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Nonbiological Photochemical Energy Conversion—Can It Compete?*

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Solar photochemical energy conversion has much in common with solar thermal energy conversion systems. As a result, it is not to be expected that photochemical systems will be much less expensive than solar thermal systems. Since direct fuel production is unique to the photochemical system, the most promising application areas are in those sectors such as transportation that have particular needs for fuels. The results of an analysis of a combined photovoltaic/thermal system applied to meeting a community energy demand is reported.

Introduction

Supplies of fossil fuels, once considered essentially infinite, now are not only limited but indeed, rapidly diminishing. Except for coal, reserves for all fossil fuels are expected to be unable to match world demand in the near future. Thus, there is at present, a major shift in energy consumption patterns. Table I reflects the current shifts taking place in one sector. The decreasing availability of traditional energy sources is clearly being felt as reflected not only in prices but also by energy consumption practices. Even while the cost of oil has risen over 800% since 1965, Southern California Edison has shifted most of its energy consumption to the more expensive imported oil due to the unavailability of other equivalent fuels. The need for expanding the alternatives to traditional energy sources is obvious.

While current practice is to switch from less available to more available energy sources, there is a distinct need to establish new energy sources. While coal, for example, is apparently plentiful, it too is nonrenewable and may also not be a suitable replacement for gas and oil in all energy consumption sectors. Direct coal burning, to some extent, may accurately be considered as a buffer, providing time to allow development of new energy sources. The objective of this paper is to investigate the potential for nonbiological photochemical solar energy conversion as one source of future energy resources.

TABLE I

ENERGY CONSUMPTION BY SOUTHERN CALIFORNIA EDISON 1965–1975

	Prices ($\$/10^6$ BTU)		Energy Consumed (%)	
Energy Form	1965	1975	1965	1975
Gas	0.31	0.87	78	16
Oil	0.326	2.671	22	60
Coal	—	0.30	—	18
Nuclear	—	0.17	—	6

What is Photochemistry?

Photochemistry may be construed in a most general sense to be simply light-induced

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chemistry. This would encompass any chemical reaction sequence initiated or promoted by light even if the primary action of the light were simply conversion to thermal energy followed by thermochemical activation. However, photochemistry is defined here as the chemistry of molecules in their excited electronic states where quantum-mechanical photon absorption is the mechanism for excitation. It is this quantum mechanism which provides photochemistry its greatest potential and most serious limitation for solar energy conversion. The goal of photochemistry is to produce excited molecular states through the absorption of light and then to allow these excited metastable species to undergo chemical reaction with a minimal loss of energy to form stable molecules having high chemical potential.

The absorption of a 700-nm photon of visible light, for example, by a molecular system is equivalent to increasing the energy of that molecule by 40.8 kcal/mole. This process is not only highly endoergic, but frequently occurs only in particular bonds or moieties of the molecule leaving the rest of the molecule unaffected. Thus, photochemistry provides a very nice mechanism for inducing high-energy chemical reactions in isolated parts of a molecular system. Equivalent thermal activation of a bond within a molecular system would require temperatures in excess of 1000°C. Also, since thermal activation is nonselective and affects all bonds within a molecule, high temperatures might well lead to undesirable bond rupture within a molecule. Thus, photoactivation can provide a means by which high-energy chemistry may be carried out in a chemical system in a uniquely controllable fashion at ambient temperatures. It is perhaps this capacity to capture and use high energy at ambient temperatures that gives photochemistry its greatest impetus for solar energy conversion.

While the photochemical quantum process provides a mechanism for carrying out high-energy chemistry at low temperatures, the quantum process also carries with it inherent limits to efficiency of solar energy conversion. If a given excited electronic state (usually the lowest electronic state) gives rise to a photochemical reaction then only energy equal to the energy of this state above the ground state can contribute to promoting the photochemical reaction. In other words, if we are speaking of energy-storing photochemical reactions, the absolute maximum quantity of energy which can be stored is that energy equal to the energy of the photoactive state above the ground state. This means, that in the area of solar energy conversion, only light within the solar spectrum more energetic than the photoactive state can promote photochemistry.

In addition, although any photon with energy in excess of the photoactive state's energy may promote the photochemical reaction, it can contribute only that quantity of energy equal to the energy of the photoactive state; energy in excess of this is lost. Thus, a quantum activation process such as light absorption must reject considerable quantities of energy in the conversion process. Bolton (*2*) has analyzed the conversion efficiency of photochemical systems incorporating quantum effects as well as other conversion efficiency limitations. He has determined that an optimistic efficiency for photochemical energy storage would be on the order of 15%. Said differently, one can expect to store at most 15% of the energy available in the solar spectrum incident on the Earth's surface through an endoergic photochemical reaction.

A Photochemical Reactor

Basically, the objective of a photochemical energy system is to deploy a photoactive material over a widespread area and then return the photoproduct to some centrally located point for use. This requires widely dispersed interconnected hardware capable of withstanding severe environmental effects. Actually, this is the basic objective of all solar

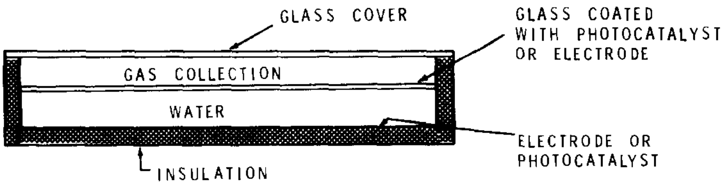

FIG. 1. Flat plate photochemical hydrogen reactor—baseline design.

energy systems and it should be expected that a photochemical system would not really differ significantly in function from a solar thermal system. For the sake of discussion, the photochemical production (*3*) of hydrogen is used as an example system.

Perhaps the most easily visualized photochemical converter concept is that of a flat plate reactor. In such a system, the reactor would remain fixed and would not incorporate any type of light concentration device. A baseline design of such a reactor might look similar to the reactor shown in Fig. 1.

This minimal design incorporates the basic components needed by a photochemical hydrogen reactor. These include an H_2 gas manifold (including a membrane to separate H_2 and O_2 if necessary), insulation to protect against undesirable temperature fluctuation in the external surroundings, transparent electrode (or photocatalyst), counter electrode (or photocatalyst), and liquid flow manifold to replenish the photoreactant (i.e., the water). While the variations on this basic design are basically limitless, the point is that a photochemical hydrogen reactor is functionally very similar in construction to a low-temperature solar thermal collector.

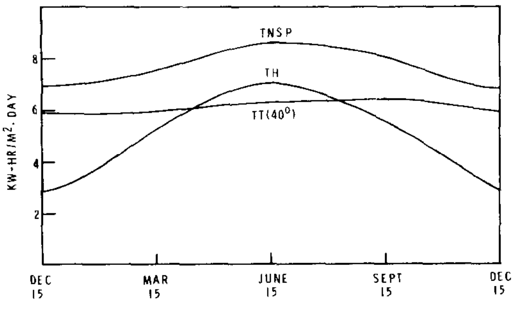

FIG. 2. Mean daily energy available in Albuquerque, NM (*4*). TNSP—Polar mounted tracking flat plate. TT—Fixed plate inclined 40°. TH—Fixed horizontal flat plate.

It is worth noting, at this point, the penalty paid in solar availability when a flat solar collector is placed on the ground and not moved throughout the day to follow the sun. Figure 2 shows the amount of solar energy available on a fixed flat plate (both horizontal and tilted 40° up from the horizontal) and the energy available to a flat plate which tracks the sun. It is clear that the loss of energy availability due to nontracking is significant.

In addition, given the potential high cost of semiconductor electrodes, semipermeable membranes, etc., which may be contained in a photochemical cell, light concentration devices seem to make sense in order to reduce the cell size. Currently, there seems to be relatively little difference between concentrating and flat plate solar thermal collector costs. Colorado State University has executed a study of the cost of various distributed concentrating collector concepts. Table II lists the component cost of a typical parabolic trough collector. The receiver tube (which would be replaced by the reaction cell in a photochemical system) constitutes about 5% of the cost of the collector. Ninety-five percent of the collector cost is for that part of the system which brings the light to focus on the receiver; these costs should remain essentially constant in going to a similar photochemical collector. Given the potential advantages of tracking concentrators, it seems reasonable to suggest that a photochemical collector of the type shown in Fig. 3 might be used.

The point of the above discussion is that, while photochemical conversion is considerably different from solar thermal conversion, the basic reactor hardware system will prob-

TABLE II

ITEMIZED COSTS FOR THE SANDIA PARABOLIC TROUGH AS MODIFIED BY WESTINGHOUSE AND COLORADO STATE UNIVERSITY

	$/m^2 (Projected area)	
Item: installed cost, without absorber	2.13 m width ($)	4.26 m width ($)
Materials		
Shell (honeycomb core)	15.90	17.50
Reflective surface (back-silvered glass)	3.40	3.40
Drive (motor, gear reduction, shafts)	27.70	30.60
Sensor	1.20	0.60
Labor and overhead to manufacture	11.30	11.40
Base and related hardware	4.80	6.20
Foundation	15.70	10.60
Transportation	1.40	1.50
Installation	8.00	8.00
Subtotal	89.40	89.80
Contingency (5%)	4.50	4.50
Total	93.90	94.30
Absorber (90 kg/cm^2)	(2.5 cm)	(5.1 cm)
Materials		
Carbon steel tube	0.50	1.00
Borosilicate glass tube	0.30	0.60
Flexible couplings	1.60	1.60
Other	0.50	0.60
Labor and overhead to manufacture and installation	1.90	3.00
Subtotal	4.80	6.80
Contingency (5%)	0.20	0.30
Total	5.00	7.10
Grand total	98.90	101.40

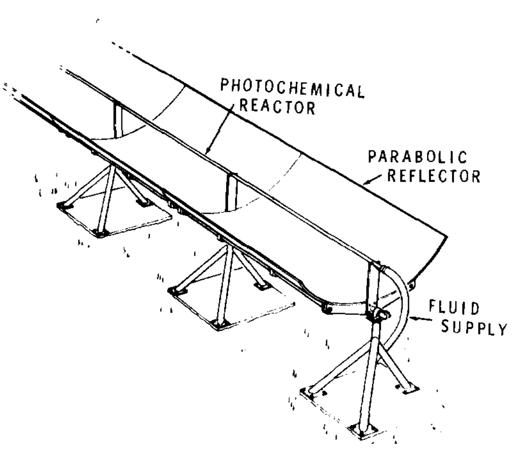

FIG. 3. Basic design of parabolic trough collector.

ably be similar to designs now evolving for solar thermal collectors, either nonconcentrating flat plates or concentrating collectors. Thus, a photochemical collection system will probably not be less expensive than solar thermal collection systems and, indeed, may be considerably more expensive given their added complexity of providing an enviroment for chemical reactions. In addition, it is reasonable to expect the maintenance of a photochemical system to be higher than a comparative solar thermal system since the photoactive material will undoubtedly require periodic replacement. If, for example, a photochemical cell 1 cm thick contains a photoactive material with an average ε of 10^4, 1.2×10^{21} molecules would be contained in each square meter of cell assuming 99% absorption. Since the photon flux (*6*) at the surface of the earth is approximately 10^{21} photons/sec/m^2 each molecule will, on the average, be excited each second or 28,800 times per day in a perfectly tracking system. Thus, if one photoactive molecule in 10^9 did not return to its original form after the photoreaction, the photoactive material would degrade at the rate of 3% per year.

Application Areas

Perhaps the primary area of interest in photochemical energy conversion is the storage of light energy in the form of some sort of chemical fuel. This chemical fuel may then be used as needed in transportation, heating and cooling, power generation, or for other energy consumption. This section examines areas of solar utilization to determine if photochemically produced fuels may play a role.

One area in which a photochemically produced fuel, such as hydrogen, might be used is in the generation of electrical power. It is doubtful, however, that such applications would ever find widespread favor. This process would involve at least two inefficient processes; one is the 10% (*2*) efficient photoproduction of H_2 and another is the 30–35% efficient thermodynamic generation of electricity by burning H_2. This would yield an overall conversion efficiency of solar energy to electricity of about 3–4%. Even if an H_2/air fuel cell (50% efficient) were employed for power production, the solar to electric conversion efficiency would be only 5%.

On the other hand, current predictions for the conversion of incident solar energy to electric power in a solar thermal system is from about 15 to 25% assuming 55–70% collection efficiency. Neither of these solar to electric conversion efficiencies include the geometric solar losses due to nonperfect tracking of the sun. Thus, they represent the best that can be done assuming that the collection techniques for both the photochemical and solar thermal systems are equivalent.

In summary, the above simply points out that one cannot afford to introduce an inefficient two-step process in place of a one-step process just for the sake of generating a fuel. While the generation of a fuel implies a ready mechanism for energy storage, the price for this convenience may be too high. Any photochemical storage mechanism will have to compete with other techniques such as sensible, latent, and thermochemical heat storage. It is estimated that energy storage will find only limited use unless the extra cost to the solar plant for providing storage increases the produced energy cost by less than 20%. From the point of view of large-scale electric power production, the most immediate application of solar power is for intermediate and peaking power plants which would require minimum storage. Solar power may not significantly impact baseload power production for a long time to come (*7*). Since, as we have discussed above, a photochemical system would not be less expensive than the equivalent solar thermal system, it is hard to see how photochemical solar power generation would find significant large-scale utilization.

In order for a photochemical energy conversion system to complete effectively, it must exploit its unique capability to produce a fuel. One area in which fuels fulfill a unique requirement is in the field of transportation. The transportation complex within the U.S. is highly dependent upon fuels which store large densities of energy. Fuels, for light-weight, high-compact energy storage are unsurpassed. In addition, the transportation sector has traditionally been willing to pay higher prices for fuel energy than other sectors. For example, natural gas currently sells at about \$1.30/GJ in Albuquerque, while gasoline sells at about \$4.00/GJ (i.e., \$0.50/gal). Much has been written about the advantages of hydrogen fuel in transportation (*8*).

Given the rather low photochemical conversion efficiency, systems which maximize the utilization of the solar energy incident on the

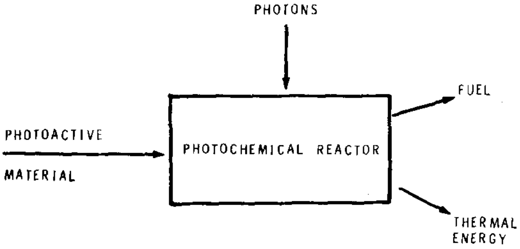

FIG. 4. Photochemical/thermal solar energy utilization.

collector should be devised. Solar total energy systems employing not only the electricity generated by a solar thermal power generation facility, but also the rejected thermal energy for heating and cooling have been studied (*9*). Such systems increase the overall utilization of collected thermal energy from 25 to 35% for electric-only systems to about 70% for the total energy systems. A similar technique for a solar photochemical fuel production system can be used to increase its cost effectiveness.

Since it would be advantageous to utilize fuel as the product of the photochemical conversion process, the concept shown in Fig. 4 which produces both fuel and low-temperature thermal energy was studied. In order to produce useful thermal energy, the photochemical cells must be operated near 60°C (140°F) if space heating is desired and near 93°C (200°C) if cooling is to be provided using an absorption chiller. This basic system was applied to a hypothetical community located in Albuquerque, New Mexico, previously studied with respect to applications of solar total energy (*10*). As done with the total energy system, the photochemical system was sized for maximum solar energy utilization by designing the system to meet the winter thermal demand. The energy needs of that community are reported in Table III.

The collector area needed to service this community's thermal energy needs (based on an average winter day) was computed to be about 49,000 m^2 based upon parabolic troughs mounted on an E–W axis operating at 60°C. The average daily energy intercepted by an E–W tracking parabolic trough is about 19.8×10^6 J/m^2. Thus, on the average, the 49,000 m^2 collector field receives approximately 976 GJ/day of solar insolation. Bolton (*2*) has estimated that for hydrogen production, 10% of the solar energy would be converted to hydrogen bond energy. Thus, the above system might produce 98 GJ/day of hydrogen. A recent analysis (*11*) of fuel consumption by urban communities reports that the average fuel consumption for automobiles in Texas communities with population densities similar to the hypothetical community under study here is about 300 gal/year/per person which converts to 820 GJ/day for the entire community. Thus, a combined photochemical/thermal generating H_2 gas could provide roughly 12% of the fuel energy a 2000-dwelling unit community needs for transportation.

Conclusion

Photochemical energy conversion—can it compete? It depends!

TABLE III

AVERAGE DAILY COMMUNITY THERMAL LOADS (GJ)

	SFD (139m²)			SFA (116m²)			LR (850m²)			HR (113m²)			3 Schools (7587m²)			Commercial (7432m²)		
	Heat	A/C	HW	Heat	A/C	HW	Heat	A/C	HW	Heat	A/C	HW	Heat	A/C	HW	Heat	A/C	HW
Spring	78.6	0	32.9	67.1	0	52.9	27.1	0	31.4	22.9	0	14.3	4.3	0	1.1	2.9	0	0
Summer	0	112.9	27.1	0	111.4	42.9	0	54.3	25.7	0	28.6	11.4	0	0	0	0	15.7	0
Fall	2.9	1.1	25.7	0	1.3	40.0	0	0.6	24.3	0	0.1	11.4	0	1.0	0.9	0	1.0	0
Winter	129.2	0	32.9	104.3	0	52.9	47.1	0	31.4	37.1	0	14.3	8.6	0	1.1	4.3	0	0
Year	52.7	28.5	29.7	42.9	28.2	47.2	18.6	13.7	28.2	15.0	7.2	12.9	3.2	0.3	0.8	1.8	4.2	0

SFD = 504 Single Family Detached Dwelling Units
SFA = 800 Single Family Attached Dwelling Units
LR = 480 Low Rise Dwelling Units
HR = 216 High Rise Dwelling Units

From a system point of view, photochemical solar energy conversion should be relatively similar to solar thermal systems. Thus, in an area such as power generation, solar thermal systems can be expected to strongly compete with photochemical concepts. Since photochemical systems are expected to be less efficient and probably more complex than an equivalent solar thermal system, photochemical systems probably will not see much penetration in electrical power generation if indeed solar penetrates this market at all. Photochemical systems must exploit their unique ability for direct production of fuel as well as maximize utilization of the solar energy collected to achieve cost effectiveness.

A solar photochemical fuel/thermal combined system can increase the utilization of a solar system to 60–70%. Such a system operating at elevated temperatures can provide most of the thermal needs (heating, cooling, and hot water) of a community, as well as provide 10–15% of the fuel needs for transporting within the community. Similar systems, providing industrial process heat could also be formulated. Such systems might service a large percentage of an industrial process heat demand and also provide a fuel which might be used internally or sold. In addition communities in colder climates than Albuquerque (the site of the analysis) would have higher demands for thermal energy and thus be able to beneficially use photochemical/thermal systems generating more fuel and thermal energy. For example, Omaha, Nebraska, with 6612 heating degree days would require almost 50% more space heating energy than Albuquerque (4348 heating degree days) without much reduction in the solar intensity available to a tracking solar collection system (*4*). Thus, a solar photochemical/thermal system in Omaha designed to meet the winter thermal needs of a community would produce considerably more fuel for community use than the Albuquerque design.

Perhaps the largest problem facing any photochemical system is the stability of the photoactive species. Enzymatic catalysts seem remarkably stable in controlled environments. However, industrial catalysts have relatively short lives. Unless the photoactive species are stable over many cycles of photoactivation–reaction-regeneration, replacement of the photospecies will be prohibitively expensive. This is perhaps an advantage of the self-synthesizing biological photosystems over man-made systems. The outlook for biological systems has been reviewed by Pollard (*12*).

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