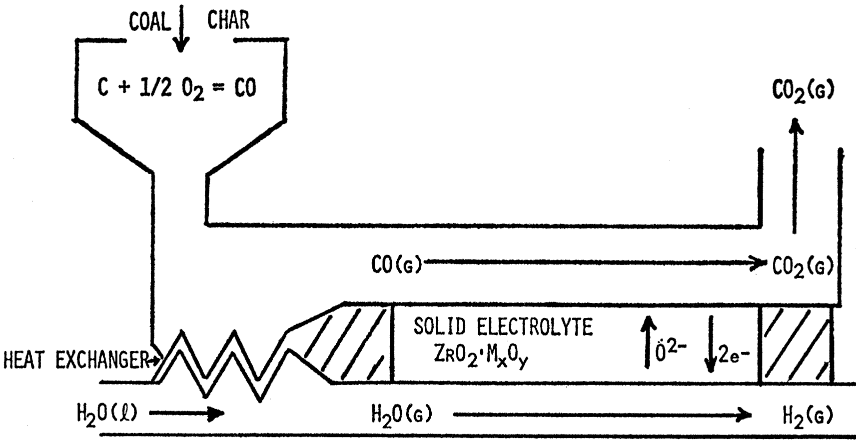

Fig. 1. Solid-membrane, open-cycle hydrogen generation process.

The above considerations also apply to cycles composed of *n* chemical steps. At least one step must be carried out at relatively low temperature, and the required $\Delta S°$ and $\Delta H°$ may be divided among $n - 1$ or fewer steps in many ways, depending upon the chemical reactions involved. However, practical and economic considerations appear to limit the number of steps to no more than eight.

Several separation or regeneration steps for intermediate products and reactants are generally required in closed-cycle thermochemical processes. Such separation techniques include mechanical, electrical, magnetic, condensation, adsorption, nonequilibrium quenching, precipitation, distillation, selective membrane diffusion, and other methods. It is important that the separation methods do not require substantial energy penalties. Movement of a product phase from one temperature to another temperature for a subsequent reaction must also be accounted for in the overall enthalpy balance.

In all potentially viable thermochemical processes it appears that a change in the oxidation state of one or more chemical elements (either anion or cation) will be a necessary requirement. The primary candidate elements for anions include sulfur, chlorine, bromine, iodine, and possibly nitrogen and phosphorus. Primary candidate elements for cations include iron, nickel, cobalt, manganese, copper, vanadium, and other transition and multivalent metals or complexes.

Some processes may be deterred from further consideration on the basis of high heats of reaction which limit the overall thermal efficiency to a relatively low value. For example, processes can be devised in which a sulfate undergoes decomposition to produce a metal oxide, SO_2, and O_2. However, such decompositions require so much heat at high temperatures that, even if all the other steps in the process require no heat, the overall thermal efficiency is seriously limited. For example, the evolution of $\tfrac{1}{2}O_2$ from $CuSO_4$ or $FeSO_4$ at 1000°K requires enthalpy inputs of 72.9 and 102 kcal/mole, respectively, for this step alone (*7*).

In devising processes, one can begin by considering all reactions which yield H_2 and O_2 from readily available materials with acceptable enthalpy changes and then try to fit them together in some way so that no by-products are left over. This can be done with the aid of a computer if sufficiently reliable thermodynamic data are available, but it is equally fruitful to review the chemical literature while keeping certain ideas in mind, such as the meshing of sets of reactions, their completeness, and their suitability for large-scale operation. After a set of promising reactions has been selected for a process, the reactions need to be studied in the laboratory to decide about the degrees of completeness and the rates. Tests also will be needed to determine the nature of a reaction in terms of the heat and material fluxes and the physical states of the products. For example, the formation of a glassy, sticky solid product would make the reaction difficult to use on a large scale.

After the suitability of the reactions has been ascertained, flow charts can be made. It is difficult to estimate the thermal efficiency of a process without constructing a flow chart to see how heat is to be best provided and rejected in the various steps and how products are to be separated. If all still looks favorable on both technical and economic grounds, more detailed studies of key reactions will need to be made and a small pilot plant will need to be constructed and operated.

Using the concepts and methods described above, we have devised one dozen closed-cycle thermochemical processes. Many other thermochemical processes have been proposed in other laboratories (*9*). Three of our processes, processes A, B, and C, are described below, each suitable for a particular range of maximum temperatures. The thermodynamic data used in these studies were drawn from standard references (*7, 8*). We found comprehensive chemistry texts such as those by Sidgwick (*10*) or Gmelin (*11*) helpful in the selection of reactions and processes based on the criteria outlined above. We have carried out experimental work on most of the reactions given in these processes, confirming that they proceed to an acceptable degree.

Process A

In this process hydrogen, oxygen, iron, chlorine, and magnesium atoms are cycled through the following steps (see Table 1):

$$3FeCl_2\ (c) + 4H_2O\ (g) \rightarrow Fe_3O_4\ (c) + 6HCl\ (g) + H_2\ (g) \qquad (A1)$$

$$Fe_3O_4\ (c) + 8HCl\ (aq) \rightarrow FeCl_2\ (aq) + 2FeCl_3\ (aq) + 4H_2O\ (\ell) \qquad (A2)$$

$$2FeCl_3\ (c) \rightarrow 2FeCl_2\ (c) + Cl_2\ (g) \qquad (A3)$$

$$Cl_2\ (g) + Mg(OH)_2\ (aq) \xrightarrow{Co^{3+}} MgCl_2\ (aq) + \tfrac{1}{2}\ O_2\ (g) + H_2O\ (\ell) \qquad (A4)$$

$$MgCl_2\ (c) + 2H_2O\ (g) \rightarrow Mg(OH)_2\ (c) + 2HCl\ (g) \qquad (A5)$$

This process can operate at relatively low temperatures if necessary, which limits the thermal efficiency by comparison with processes for which heat is available at higher temperatures. On the other hand, at lower temperatures, cheaper heat, such as solar energy or lower temperature nuclear heat rejected from another coupled process, can be used, and corrosion problems are less severe.

In practice, the indicated reactions are to be carried out as continuous processes and the reactions may not go to equilibrium. Various separations are required, and the overall efficiency of the process depends on how they are carried out. Let us now consider each of the above steps in more detail.

Table 1. Thermochemical data for process A.

Step	Reaction temperature (°C)	Energies (kcal) for reactions as written	
		$\Delta H°$	$\Delta G°$
A1	450° to 900°	78 to 68	30 to − 5
A2	50° to 110°	− 50	− 1 to 7
A3	300°	28	4
A4	50° to 90°	− 38	− 42 to − 48
A5	350°	4	8

Step A1. Steam passes over solid $FeCl_2$ at 450° to 900°C (depending upon the heat source), and magnetite (Fe_3O_4), HCl, and H_2 are the products. If the temperature is slightly lower, the main products appear to be $Fe(OH)_2$ and HCl. The estimated enthalpy change at 450°C is about 78 kcal (or 68 kcal at 900°C) per mole of H_2, endothermic, based on the steam feed described below. The great stability of Fe_3O_4 prevents the oxidation reaction from proceeding completely to the Fe^{3+} state, and thus some Fe^{2+} is recycled without contributing to H_2 formation.

In one version of the reaction procedure, superheated $FeCl_2$ solution is fed to a heated rotating drum and allowed to flash to yield small particles for a large reaction surface. Magnetite beads could be used to assist stirring and heat transfer. The outgoing Fe_3O_4 gives up its heat to incoming feed. The outgoing H_2O and HCl are condensed to acid and thereby provide heat to some other stream; the condensed acid reacts with Fe_3O_4. The sour H_2 is scrubbed with Fe_3O_4 and water before being compressed for shipment or storage.

Step A2. The Fe_3O_4 from step A1 gives up its heat to the solution supplied to step A1 and then is dissolved in aqueous HCl at 50° to 110°C to form $FeCl_2$ and $FeCl_3$. Part of the HCl comes from step A1 and part from step A5. The dissolution is exothermic with 50 kcal liberated per mole of Fe_3O_4, enough to boil all the water formed in the reaction. The heat can be used in other endothermic steps, such as water preheating and steam generation for step A1.

In the presence of excess HCl, the $FeCl_3$ can be extracted with diethyl or di-isopropyl ether at 25° to 30°C. Very little $FeCl_2$ dissolves in the ether phase. The ether is evaporated and recycled. The $FeCl_2$ solution, after being stripped of ether and HCl, is fed into step A1. The ether solution of $FeCl_3$ contains some water and HCl which must be removed to produce dry $FeCl_3$ for step A3. The drying of 2 moles of $FeCl_3$ theoretically requires 62 kcal; this can be supplied by the heat of solution of less than 4 moles of HCl from step A1. Most of the ether can be evaporated at less than 50°C where abundant heat is available; in addition, step A4, described below, can supply 10 kcal at 50° to 90°C.

Step A3. This reaction takes place at around 300°C. It is possible to have liquid or solid $FeCl_3$ in equilibrium with solid $FeCl_2$ and Cl_2 vapor by changing the temperature slightly. At 1 atm, the melting point of $FeCl_3$ is 282°C and the boiling point is 315°C. According to Ringwald (*12*), the equilibrium ratio of Cl_2 to Fe_2Cl_6 vapor at 287°C is about 0.083; the ratio falls with increasing temperature because of the rapid rise of the vapor pressure of Fe_2Cl_6, and reaches 0.064 at 302°C. The heat of dissociation from solid $FeCl_3$ is about 26 kcal per mole of Cl_2; from liquid $FeCl_3$ the heat required is only about 5 to 6 kcal per mole of Cl_2, owing to the large heat of fusion of $FeCl_3$. The vaporization of a mole of solid $FeCl_3$ requires about 34.5 kcal of heat.

One way to carry out the reaction is to operate where $FeCl_3$ is liquid and to separate the solid product $FeCl_2$ from the liquid while condensing liquid $FeCl_3$ from the vapor mixture of Cl_2 and Fe_2Cl_6 at a slightly higher pressure. Traces of water hydrolyze the $FeCl_3$ to oxide or oxychloride which separates as a solid with the $FeCl_2$. The HCl leaves with the Cl_2 and forms $MgCl_2$ with the $Mg(OH)_2$ fed to step A4. Thus the presence of water in step A3 decreases the overall efficiency of the process.

Step A4. The absorption of Cl_2 by aqueous $Mg(OH)_2$ produces hypochlorite early in the reaction sequence. A basic hydrated cobaltic oxide, which forms if a cobalt salt is added to the mixture, catalyzes the decomposition of hypochlorite to O_2 and Cl^- (*13*). The Co^{3+} circulates with the Mg^{2+}; Ni^{2+} may be used in place of Co^{3+}. In laboratory tests the rate of O_2 evolution appeared to be limited by the dissolution rate of Cl_2.

Another way to form O_2 from Cl_2 and water vapor is to use the reverse of the well-known Deacon process: $Cl_2 + H_2O \rightarrow 2HCl + \tfrac{1}{2}\ O_2$. This reaction is also catalyzed by a number of heavy metal salts such as those of copper, iron, nickel, or cobalt. A practical difficulty with this reaction is that the temperature needs to be fairly high, for example, 650°C, for reasonable rates, and also one is left with the problem of separating O_2 from a hot, corrosive mixture of gases. Therefore, it seems useful to form Cl_2 at temperatures below about 100°C according to step A4, where equilibrium favors the production of O_2.

At 25°C, step A4 is estimated to liberate about 38 kcal per mole of $MgCl_2$ formed in dilute aqueous solution, but the heat liberated will be less if less water is present, down to a minimum of 10.5 kcal if $MgCl_2 \cdot H_2O$ forms; we assume this latter situation for heat estimates.

Step A5. The hydrolysis of $MgCl_2$ is a well-known reaction used in times past for HCl and Cl_2 manufacture. Other possible products are MgO and MgOHCl. MgOHCl readily reacts with steam above 300°C and loses its chloride as HCl; MgO has both a strong physical and a strong chemical affinity for water. The water pressure at equilibrium at 350°C over $Mg(OH)_2$, calculated from standard data (*8*), is about 19 atm, and the heat of hydration is about 9 kcal/mole. However, the physical states of the $Mg(OH)_2$ and MgO affect the water content. In succeeding reactions it matters little whether MgO or $Mg(OH)_2$, or both, are present, and to describe the process we have simply used $Mg(OH)_2$.

Part of the feed for step A5 is the concentrated, essentially oxygen-free $MgCl_2$ solution from step A4; for energy balance purposes we assume it has the composition $MgCl_2 \cdot H_2O$. A mole of water, destined to be split, is also fed here as steam. It is to be fed countercurrent to the $MgCl_2$ for greater conversion to HCl. If we assume it fed as steam at 350°C, the heat requirement for step A5 is about 24 kcal. However, initially the mole of H_2O is liquid; surplus heat is available at 100°C to vaporize it, but an extra 2.5 kcal will be needed to bring it to 350°C. Thus the total heat requirement for step A5 is about 26.5 kcal.

The solution and dehydration of various chlorides in this process involve moderate amounts of heat at low temperature. Without detailed experimental data on each of these steps, the exact heat requirements for the entire process are difficult to calculate. However, if we assume that these steps are in approximate thermal balance, then most of the heat required in process A is used at 300°, 350°, and 450° to 900°C in steps A3, A5, and A1, respectively; the total heat requirement for these steps is about 126 ± 5 kcal per mole of H_2 formed. About 53 kcal is liberated at about 50° to 100°C in steps A2 and A4. The difference is 73.5 kcal, larger than the heat of formation of liquid water, 68.3 kcal, because not all the heat released at lower temperatures can be used. In addition to the ~ 126 kcal for heats of reaction, more heat will be needed for supplying pumping power and to make up for miscellaneous losses. By analogy with other industrial chemical processes, this extra heat requirement is estimated to be a minimum of 15 kcal per mole of H_2. For example, about 5 to 10 percent of the input of an oil refinery is used for such functions.

Table 2. Thermochemical data for process B.

Step	Reaction temperature (°C)	Energies (kcal) for reactions as written	
		$\Delta H°$	$\Delta G°$
B1	100°	− 8	2
B2	30° to 100°	30	38
B3	500° to 600°	30	0
B4	80°	− 38	− 46
B5	350°	4	8

The overall thermal yield efficiency of the plant ε, assuming that the product H_2 is converted to water vapor, then would be $57.8/141 = 0.41$; that is, 41 percent of the input heat is available as hydrogen fuel [lower heating value (LHV)]. The limiting Carnot efficiency for the temperature interval 723° to 300°K, for example, would be $423°/723° = 0.586$ even if $\beta = 1$, but one must consider this using the free energy of formation of water vapor. Since 54.6 kcal of work is available from $H_2 + \frac{1}{2}O_2$ in a perfect fuel cell, the work efficiency is $54.6/141 = 0.385$. For this example, the value of β given in Eq. 1 is ~ 0.66. A simplified flow chart for process A is shown in Fig. 2.

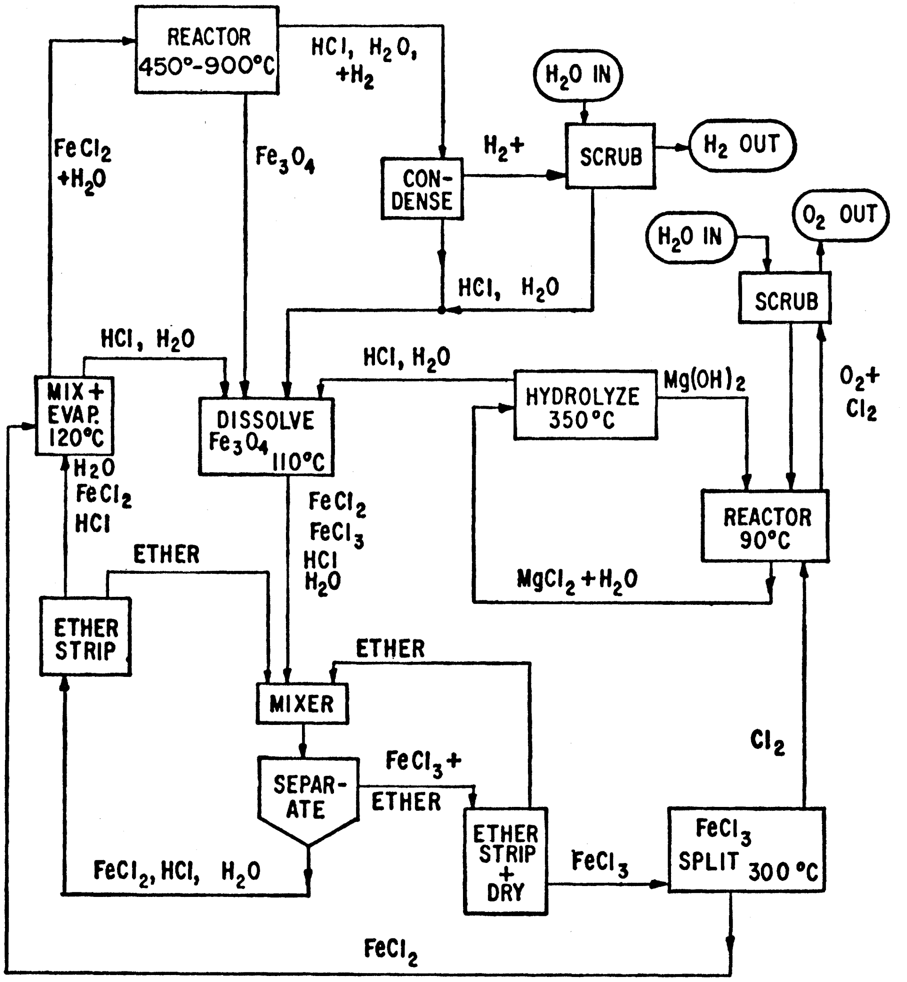

Fig. 2. Simplified flow chart for process A.

Process B

In this process copper, chlorine, hydrogen, and oxygen atoms are cycled through the following basic steps (see Table 2):

$$2Cu\,(c) + 2HCl\,(aq) \rightarrow 2CuCl\,(c) + H_2\,(g) \qquad (B1)$$

$$4CuCl\,(c) \rightarrow 2CuCl_2\,(c) + 2Cu\,(c) \qquad (B2)$$

$$2CuCl_2\,(c) \rightarrow 2CuCl\,(c) + Cl_2\,(g) \qquad (B3)$$

$$Cl_2\,(g) + Mg(OH)_2\,(aq) \rightarrow MgCl_2\,(aq) + H_2O\,(\ell) + \tfrac{1}{2}\,O_2\,(g) \qquad (B4)$$

$$MgCl_2\,(c) + 2H_2O\,(g) \rightarrow Mg(OH)_2\,(c) + 2HCl\,(g) \qquad (B5)$$

The last two steps are the same as the last two steps in process A. Their advantage is that they proceed at relatively low temperatures where the equilibrium favors the production of O_2.

Step B1. This reaction is conveniently carried out in aqueous solution at about 100°C on the finely divided copper from step B2. About 8 kcal are liberated per mole of H_2 formed, with the use of the gaseous HCl input from step B5. Literature data indicate that, at 80° to 100°C, about 1 mole of CuCl will dissolve in 9 moles of H_2O mixed with 2 moles of HCl. At lower temperatures, the CuCl is considerably less soluble and so it can be separated by cooling the solution, preferably countercurrently, with weak solution so that the overall heat needed for separation is approximately zero; the 8 kcal liberated by step B1 is also available.

Step B2. Two moles of CuCl come from step B1, and 2 moles come from step B3. Step B2 actually consists of two substeps, B2a and B2b.

$$4CuCl + \chi \rightarrow 2CuCl_2 \cdot \chi + 2Cu \qquad (B2a)$$

The disproportionation of CuCl is ordinarily rather small ($\Delta G° = 38$ kcal), but, if the product $CuCl_2$ can be removed, the reaction will proceed indefinitely. It is possible to remove the CuCl by complexing it with another substance, here designated by χ.

The complex $CuCl_2 \cdot \chi$ is thermally decomposed to yield χ for step B2a and solid $CuCl_2$ for step B3:

$$CuCl_2 \cdot \chi \rightarrow \chi + CuCl_2\,(c) \qquad (B2b)$$

The reaction conditions to be used in these two substeps depend on the nature of χ. In one method, χ is a chelating agent such as propylenediamine which selectively dissolves the $CuCl_2$. In another method, Cu^{2+} is preferentially absorbed on an ion-exchange resin, from which $CuCl_2$ is regenerated by HCl solution. In a third method, χ is water containing enough HCl to prevent hydrolysis but not so much as to make CuCl very soluble or to dissolve the copper formed.

The choice for χ affects the temperatures at which heat is supplied or rejected in the B2 substeps, but the overall heat demand will be approximately the same because the initial and final stages are the same and the heat used for evaporation can be recovered upon condensation and used to heat liquid with only a small loss. Thus one might base the heat demand for step B2 on the hypothetical solid-to-solid reaction:

$$4CuCl \rightarrow 2CuCl_2 + 2Cu$$

for which the available data indicate a demand of about 30 kcal at 25°C, although step B2 may actually need heat at 100° to 200°C.

Step B3. The well-known decomposition of $CuCl_2$ occurs readily at temperatures in the range 450° to 500°C. Nearly all the vapor is Cl_2, and its pressure is about 0.037 atm at 450°C, 0.54 atm at 510°C, and 1.17 atm at 550°C. Pure CuCl has a melting temperature of about 425° to 430°C; its vapor pressure is only about 0.0013 atm at 500°C. Thus, by heating $CuCl_2$ at 600°C, one obtains Cl_2 vapor and molten CuCl which may contain a little $CuCl_2$. Pure $CuCl_2$ melts at approximately 630°C. The decomposition absorbs about 30 kcal per mole of Cl_2.

Steps B4 and B5 are identical to those described above under process A and hence will not be discussed further here. A simplified flow chart for process B is shown in Fig. 3.

The main heat requirements for process B are found in steps B2 (30 kcal at 100° to 200°C), B3 (30 kcal at 500° to 600°C), and B5 (26.5 kcal at 350°C, on the assumption that the feed water can be vaporized at about 100°C by the heat from step B4), for a total of 86.5 kcal. Here again, the net heat requirement for a practical process exceeds 68.3 kcal because not all the low-temperature heat released can be used. In the most favorable case, the chelating agent χ might be chosen to permit the use of perhaps 5 to 6 kcal of the heat liberated in step B1 for a net demand of 81 kcal.

If to 86.5 kcal we add $\geqslant 15$ kcal for the inevitable losses and other requirements, the total heat demand is $\geqslant 101.5$ kcal and the thermal yield efficiency ε is $57.8/101.5 \leqslant 0.57$. The thermodynamic process efficiency n^* is $54.6/101.5 \leqslant 0.538$. The ultimate Carnot efficiency between 550° and 30°C is 0.63, and $\beta \leqslant 0.85$. Process B is more efficient than process A because it operates at a higher maximum temperature, and, fortuitously, less heat is circulated internally, that is, only about 10 to 15 kcal per mole of H_2 in process B instead of at least 50 kcal in process A.

Process C

This process appears to be the most eligible of a small family of processes founded mainly on iodine. The following key steps are the basis for the process (see Table 3):

$$3I_2\,(\ell) + 6LiOH\,(aq) \rightarrow 5LiI\,(aq) + LiIO_3\,(aq) + 3H_2O\,(\ell) \qquad (C1)$$

$$LiIO_3\,(c) + KI\,(aq) \rightarrow KIO_3\,(c) + LiI\,(aq) \qquad (C2)$$

$$KIO_3\,(c) \rightarrow KI\,(c) + 3/2\,O_2\,(g) \qquad (C3)$$

$$6LiI\,(\ell) + 6H_2O\,(g) \rightarrow 6HI\,(g) + 6LiOH\,(\ell) \qquad (C4)$$

$$6HI\,(aq) + 3Ni\,(c) \rightarrow 3NiI_2\,(aq) + 3H_2\,(g) \qquad (C5)$$

$$3NiI_2\,(c) \rightarrow 3Ni\,(c) + 3I_2\,(g) \qquad (C6)$$

Step C1. Liquid iodine at about 115°C from step C6 reacts with concentrated aqueous LiOH at about 100°C from step C4. About 44 kcal of heat are evolved per mole of $LiIO_3$ formed. The reaction is already quite rapid at 80°C, but in the process described here we propose to let it run at 100° to 190°C so as to use the heat to evaporate liquid in other steps.

Iodine does not liberate O_2 directly from water in alkaline solution as does Cl_2 or Br_2. Thus the production of O_2 from I_2 requires several steps.

In preparation for step C2, ethanol is added to the concentrated aqueous solution from step C1; $LiIO_3$ is rather insoluble in ethanol-rich solutions, and nearly all of it precipitates. After this separation, the ethanol is evaporated from the LiI solution and is recycled. The long-term stability of tincture of iodine indicates that the oxidation of ethanol should be minor as long as the solution is not alkaline; no iodoform was observed to form in short-time laboratory tests of the $LiIO_3$ separation step. Ethanol can be evaporated in double-effect evaporators to make more efficient use of the low-temperature heat evolved in other steps.

Step C2. The $LiIO_3$ is dissolved in the minimum amount of water and mixed with a concentrated aqueous solution of KI, the product of step C3. The solution is then cooled to approximately 0°C, whereupon most of the KIO_3 precipitates. The remaining solution, which contains K^+, Li^+, I^-, and IO_3^-, is partially dewatered and then returned to the ethanol solution where LiI is preferentially taken into solution so that the K^+ remains in the KI-KIO_3 loop.

Step C3. This step is the thermal decomposition of molten KIO_3 to KI and O_2 at 560° to 650°C and 1 atm. If the KIO_3 is free of Li^+, no I_2 is evolved. In practice, some $LiIO_3$ may be carried along; the $LiIO_3$ decomposition yields I_2 and O_2 at slightly lower temperatures, around 500°C, and this I_2 will have to be removed with a small amount of LiOH. A good heat-transfer medium for the decomposition of KIO_3 appears to be pure O_2. About 51 kcal are required per mole of KIO_3 in step C3.

It appears that KIO_3 is a good choice for an O_2 source because of its clean decomposition to O_2 and its relatively low solubility; $LiIO_3$, and other iodates such as $Ba(IO_3)_2$ which might be easier to form, are unsatisfactory because at temperatures below 850°C they decompose to O_2, I_2, and rather insoluble, intractable paraperiodates such as $Ba_5(IO_6)_2$. Magnesium iodate and some other iodates easily decompose to the metal oxide, I_2, and O_2, but these metal oxides form bases that are either too weak or too insoluble to be of practical use. The sometimes obscure laws of conservation of energy are subtly buried in chemical considerations of this type.

Step C4. Concentrated aqueous LiI reacts with superheated steam at about 475°C or higher and 1 atm to form HI and LiOH. Steam comes along with the HI; in preliminary laboratory tests the condensate contained about 1 percent HI (by weight). Both LiI and LiOH are molten at this temperature and dissolve in each other, thereby lowering the fugacity of the LiI and reducing the HI yield. It is practical to plan on no more than two-thirds of the LiI being hydrolyzed and to feed the steam countercurrently for greater HI yield. The hydrolysis conditions are rather corrosive but carbon seems to survive well as a reactor vessel material. The reaction requires about 19 kcal to produce 6 moles of HI; this heat is supplied by the superheated steam feed. The $\Delta G°$ value of 108 kcal/mole is spread over 6 moles of HI gas, and hence the reaction can proceed appreciably as shown.

Table 3. Thermochemical data for process C.

Step	Reaction temperature (°C)	Energies (kcal) for reactions as written: $\Delta H°$	Energies (kcal) for reactions as written: $\Delta G°$
C1	100° to 190°	−44	−25
C2	0°	~ 0	~ 0
C3	650°	51	~ 0
C4	450° to 600°	19	108
C5	150°	−58	−20
C6	700°	99	~ 0

The mixture of hot HI and steam leaving the hydrolysis step is condensed to supply low-temperature heat for other steps and is concentrated by partial condensation and distillation. It is then pumped into the reaction vessel for step C5.

Other salts, such as MgI_2, hydrolyze more easily than LiI, but the resulting oxides or hydroxides are too weak as bases to combine with I_2 vigorously and in concentrated solution as in step C1. A stronger base used in step C1, such as $Ca(OH)_2$ or NaOH, is more difficult to hydrolyze, and hence LiOH is a compromise.

Step C5. Hot nickel sponge from step C6 reacts at roughly 10 atm and 150°C with the condensed HI solution to form H_2 and a strong solution of NiI_2. Operating the reaction at a modest pressure eases purification and compression requirements for the product H_2. The H_2 could be conveniently freed of HI if the gas is passed over more nickel sponge. The reaction liberates about 58 kcal for 3 moles of NiI_2 formed. Some of this heat is recovered by condensing water vapor from the H_2 stream; the rest is used to flash water from the NiI_2 solution.

The NiI_2 solution is evaporated by simple heating without appreciable hydrolysis to yield dry NiI_2 for step

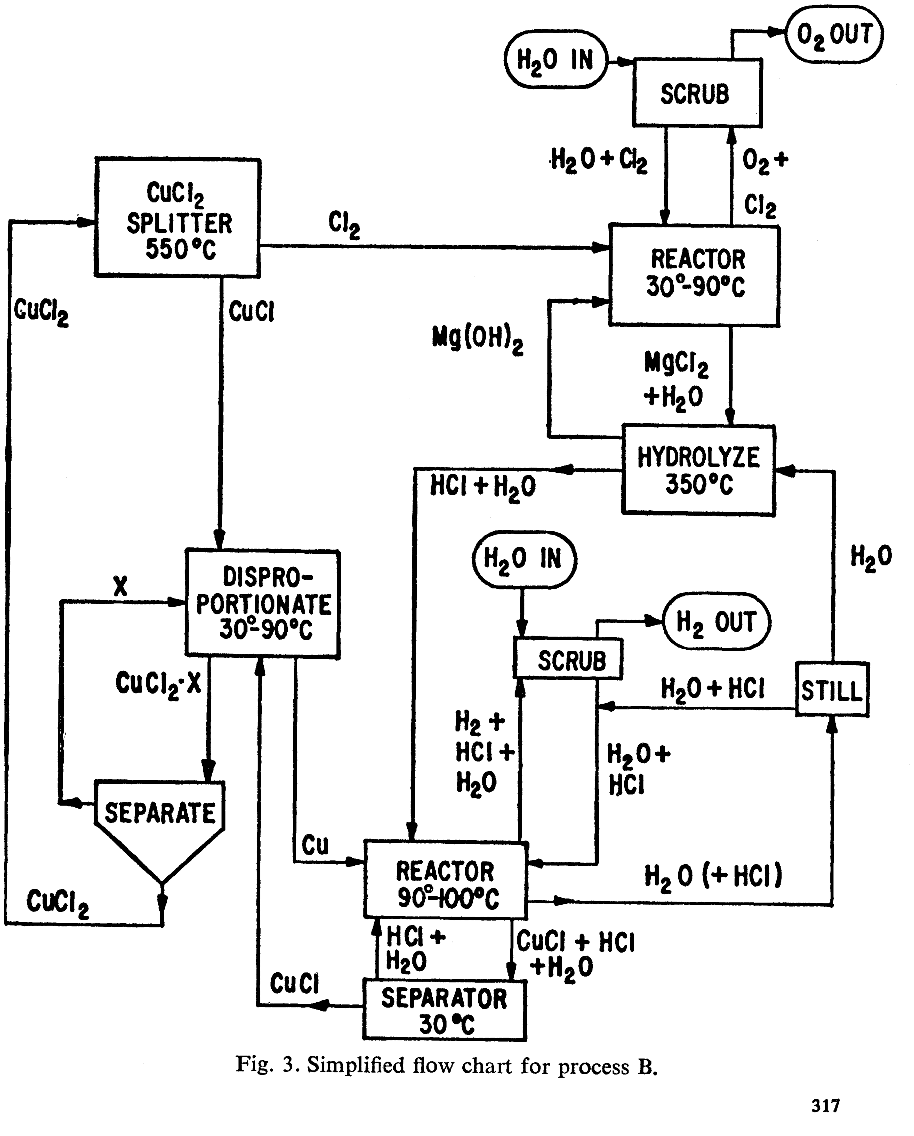

Fig. 3. Simplified flow chart for process B.

C6. If one wanted to go to the trouble of drying the HI, one would not need to dry the NiI_2 and then one might operate with fixed beds of Ni/NiI_2. At present, it seems simpler to dry the NiI_2.

Step C6. Dry NiI_2 is thermally cracked at 600° to 750°C to yield nickel sponge and I_2. The incoming salt may be heated directly by the outgoing I_2 and by condensation of any NiI_2 which sublimes without decomposition. Some sort of rotary, inclined kiln may be useful here. The pressure of I_2 is approximately 0.25 atm at 700°C. The reaction is endothermic, about 99 kcal for 3 moles of I_2 formed, and is the largest consumer of high-temperature heat in the process. The hot nickel sponge is used to make H_2 in step C5. Cobalt might be substituted for nickel in steps C5 and C6, although CoI_2 is a little more difficult to decompose. It will be necessary to avoid undesired oxidation of I^- by excluding O_2 in certain steps of the process.

A simplified flow chart for the various streams is shown in Fig. 4. A rough estimate of heat requirements for the separate steps of process C indicates that about 75 kcal are needed per mole of water decomposed. If to this one adds $\geqslant 15$ kcal for estimated losses, pumps, and the like, one needs $\geqslant 90$ kcal to produce 1 mole of H_2 which yields 57.8 kcal on burning to water vapor; the thermal yield efficiency is thus $57.8/90 \leqslant 0.64$. The value of n^* is $54.6/90 \leqslant 0.61$ compared with a limiting Carnot factor of 0.73, and $\beta \leqslant 0.61/0.73 = 0.83$. More laboratory studies on certain parts of the process will be needed before more precise estimates and design work can be done.

From a general chemical viewpoint, a comparison of processes A and B with process C shows that in going from Cl_2 to I_2, one eases problems of H_2 formation but makes O_2 formation more difficult. Bromine appears to resemble Cl_2 more than I_2 in processes of this type, and there seems to be little incentive to use it.

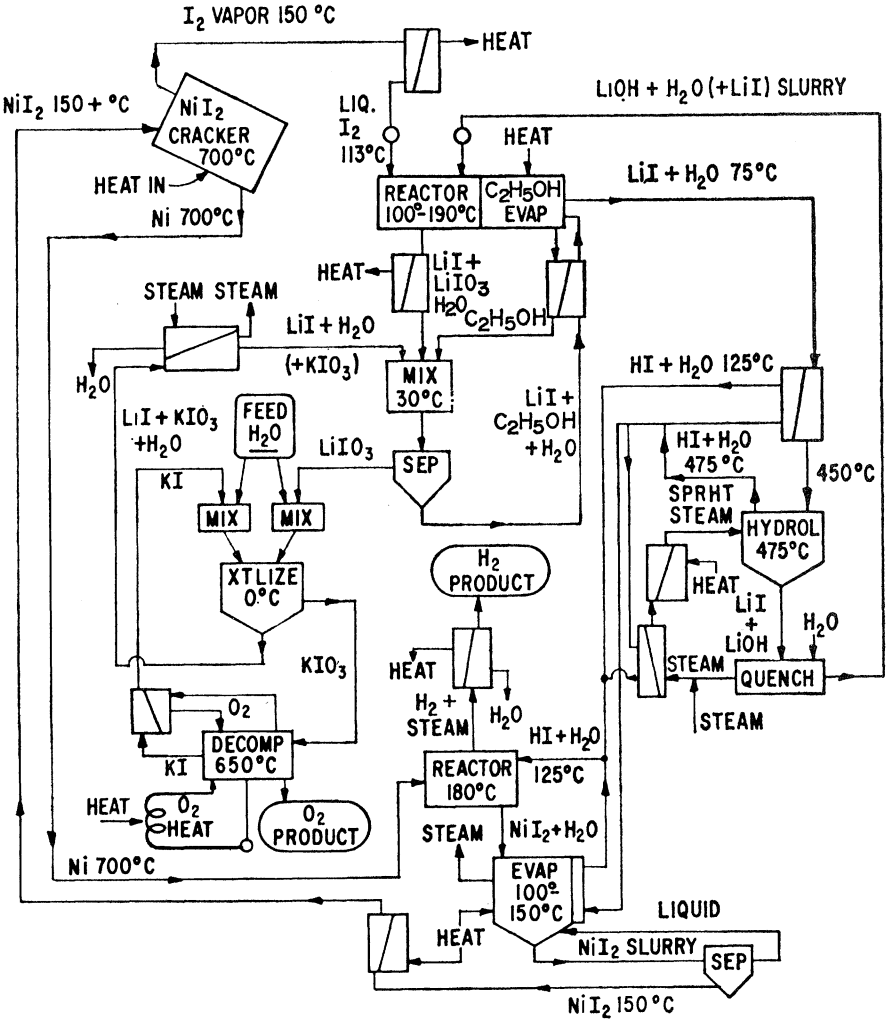

Fig. 4. Simplified flow chart for process C.

Other Processes

Mixed thermochemical-electrolytic processes for the generation of hydrogen also offer promise in spite of the fact that they have received little mention in the literature. In such systems electrolytic energy is generally applied to one step of a multistep process, which requires considerably less voltage and losses than direct water electrolysis. The remaining steps of the process then include combinations of the closed-cycle thermochemical processes outlined above. Such mixed-cycle systems may be more readily coupled to utility needs for off-peak energy storage than straight thermochemical systems.

Other approaches to hydrogen production based on biological or photolytic concepts have been suggested (*14*). Photochemical processes based on sunlight offer a genuine, long-term solution to energy supply problems, but the capital investment required could be large so that the energy made available would not necessarily be cheap. Future closed-cycle processes might be involved in converting solar energy to chemical forms, and some of the concepts discussed in this article should be helpful in devising appropriate cycles.

Economic Comparisons and Uses

The cost of hydrogen generated from closed-cycle thermochemical processes can be approximately estimated on the basis of the known costs of high-temperature nuclear heat, the expected process efficiency, and estimates of the capital and operating costs of the thermochemical process equipment itself. The future capital cost of high-temperature gas-cooled reactors in the United States in the 2000- to 4000-megawatt (thermal) size range is estimated to be \$120 to \$200 per kilowatt (thermal), in current dollars, not including electrical generation and thermochemical process equipment. Based on utility financing, a 90 percent duty cycle, and nuclear fuel cycle costs of \$0.20 per 10^6 kilojoules, the total cost of input nuclear heat will be \$0.92 to \$1.38 per 10^6 kj (that is, \$0.87 to \$1.30 per 10^6 British thermal units).

The most economical closed-cycle processes will utilize significant displacements from thermodynamic equilibrium so that systems with overall thermal efficiencies of the order of 50 percent are judged to be more likely practical candidates for eventual commercial use. Accordingly, the heat costs alone for hydrogen generation would range from \$1.85 to \$2.75 per 10^6 kj at 50 percent efficiency. An approximate analysis of the processes described above yields a minimum additional capital plus operating cost of at least \$1 per 10^6 kj. Thus hydrogen from closed-cycle processes is expected to have a minimum potential cost of at least \$2.75 per 10^6 kj at the generation plant for processes with 50 to 60 percent efficiency.

The costs of hydrogen produced by electrolysis and by more conventional fossil fuel–based methods have been discussed by several authors (*15–17*). The cost of electrolytic hydrogen in 1985, based on the use of solid polymer electrolysis cells, is projected (*15*) to drop to:

$$C_E = 0.312C_0 + 0.227$$

where C_E is the hydrogen combustion energy expressed in current dollars per 10^6 British thermal units (LHV) and C_0 is the cost of electrical energy in mills per kilowatt-hour. Thus, for off-peak power at 9 mills per kilowatt-hour, C_E would cost over \$3.20 per 10^6 kj in 1985. With current technology this hydrogen would cost well over \$4.50 per 10^6 kj.

The cost of hydrogen produced from open-cycle thermochemical processes has been calculated for various gaseous and liquid hydrocarbon feedstocks by Goff (*16*), who shows that the minimum cost of such gaseous hydrogen should vary from more than \$1.30 to over \$2 per 10^6 kj as the cost of fluid hydrocarbon feedstock varies from about \$0.50 to \$1 per 10^6 kj.

With rapidly rising feedstock prices, coal is becoming increasingly competitive to all of the above technologies as a source of hydrogen. Preliminary estimates indicate that hydrogen may be made at a cost of \$1.60 to \$2.20 per 10^6 kj assuming that coal or coal char will be available at approximately \$0.50 per 10^6 kj. It appears therefore that coal-based processes will prevail as an increasingly important source of hydrogen in the next two decades or more. However, when and where coal or other fossil fuels become more costly or chemical pollution problems are severe, nuclear thermochemical hydrogen production may be economical, and thermochemical processes of the type discussed in this article may prove to be useful.

The projected costs of hydrogen appear to indicate that it will not serve as a universal energy medium for the next few decades at least. Rather, hydrogen is expected to play a major role as an increasingly important chemical feedstock for industrial and petrochemical processes and in the conversion of coal into clean fluid synthetic fuels. If it can be made at a sufficiently low cost: liquid hydrogen would be a serious candidate fuel for aircraft toward the end of this century, principally because of its outstanding thrust-to-weight ratio and low pollution effects (*18*).

Over the longer term, when synthetic natural gas and related fossil-based fuels become increasingly expensive or unavailable, hydrogen offers the potential for widespread use in distributed electrical generation systems and as a more general fuel. Other technologies such as closed-loop chemical energy transmission (*19*) and advanced electrical transmission systems will compete with hydrogen as major energy transmission media in the next century.

Conclusions

The basic concepts for thermochemical hydrogen generation processes have been summarized in this article. A useful set of criteria has been described for the screening and selection of potentially viable, multistep, closed-cycle thermochemical processes for hydrogen generation. Three illustrative, new closed-cycle processes have been discussed, indicating potential, overall thermal efficiencies ranging from approximately 40 to 60 percent. Combined thermochemical-electrolytic schemes also warrant further consideration. Principal technical problems in the development of such thermochemical closed-cycle and mixed-cycle processes are expected to include primarily materials compatibility, reaction kinetics, separation techniques, and heat-exchanger systems.

As natural gas supplies decline and prices rise, new open-cycle thermochemical processes based on water and other fossil fuel feedstocks will be the first important new technology in supplying the growing hydrogen needs of industry for at least the next two decades. Conventional electrolysis technology does not appear to be a competitor for large-scale supplies in this century unless very low off-peak electrical power rates become available, although electrolysis will be the best technique for some small-scale uses. Further analysis will be required to determine if closed-cycle thermochemical or mixed-cycle methods will displace electrolysis or other methods as the principal technology for the production of hydrogen on a large scale for the longer term.

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