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THERMOCHEMICAL PROCESSES FOR SOLAR HYDROGEN PRODUCTION

AUTHOR(S)

Melvin G. Bowman

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

THERMOCHEMICAL PROCESSES FOR SOLAR HYDROGEN PRODUCTION

Melvin G. Bowman
Los Alamos National Laboratory
P.O. Box 1663, MS C348
Los Alamos, New Mexico
87545 USA

ABSTRACT

The use of solar energy to produce hydrogen from water is an attractive concept that merits a continuing research and development effort. The base technology being developed for solar thermal power can be applied effectively in the production of hydrogen from water. Hydrogen production could be based on advanced water electrolysis and economic solar hydrogen become an eventual reality even if advanced processes do not prove to be feasible. Thermochemical cycles for decomposing water promise higher efficiencies if cycles can be developed that match the characteristics of solar heat sources. At present, cycles based on sulfuric acid are the most fully developed processes and they can be adapted to solar thermal systems and serve as standards of comparison for new cycles as they are discovered and developed. Advanced cycles based on solids decomposition reactions should interface advantageously with solar thermal systems and several cycles based on such reactions are under experimental evaluation.

1. INTRODUCTION

The potential advantages of hydrogen as an energy carrier and as a fuel have been emphasized many times over the past several years. Hydrogen is also a prime intermediate in the production of fuels and chemicals and the demand for hydrogen is projected to increase rapidly. Consequently, the use of solar energy for the production of hydrogen from water is a very appealing concept and if production processes can be coupled economically with solar energy systems, the resultant technology will be extremely valuable. The production of hydrogen would also help fulfill the important function of energy storage that is an inherent requirement for most large-scale uses of solar energy.

Since hydrogen must eventually be produced in high volume at low cost in order to become an important part of the energy economy, it is relevant to note that the decomposition of water is a high energy process and only a small fraction of the solar spectrum has sufficient energy for a one-step quantum reaction. Further, sunlight is a diffuse energy source and the cost per unit area of the material that intercepts the sunlight will be a controlling part of the overall investment in a solar hydrogen system. As a consequence, it appears that practical processes for solar hydrogen production must be based on optimized thermal processes that utilize concentrated sunlight with high efficiency.

2. PRODUCTION TECHNOLOGIES

At the present time major efforts in the development of solar thermal technology are directed primarily toward coupling existing power production techniques to different concentrator systems under development. An important part of such development is directed toward the incorporation of high temperature energy storage systems that permit a relatively constant rate of power production. This approach is practical and prudent since most of the available effort can be focused on the crucial problems of developing methods and components for concentrator systems (heliostats), receiver systems and energy storage and retrieval systems for a known and valuable application. However, most of this basic solar thermal technology will be of direct application in the solar thermal production of fuels and chemicals, with additional effort eventually required to develop the technology that is unique to each production process.

2.1 Electrochemical Hydrogen Production

The electrolysis of water is a well known technique and although present electrolyzers are relatively inefficient, a worldwide effort is underway to develop advanced methods for acid solutions (1), for alkaline solutions (2) and for the high-temperature electrolysis of steam by the use of an ion-conducting ceramic as an electrolyte (3) excellent progress is being made and it is probably not overoptimistic to project the eventual availability of electrolyzers with voltage efficiencies of 85-90 per cent. Therefore, if efficient systems for solar thermal electricity can be developed and coupled with an appropriate thermal storage unit, it should be possible to design a solar-electrochemical hydrogen plant in which the expensive electrolyzer units, as well as the power generation units, are operated in a continuous mode at near design capacity. Thus, economic solar hydrogen production might become an eventual reality even if the more promising advanced processes do not prove to be feasible.

2.2 Thermochemical Hydrogen Production

It is widely recognized that for high temperature heat sources, production processes based on thermochemical cycles can yield higher efficiences than an overall path where heat is converted to electricity and water decomposed electrochemically. Consequently, there is a worldwide effort to develop cycles to exploit the potential of thermochemical water splitting. It should be noted that the total effort is small in comparison to the effort actually necessary to develop a new technology. In addition, most of the programmatic support has been given to applied programs concerned with early selection and engineering design of a specific cycle rather than studies which might lead to the identification of better cycles. Nevertheless, several thermochemical cycles have been shown to be technically feasible and three H_2SO_4 based cycles are at a bench-scale level of development. The progress is encouraging, but in principle, more efficient cycles are possible and studies to discover and develop better cycles should continue.

For maximum efficiency, one would wish to discover and develop cycles that approximately fulfill the criteria for an "ideal" cycle for each heat source. Such criteria have been described previously (4,5) and emphasize that large entropy changes for high temperature endothermic steps permit lower maximum temperatures and also minimize the number of reaction steps required for a thermochemical cycle. Sulfate decomposition reactions exhibit large entropy changes and H_2SO_4 decomposition is a special example of sulfate decomposition. However, the decomposition of a metal sulfate to an oxide or oxysulfate is essentially an isothermal step while sulfuric acid cycles can accept heat over a wide temperature range. Thus, sulfuric acid decomposition is a better match for the heat delivery characteristics of a high temperature gas-cooled reactor. Until recently, most thermochemical hydrogen programs have considered such reactors as the "target" heat source.

2.2.1 Sulfuric Acid Based Cycles

Four different reactions for the formation of sulfuric acid have been studied for use in thermochemical hydrogen cycles. They may be described by the following equations,

$$SO_2 + 2H_2O \longrightarrow H_2SO_4 + H_2 \qquad [1]$$

$$SO_2 + 2H_2O + I_2 \longrightarrow H_2SO_4 + 2HI \qquad [2]$$

$$SO_2 + Br_2 + 2H_2O \longrightarrow H_2SO_4 + 2HBr \qquad [3]$$

$$3/2SO_2 + H_2O \longrightarrow H_2SO_4 + 1/2\ S \qquad [4]$$

In the first reaction SO_2 in solution (sulfurous acid) is oxidized at the anode and hydrogen evolved at the cathode of an electrolysis cell. This electrochemical step in the "hybrid" sulfuric acid cycle has been under extensive development at the Westinghouse Laboratory in this country (6) and at the Juelich Nuclear Research Center in Germany (7). The second equation describes the prime reaction in the thermochemical cycle under development at the General Atomic Co. (9). The reaction is conducted with excess iodine and the key result is the formation of two immiscible liquids: a relatively concentrated H_2SO_4 solution and an iodine-rich HI solution. Hydrogen formation is effected by the thermal decomposition of HI after it is separated from water. The third equation describes the use of bromine to oxidize SO_2 in solution to form quite concentrated H_2SO_4 and yield gaseous HBr. In the most fully developed version of the overall cycle, the HBr is dissolved in water and an electrolysis step is used to evolve hydrogen and regenerate bromine (9). The fourth equation actually represents equilibrium in the SO_2-H_2O system (10) and although the normal reaction rate is extremely slow, fairly rapid reaction rates can be achieved by means of catalysts. The reaction was studied at Los Alamos several years ago (11), but was tabled because methods developed for the use of sulfur in reactions to complete the cycle were not really satisfactory.

The oxygen evolution in sulfuric acid cycles results from the overall thermal decomposition of the acid as represented by the following equation.

$$H_2SO_4 \longrightarrow H_2O + SO_2 + 1/2\ O_2. \qquad [5]$$

It is important to note that all of the formation reactions listed above produce the acid in aqueous solution and excess water must be removed in an initial step. After "drying," the $H_2SO_4(\ell)$ is vaporized to form $H_2SO_4(g)$ at ∼650 - 700 K (depending) on pressure). This step requires about 40% of the total energy needed for the decomposition of $H_2SO_4(\ell)$. With increasing temperature the

H_2SO_4(g) decomposes to H_2O(g) and SO_3(g) and the SO_3(g) then decomposes to SO_3(g) and O_2(g). At the projected operating pressures (25-30 atm), a temperature near 1300 K is required for high yield. Consequently, the overall process of sulfuric acid decomposition requires heat over a wide temperature range and in this feature, is reasonably well matched with the heat delivery characteristic of a cooling gas stream, e.g. from a circulating gas-cooled reactor. However, the desired maximum temperature is higher than a realistic "process temperature" for high temperature reactors and the higher temperature available from solar thermal systems would be beneficial to all sulfuric acid cycles.

Reaction 5 above has been investigated at different laboratories. The results are in general agreement and several catalysts have been identified that are effective in promoting the final SO_3 decomposition. Extensive corrosion studies have been conducted on possible container materials for the overall H_2SO_4 decomposition process. Materials have been identified that perform adequately in tests at atmospheric pressure. It is generally agreed that the most corrosive conditions are associated with liquid H_2SO_4 at its vaporization temperature.

At the present time, workers at the European Communities Research Center in Ispra, Italy are constructing a well designed system with good instrumentation for studying the concentration and decomposition of sulfuric acid on a semi pilot plant scale (about one metric ton of H_2SO_4 per day). The system is being constructed from components that are available commercially. The acid concentration and vaporization units are constructed of a ceramic lining (bricks) inside carbon steel. Heat for the sulfuric acid vaporization step will be supplied by injecting hot air, at an initial temperature near 1075 K, into the acid in the vaporizer unit. The overall process is called "Christina" by the Ispra workers (12). The advantages cited for the process are counterbalanced by the necessity of heating and circulating relatively large volumes of air in the various process steps. In addition, the pressure of oxygen in the air suppresses the decomposition of SO_3 in the high temperature step. For example, for the assumed maximum temperature available from a reactor, only 40% of the SO_3 cycled through the Christina system is decomposed in the high temperature step. The result is a serious decrease in the overall thermal efficiency of the process

The results of the Christina experiment will be of interest and importance in the development of sulfuric acid cycles. It would be valuable to conduct sulfuric acid decomposition experiments on a similar scale utilizing heat exchanger systems in place of the adiabatic systems. It is also of value to note that the efficiency of the Christina process would increase with an increase in the maximum temperature. Thus, it might be of unique value for solar thermal systems in contrast to gas cooled reactors.

2.2.2 Metal Sulfate-Sulfuric Acid Cycles

As indicated above, one disadvantage of sulfuric acid cycles is the fact that the acid is produced in aqueous solution and excess water must be removed before the acid is vaporized and decomposed. In principle, this energy intensive step could be avoided by the formation of insoluble metal sulfate from the reaction of H_2SO_4 in solution with a metal oxide (or an oxysulfate). The dried sulfate would then be decomposed at high temperature.

The resultant procedures may be described as sulfuric acid-metal sulfate cycles. For such cycles, the "ideal" sulfate would be insoluble, would not be highly hydrated and would not require excessive temperature (excessive heat) for its decomposition. Bismuth sulfate was chosen for the first study of this type of cycle since literature data indicated that it approximated the above characteristics. The relatively high cost of bismuth is undesirable, but would be acceptable in a cycle with a reasonable recycle period. Further, of several obvious sulfates considered, bismuth sulfate appeared to be essentially the only one that would form by reaction with dilute acid and also decompose at a temperature low enough to permit reasonable coupling with a high temperature process heat reactor.

Bismuth sulfate decomposes through a series of intermediate oxysulfates rather than directly to bismuth oxide. The following equations describe the decomposition steps that are relevent to the cycle.

$$Bi_2(SO_4)_3 \longrightarrow Bi_2O(SO_4)_2 + SO_3 \qquad [6]$$

$$Bi_2O(SO_4)_3 \longrightarrow Bi_2O_2SO_4 + SO_3 \qquad [7]$$

$$Bi_2O_2SO_4 \longrightarrow Bi_2O_{2.3}(SO_4)_{0.7} + 0.3\ SO_3 \qquad [8]$$

Enthalpies for Reactions 6 and 7 were measured experimentally (13). The values are 161 and 172 kJ/mol respectively. Although the enthalpy for Reaction 8 was not determined, it should approximate that for Reaction 7 (per mole of SO_3) since the decomposition proceeds rapidly to the oxysulfate produce of Reaction 8. $Bi_2O(SO_4)_2$ is the stable sulfate in contact with sulfuric acid in the concentration range of 3.0 to 52.7 wtT at ambient temperatures. This oxysulfate contains three waters of hydration. At acid concentrations higher than 52.7 wt% the stable sulfate is $Bi_2(SO_4)_3$ with no waters of hydrogen. From such studies it is clear that there are two alternate bismuth sulfate cycles based on an initial reaction to form sulfuric acid. These may be described as Alternate I and Alternate II.

Both cycles contain an additional step for the decomposition of SO_3 to SO_2 and O_2.

ALTERNATE I

$$Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ H_2SO_4 \longrightarrow Bi_2(SO_4)_3 + 2.3\ H_2O \qquad [9]$$

$$Bi_2(SO_4)_3 \longrightarrow Bi_2O_{2.3}(SO_4)_{0.7} + 2.3\ SO_3 \qquad [10]$$

ALTERNATE II

$$Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ H_2SO_4 \longrightarrow Bi_2O(SO_4)_2 + 1.3\ H_2O \qquad [11]$$

$$Bi_2O(SO_4)_2 \longrightarrow Bi_2O_{2.3}(SO_4)_{0.7} + 1.3\ SO_3 \qquad [12]$$

Alternate I requires higher strength sulfuric acid, but for each mole of SO_3 finally decomposed, requires a lower bismuth inventory and less energy for drying the solid sulfate. However, the fact that the solid retains significant quantities of solution (that must be removed by evaporation) seriously degrades the advantages of metal sulfate cycles based on high strength acid.

Alternate II requires lower strength sulfuric acid. Its potential advantage would be in combination with the hybrid sulfuric acid cycle and depend on the possibility that significantly lower voltages would be required in electrolyses to form dilute acid. Up to the present time, such lower voltages have not been realized in the electrolysis of SO2 to form dilute acid in comparison to electrolysis in more concentrated acid. Therefore one may conclude that additional development will be required before the advantages of metal sulfate-sulfuric acid cycles are actually realized.

2.2.3 The Magnesium Sulfate-Iodide Cycle

For several years, efforts at Los Alamos and other laboratories have been directed toward the development of sulfate cycles that do not include the formation of sulfuric acid as an intermediate step. Such efforts have been largely unsuccessful. However, in recent studies at Los Alamos, reasonable yields have been achieved at a temperature of 425 K for a reaction in which gaseous iodine was employed to oxidize $MgSO_3$ in the presence of excess MgO and yield solid $MgSO_4$ and solid MgI_2 (14). The reaction may be described by the following equation

$$MgSO_3 \cdot YH_2O + MgO + I_2(g) \longrightarrow MgSO_4 + MgI_2 + YH_2O(g) \qquad [13]$$

the $MgSO_3 \cdot 6H_2O$ used in the experiments was partially dehydrated at the temperatures and the possible role of water vapor in reaction 13 remains to be determined. Nevertheless, reasonable yields have been achieved and additional reactions confirmed (in our Laboratory or in other laboratories) for a sulfate based cycle that does not include solutions as intermediates. The cycle is closed by the hydrolysis of MgI_2 (in the presence of $MgSO_4$) to form HI which is then thermally decomposed to give hydrogen and iodine.

2.2.4 Oxide Based Cycles

With the development of solar thermal systems as viable heat sources for thermochemical water splitting, it is apparent that cycles based on solid oxide decomposition as the high temperature step may offer unique advantages for coupling with a solar furnace, since the oxide can be heated and decomposed in air at temperatures where the oxygen dissociation pressure exceeds the pressure of oxygen in the atmosphere. Thus, the oxide could be heated directly by solar radiation entering through an "air window" and the difficult problem of transmitting heat to the process, either through a container wall or a quartz window, might be greatly simplified. Therefore, studies have been initiated to determine practical conditions for the low-temperature steps in oxide cycles. Oxide decomposition reactions are also being evaluated in rotary kiln and fluidized bed systems. Some of the decomposition reactions being considered (and decomposition temperatures) are:

$$3Fe_2O_3 \longrightarrow 2Fe_3O_4 + 1/2\ O_2\ (\sim 1800K) \qquad [14]$$

$$2CuO \longrightarrow Cu_2O + 1/2\ O_2\ (\sim 1350K) \qquad [15]$$

$$Co_3O_4 \longrightarrow 3CoO + 1/2\ O_2\ (\sim 1225K) \qquad [16]$$

$$3Mn_2O_3 \longrightarrow 2Mn_3O_4 + 1/2\ O_2\ (\sim 1225K) \qquad [17]$$

$$2MnO_2 \longrightarrow Mn_2O_3 + 1/2\ O_2\ (\sim 800K) \qquad [18]$$

One method for promoting low temperature reactions in oxide cycles involves the use of iodine in the general reaction:

$$MO + M'O + I_2 \longrightarrow MO_2 + M'I_2(aq). \qquad [19]$$

Available thermochemical data indicate that such reactions could occur where $Mg(OH)_2$ represents M'O, although in some cases they depend on the large heat of solution of MgI_2. In general, the lower the decomposition temperature (and concurrent lower requirement for high temperature heat), the larger the energy required to concentrate, dry and dehydrate the iodide solutions. Such steps are energy intensive and lead to lower efficiencies. Nevertheless it seems probable that the advantages of oxide cycles (particularly for solar heat) will overshadow the disadvantages of the solution chemistry. In some cases, it might be feasible to minimize overall energy requirements by utilizing iodides with lower heats of solution or by using alternate solvents.

Experimental studies are being made with cobalt oxides as the first example of the class of oxide cycles outlined above. The complete cycle may be descirbed by the following equations:

$$3CoO + Mg(OH)_2 + I_2 \longrightarrow Co_3O_4 + MgI_2(aq) + H_2O(\ell) \qquad [20]$$

$$MgI_2(aq) \longrightarrow MgI_2(s) \qquad [21]$$

$$MgI_2(s) + H_2O \longrightarrow MgO + 2HI \qquad [22]$$

$$2HI \longrightarrow H_2 + I_2 \qquad [23]$$

$$Co_3O_4 \longrightarrow 3CoO + 1/2\ O_2 \qquad [24]$$

$$MgO + H_wO \longrightarrow Mg(OH)_2 \qquad [25]$$

All of the reactions have been tested and, except for reaction 20, occur rapidly and in good yield. Up to the present time, reaction rates achieved for this reaction are too slow for a practical cycle. Future work will involve attempts to accelerate the low temperature reaction in the cobalt oxide cycle, as well as testing similar reactions in the other oxide systems.

3. SOLIDS DECOMPOSITION TECHNOLOGY

Thermochemical cycles based on solid decomposition reactions are well suited for use with a high temperature isothermal solar heat source such as solar. However, the validation of such cycles should include the development and testing of methods for the practical utilization of solid decomposition reactions at high temperature. Consequently, a laboratory-scale rotary kiln was constructed and used in studying the decomposition of different solids. The results suggest that these high temperature reactions are very rapid. For example, for a residence time of only one minute in the "hot-zone" of the kiln, $Bi_2O(SO_4)_2$ was 96% decomposed at 1123K, $ZnSO_4$ was 92% decomposed at 1283K and Co_3O_4 100% decomposed at 1283K. These results suggested that fluidized bed systems would be well suited for the reactions under consideration.

Attempts to study $Bi_2O(SO_4)_2$ decomposition in a fluidized bed system were unsuccessful since these sulfate particles would not fluidize satisfactorily. Therefore, a dual-particle fluidized bed system was conceived for the high temperature decomposition reactions. In this system, a bed of spherical particles of ZrO_2 approximately 450 micrometer diameter is fluidized with argon. The argon also serves as a carrier gas to transport smaller particles of the powder to be decomposed to and through the bed. A screw feeder is used to meter the powder. The decomposed material is collected down stream in a cyclone separator.

The dual-particle fluidized bed concept was tested by studies of $ZnSO_4$ decomposition. In these experiments, a constant flow of argon carrier gas (0.2 mol per minute) was passed through the fluidized bed. The quantity of $ZnSO_4$ was varied to obtain different mol ratios of carrier gas to sulfate feed. Temperatures were measured by means of a thermocouple on the exterior of the quartz tube containing the fluidized bed. The results from two deries of experiments are summarized in Table 1.

TABLE 1

Bed. Temp. (k)	Ar/Sulfate mol ratio	Sulfate Decomp. %
1175	55	55
1175	17	33
1175	11	26
1225	55	85
1225	22	61
1225	11	48

The extent of decomposition was obtained by analysis of the solid product trapped in the cyclone separator. The mean residence time for the $ZnSO_4$ in the fluidized bed was less than one second.

The fluidized bed experiments indicate that high temperature solids decomposition reactions can be coupled effectively with high temperature isothermal heat sources available from developing solar thermal technology. For sulfate decompositions, a mixture of SO_3, SO_2 and O_2 would be utilized as the fluidizing gas. For oxide decompositions, air could be used to heat and fluidize the powder.

4. CONCLUSIONS

The use of solar thermal energy to produce hydrogen from water is an attractive concept that merits continuing effort in attempts to develop a practical technology. Much of the base technology in concentrators and receiver systems already developed for solar thermal power production will be applicable to hydrogen production processes. Improvements in base technology will continue to be applicable. For example, energy storage for electric systems will also be valuable for thermochemical hydrogen production since all such processes involve low to intermediate temperature steps that require almost continuous operation. Specific technology for the transfer of heat from the solar receiver to the chemical process is an area for additional development. Some promising techniques have been identified, however, and progress already made on thermochemical hydrogen cycles indicates that the processes can be coupled effectively with solar heat.

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