outcome will depend on the policy decisions of governments as well as on institutional and financial factors and, in the United States, on how the oil and mining companies and the utilities react to the problems and challenges of geothermal energy development. In other countries, particularly developing countries, where the separation between the sectors of the economy engaged in resource development and in electric power generation may not be so clear-cut, or where the state is itself more active, geothermal resources may have a part to play in substituting at lower cost for oil, coal, or nuclear fission to meet future energy needs.

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10. This is the average investment per initial daily barrel delivered to a loading terminal in the Persian Gulf. An investment of roughly $38 per kilowatt in tanker capacity is required to deliver oil to the United States, but this investment need not be made by the company which produces the oil.
11. This is the average investment per initial daily barrel of U.S. onshore oil. Prices are from Adelman (*9*).
12. It is assumed that the average geothermal well costs $150,000 and delivers a steam production equivalent to 5 Mw, that the ratio of drilling to total development costs is 1/1.6, and that 60 percent of the wells drilled are producers.
13. W. M. Gilchrist, *Mining Eng. (N.Y.)* **21**, 30 (1969). The investment cost in mine development and mining plant construction is taken to be $20,000 per annual ton of $U_3O_8$ produced. A burnup of 3,000 megawatt-days per ton of uranium, a ratio of 1.7 tons of uranium per megawatt electric of generating plant, and a generating plant load factor of 0.75 are assumed. The cost of supplying the initial charge of unenriched uranium, in a form suitable for use in a reactor, is about $50 per kilowatt. See, for example, L. R. Haywood, J. A. L. Robertson, J. Pawliw, J. Howieson, L. L. Bodie, *Proc. U.N. Int. Conf. Peaceful Uses At. Energy 8th* (1972), pp. 185–214.

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# Solar Energy by Photosynthesis

Melvin Calvin

As we run out of the stored energy which oil, natural gas, and coal represent (*1*), the question arises as to whether we can make use of solar energy. In order to make some estimate of this possibility, we must evaluate the magnitude of the solar energy resource. The highest yearly averaged impingement is in the region of the Sahara Desert [~ 280 watts per square meter (*2*)], and there is another high-intensity region in the southern United States and Northern Mexico (about 260 watt/m$^2$). Let's relate that to the solar energy constant, that is, the total energy of the sun coming in at normal incidence outside the earth's atmosphere, which is about 2 calories per square centimeter per minute or 1 kilowatt per square meter. Only about half of that reaches the earth's surface, and this amount varies considerably, depending upon the weather conditions. The annual average insolation in the United States, taking into account the variability over day and night, winter and summer is shown in Fig. 1. The region within the contour line at 260 watt/m$^2$ consists of most of New Mexico and Arizona with parts of Nevada and Southern California. The other high points are in southern Florida and in southern Louisiana. The potential contribution of photosynthesis to the collection of solar energy merits consideration. Let us examine the photosynthetic process as such and the technologically constructed systems modeled on what we know of the natural photosynthetic apparatus. I suggest two such model systems for the direct photoconversion of the quantum into useful energy, one of them to produce storable energy (probably in the form of hydrogen), and the other to use a synthetic system based on the concepts of the structure of biological membranes, the converted quantum being taken off as electrical potential.

While the hydrogen proposal and experiments are not biological photosynthesis, they are based on what we know about the photosynthetic process (*3*). It is a "synthetic" system, in which we expect to sensitize the photodecomposition of water to hydrogen and oxygen. The hydrogen can be a fuel that can be used in various ways. The harnessing of solar energy by a natural quantum collection process includes the generation of hydrogen or the reduction of carbon dioxide. The normal way for the quantum to be used in photosynthesis is in the reduction of carbon dioxide.

Roughly 6 percent of the energy use in the United States is for the production of chemicals or materials. For this purpose, power generation or hydrogen production can be only adjuncts: only reduced carbon can contribute directly in making materials and chemicals. I therefore distinguish between the materials and fuel. The photochemical system, as now conceived, can produce only hydrogen, whereas photosynthesis itself can produce either hydrogen or reduced carbon.

## Biological (Agricultural) Photosynthetic Conversion of Solar Energy

The biological model that is the conceptual source of these two processes (*4*) is both the green plant and bacterial photosynthesis as we have learned to understand it in the last 20 years, a generalized scheme of which is shown in Fig. 2. The green part of the plant, represented in the center, is absorbing the sunlight and separating the positive and negative charge. The positive and negative charge can be used by the

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enzymatic apparatus of the green plant. The hydrogen atoms representing the negative charge can be used to reduce carbon dioxide and generate sugar; and the positive side represented by oxygen atoms can be used to oxidize water and generate molecular oxygen. The center of the diagram is the quantum converting apparatus. The carbon reduction cycle (the large circle on the outside) uses the primary reducing power produced in the chlorophyll-containing part of the plant to reduce the carbon dioxide (*3*). After the entry of carbon dioxide into the photosynthetic carbon cycle all the various plant components are synthesized (fats, hydrocarbons, proteins, carbohydrates, amino acids, nucleic acids, and others). One can use the information about the two parts of the photosynthetic process—the photochemical generation of [H] (which indicates chemical reducing power) and [O] (which indicates chemical oxidizing power) and carbon reduction—in two separate ways.

The photosynthetic carbon reduction cycle can be used as an energy source and as a material source (*5*). It does not seem possible to use the photoelectric system directly for a material source. It generates electric power, or hydrogen, neither of which are substances from which needed *materials* can be constructed. These materials represent primarily the chemicals and other nonenergy items that constitute about 6 percent of our total energy requirement (the equivalent of about 2 million barrels of crude oil per day).

One way of beginning to examine the photosynthetic cycle as an energy and material source is to inquire about the natural photosynthetic productivity in terms of reduced carbon that is spread over the earth's surface. The greatest production of reduced carbon is mainly along the equator; not the areas of the earth where the highest insolation occurs, but, rather, where the best conditions for year-round growth exist. The equatorial areas grow a very large amount of natural vegetation because of the presence of water. The overall annual production is of the order of 1 kilogram of carbon per square meter per year, mostly in the form of sugar. I say "mostly in the form of sugar" because the principal product (generally about 50 percent) of plant photosynthesis is carbohydrate.

When that fact is realized, we should then ask ourselves which plants are capable of raising that productivity

Table 1. Fermentation of alcohol: efficiency and price. $\Delta H$, heat of combustion; pound ~ 0.45 kg; gallon ~ $3.8\ 10^{-3}\ m^3$; Btu ~ $1.06 \times 10^3$ joules.

| Sugar | Ethanol |
|---|---|
| $C_6H_{12}O_6$ | $2\ C_2H_5OH + 2\ CO_2$ |
| 180 g | 92 g |
| $\Delta H$ 673 kcal | 655 kcal |
| 12.88 pounds ⟶ | 1 gallon (84,356 Btu) |
| at 5 cents per pound ⟶ | 64 cents per gallon |
| | + ~ 20 cents process cost |
| Petroleum ⟶ | ethanol |
| | (domestic) 55 cents per gallon (controlled)* |
| | foreign > $1 per gallon |

* Not available in San Francisco area.

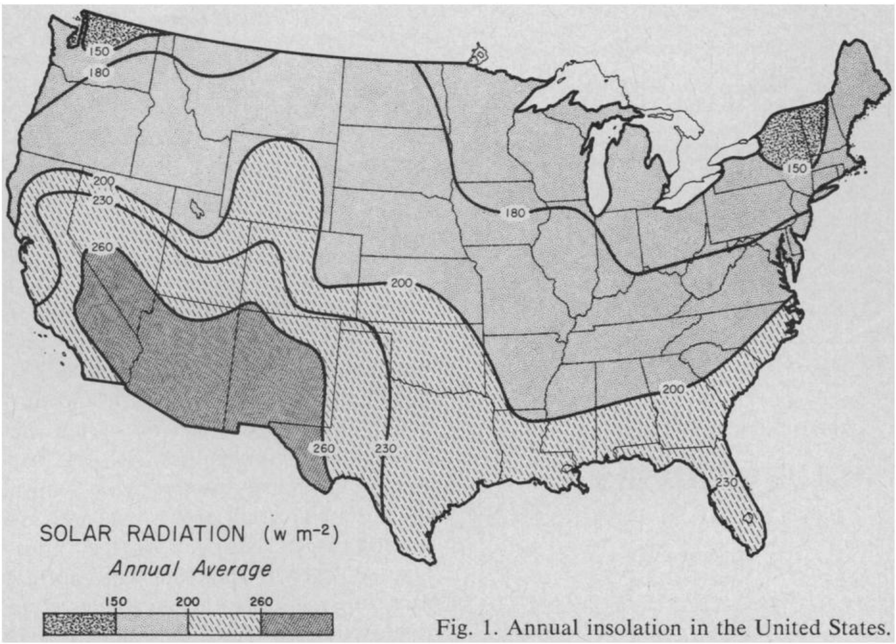

Fig. 1. Annual insolation in the United States.

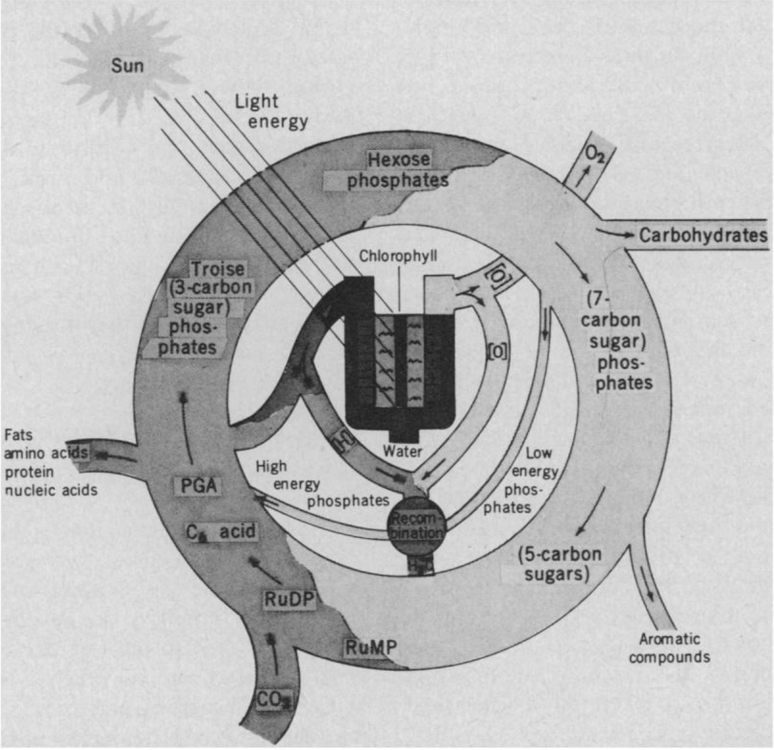

Fig. 2. Photosynthetic conversion of sunlight to energy and reduced carbon. Abbreviations: PGA, 3-phosphoglyceric acid; RuDP, ribulose 1,5-diphosphate; ribulose 5-monophosphate; [H], chemical reducing power; [O], chemical oxidizing power.

from 1 kilogram of carbon per square meter per year to something more useful. The natural efficiency is very low, a few hundredths of a percent. There is little doubt about which type of plants to use. The principal plant known today which has the highest yield of yearly, averaged photosynthesis is sugarcane (*6*). The overall efficiency is about 0.6 percent and this will be compared with several other types of plants later.

I want to suggest the use of sugar as an industrial raw material and also to suggest its end uses. You could burn sugar—it is carbohydrate, as is cellulose, and has the same caloric content. However, there are more efficient methods than burning, and one is to convert the sugar and cane cellulose into alcohol. In this process (shown in Table 1), the thermal efficiency is very good, with practically no loss in going from sugar to alcohol. It takes 12.9 pounds (1 pound ~0.45 kilogram) of sugar to make 1 gallon of alcohol, that is, 64 cents worth of sugar at 1971–1972 price of sugarcane to make 1 gallon of alcohol. It costs about 20 cents to convert the sugar, making a total of 84 cents per gallon for alcohol by fermentation. Today (January 1974) the controlled price of the petroleum source alcohol is 66 cents per gallon, if you can find any. However, the actual offshore price for petroleum source alcohol is more than $1 per gallon. The reason for presenting these numbers is that at a price of 85 cents per gallon for fermentation alcohol, even on a thermal basis, if nothing else, we are already nearly economic in the use of alcohol, at least as an additive to fuel gasoline. These sources are coming closer economically.

As an illustration of how the economics of this kind of chemistry has affected the sources of alcohol in the last 50 years, the industrial ethyl alcohol production since 1940 is shown in Fig. 3. From 1940 to 1945 (during World War II) the alcohol was made mostly by fermentation from molasses, sulfite liquors, and grain (natural sources of carbohydrate). When petroleum became available as a cheap source of alcohol around 1950, it took over, entirely, the alcohol market. Ethylene is obtained by cracking liquid hydrocarbon and hydrating the ethylene to make ethanol. The fermentation sources of ethanol disappeared entirely after 1960 because ethylene was only 2 cents per pound, and the conversion cost was very small.

Table 2. Annual productivity for *Hevea* (rubber), cane, and beet crops.

| Crop | Yield |
|---|---|
| *Hevea* | 1 ton of rubber per acre |
| Cane | 4 tons of sugar per acre<br>2 tons of ethanol<br>1.2 tons of ethylene<br>$68 \times 10^6$ Btu (0.23 percent of incident sun)<br>4 tons of bagasse per acre |
| Beet | 2 tons of sugar per acre<br>0.7 ton of pulp per acre |

The price of ethylene is roughly of the order of 10 cents per pound and rising, whereas a year or two ago it was around 2 cents per pound. Thus, the economic facts of high price and scarce supply have brought back the possibility that fermentation alcohol could become a significant source of hydrocarbon (Table 2).

Sugarcane makes 4 tons of sugar per acre (1 acre $\sim 4.05 \times 10^3$ square meters) per year, from which is obtained 2 tons of ethanol and 1.2 tons of ethylene, with an overall efficiency of 0.23 percent of incident sunlight, if only the sucrose is counted. There is, however, an equal amount of cellulose in the cane, in the form of bagasse (the cellulose residue of the sugarcane), with a yield of 4 tons of bagasse per acre per year. The total therefore appears to be 8 tons of carbohydrate per acre of cane, raising the efficiency of solar energy conversion (agricultural solar energy conversion) for cane to about 0.5 percent. Sugar beets give 2.3 tons of sugar per acre, with 0.7 ton of pulp per acre, per year; but beets, unlike sugarcane, do not grow all the year round.

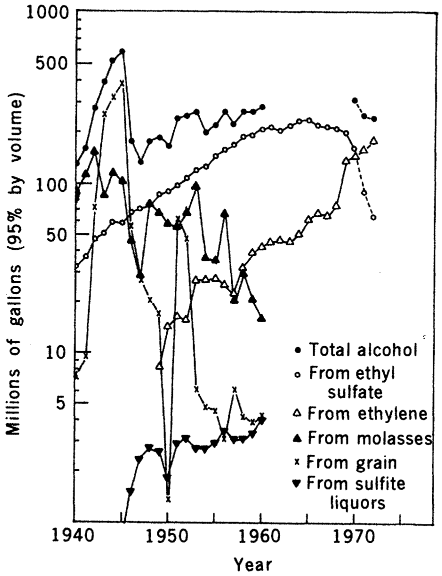

Fig. 3. Industrial alcohol production (1971).

It occurred to me that we are going to a great deal of trouble to convert a carbohydrate (sugar) into a hydrocarbon (ethanol-ethylene-polyethylene). Would it not be possible to find a plant source that would make hydrocarbon directly (Fig. 4)? There is at least one, already available, very well known source: the *Hevea* rubber plant which was first found wild in Brazil and now is grown almost exclusively in plantations in Malaysia and Indonesia. Today the yield of rubber (which is already a hydrocarbon with no oxygen in it) is about 1 ton per acre per year, which is about half the yield of cane, and only about 20 percent less in terms of ethylene potential. The rubber growers are very optimistic that they can, and will, be able to raise the yield of rubber from 1 to 3 tons per acre per year (*7*). If they are able to harvest 3 tons of rubber per acre per year (that is, 3 tons of hydrocarbon), this type of plant may also become a seriously considered possibility for a direct photosynthetic source of hydrocarbon for use in chemicals and materials.

The rubber story is very similar to the industrial alcohol (ethanol) story, and, in a sense, is even a little more spectacular. After World War II, synthetic rubber (that is, butadiene and styrene) made from petroleum practically eliminated rubber plantations as a source of this material. The rubber growers then began to improve the yield, which at the end of World War II was only about 400 pounds of rubber per acre per year (*8*). The figure today is about 2300 pounds of rubber per acre per year. About one-third of the rubber used today comes from natural sources, and two-thirds from synthetic sources.

If the price of petroleum continues to rise, and the yield of natural rubber can be raised another twofold, we will again have reached another crossing point where a natural photosynthetic system for converting carbon dioxide and sunlight into hydrocarbon can be used. There are also many other types of hydrocarbon resources such as gutta, terpenes, and the like, which have not yet been explored as such. It is quite possible that breeding programs, such as have been devised to improve the *Hevea* rubber plant yield from 400 to

2400 pounds per acre per year, could be used to develop other souces of natural hydrocarbon. This could perhaps be done in a shorter period of time than was required for *Hevea* (a 7-year crop), provided that some of the annual plants were explored and that elasticity is not a special requirement.

Probably the first natural photosynthetic process which will be developed economically as a hydrocarbon source will be the conversion of carbohydrate. If the sugar planters in Hawaii, where gasoline is now rationed, would convert about one-third of their molasses directly into fuel alcohol, they would not have to purchase the 15 million gallons of petroleum which they now do to run their agricultural machinery. Another special situation seems to be developing in Nebraska which has about 7 million bushels of spoiled grain per year. This should yield more than 20 million gallons of alcohol, which, as a 10 percent additive to gasoline, would give 200 million gallons of "gasohol." This is the name used by the Nebraska legislature to designate a composition which would qualify for a 3 cent state tax credit (*9*).

As a final comment on the natural photosynthetic sources of hydrocarbon, let me remind you of our use of about 2 million barrels per day of oil equivalent as a source of chemicals and materials. If we were to try to supply this entire need from sugarcane we would require about 60 million acres of cane if we used only the sucrose and only about 30 million acres if the cellulose could be used as well, a capability soon to arrive (*10*). In 1971 there were 0.7 million acres under cane cultivation and about 1.4 million acres in sugar beets in the United States.

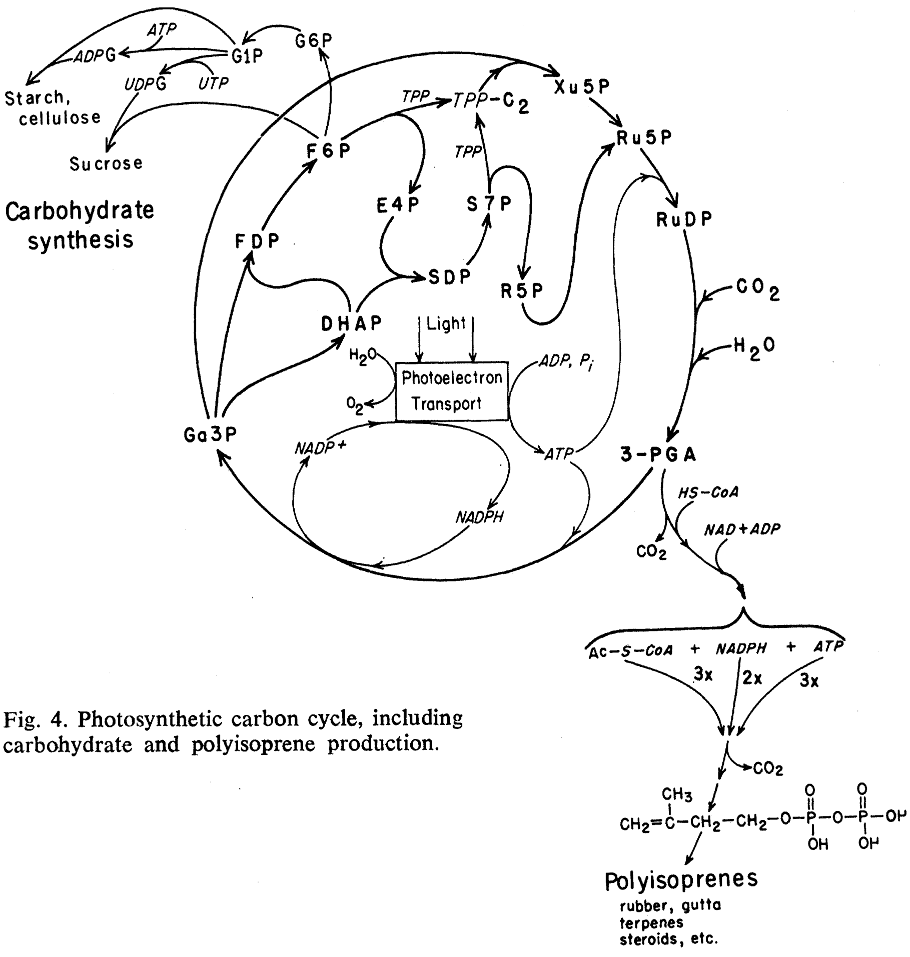

Fig. 4. Photosynthetic carbon cycle, including carbohydrate and polyisoprene production.

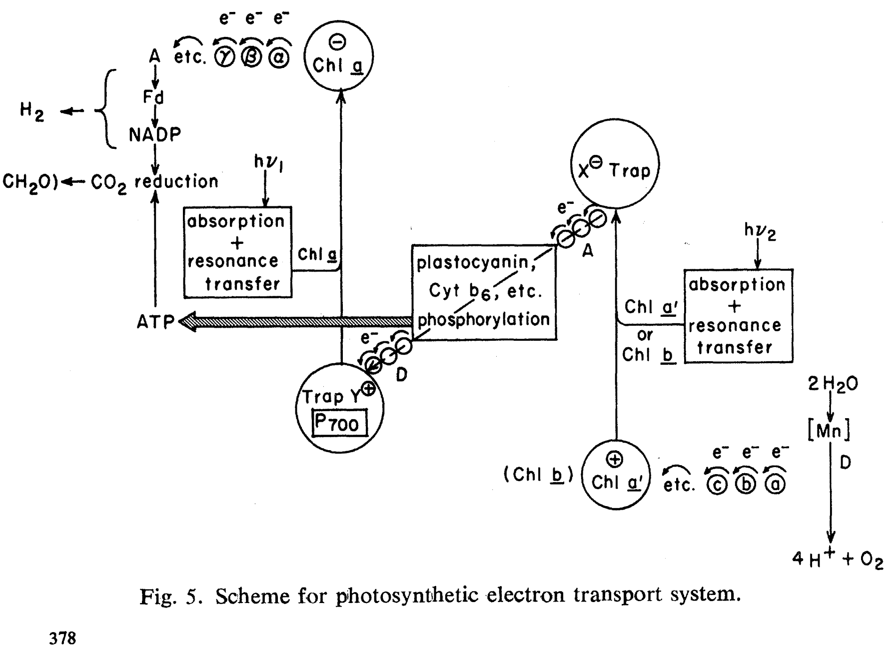

Fig. 5. Scheme for photosynthetic electron transport system.

## Model Systems of Photosynthetic Solar Energy Conversion

A great deal is known about how the plant makes carbohydrate, and we also know how the plant makes hydrocarbon (polyisoprene, for example, rubber). We are learning more about the way in which the plant captures the quantum of energy (*11, 12*). The knowledge of the plant's quantum conversion system is not nearly so complete as the knowledge of the photosynthetic carbon reduction cycle and subsequent processes. The primary quantum conversion process is still uncertain. But using what knowledge we have of the quantum conversion process, we can ask if the concepts generated in photosynthesis research—how the plant actually captures the quantum and converts it into useful potential, or electron flow—can guide us in simulating some parts of that process by purely synthetic methods. We then might be able to use that quantum conversion (solar energy conversion) process to help solve some of the energy problems with which we are faced.

The same photosynthetic carbon cycle that is shown in Fig. 2 is more elaborately displayed in Fig. 4. The entry of carbon dioxide into the photosyn-

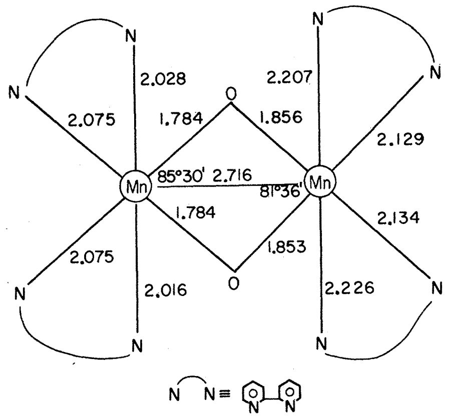

Fig. 6. Structure of the binuclear manganese photocatalyst di-$\mu$-oxotetrakis(2,2′-bipyridine)dimanganese (III, IV) perchlorate.

thetic carbon cycle and the exit of carbon into sucrose, starch, and cellulose, as well as hydrocarbon, is shown in some detail. The energy which drives the carbon cycle is represented by the photoelectric cell shown in the center of Fig. 2. Here, in Fig. 4, light enters the black box, which takes oxygen from the water and expels it into the atmosphere, and uses the remaining hydrogen to generate the reduced pyridine compound (NADPH) which, together with the adenosine triphosphate (ATP), drives the carbon reduction cycle. All of the driving chemicals—the ATP and NADPH—come from the light source.

How much do we know about this black box? We know a good bit about what is occurring inside the "photoelectric cell" of the green plant (Fig. 5). There are two successive quantum absorptions; the first one (photosystem 2) produces a strong oxidant and an intermediate reductant energy state, that is, raising the energy of the electron so that it may pass through electron transfer agents back to another previously oxidized chlorophyll molecule at a lower oxidation potential (*12*). After it has reduced the second chlorophyll to its normal state, it is again raised by another light action (photosystem 1) to a still higher reduction potential and then it comes down through a series of carriers, of which NADPH is one, and eventually goes into the carbon dioxide reduction process. Whereas Fig. 4 emphasized the carbon reduction cycle, Fig. 5 emphasizes the quantum conversion (electron transfer) scheme of photosynthesis.

An analysis of this photosynthetic electron transfer scheme can give us some clues as to how we might be able to construct a system which might be a device for converting solar energy into some useful form. One method might simply be to try to isolate a particle which would contain the entire system asymmetrically arranged with an acceptor, perhaps ferredoxin (Fd), on one side and an oxygen generator on the other, and use that particle (if it exists) in an asymmetric membrane. Light would then transfer electrons from the oxygen-generating side (donor) of the system to the acceptor (or hydrogen-generating) side. Suitable electrode-active redox couples could be placed in the solutions on either side of the membrane to couple this electron transfer process to electrodes, and so generate a current for use. While the successful construction of such a system would be very illuminating, it is not likely to be easily constructed or to be very stable if, as now appears, it must depend on complex structures isolated from plants and placed in an unnatural environment.

## Photochemical Hydrogen Production

In some green plants and bacteria it is possible to modify the end result of this type of photochemistry. Instead of the active hydrogen reducing carbon dioxide to make sugar, it is possible to limit the amount of carbon dioxide available to the plant and, by keeping the oxygen level very low, induce the plant to use the light energy to generate molecular hydrogen (*13*). The oxygen must be swept out, or used up, because the enzyme system which generates the molecular hydrogen is sensitive to oxygen. This is one of the problems. However, it appears possible to alter the conditions in such a way that the photosynthetic apparatus will generate hydrogen instead of reducing carbon. Thus we know that it is possible to have catalytic systems in the plant which can use sunshine (solar energy) to generate hydrogen from the water (*14*). This fact has been known for more than 20 years (*13*), but recently a system was described in which a blue-green alga, *Anabaena*—which contains in it the entire photosynthetic apparatus, and, additionally, a heterocyst cell that has no oxygen-producing apparatus— but has in it the hydrogen-generating apparatus (*15*). The reduced compounds are made in the green part of the plant (the oxygen-producing cells) and then diffuse into the nongreen part (heterocyst) with resultant evolution of hydrogen.

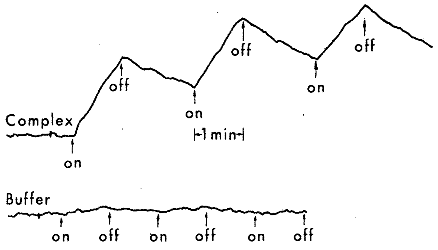

Fig. 7. Oxygen production by photolysis of binuclear manganese compound.

The fact that the plant has in it an apparatus capable of capturing the quanta and liberating molecular hydrogen was sufficient to make me feel that if I knew more about the details of the quantum conversion (*16*) and about the enzymatic systems involved I might be able to devise a simpler set of chemicals which would perform the same function, that is, generate hydrogen and oxygen from water. It would not be necessary, then, to reduce carbon, or have the whole skeleton of construction of a green plant which is required to make another green plant. I wanted to derive a system which would not be as complex as the one the green plant has in order to reproduce itself. To do that, however, it was necessary to have a concept of how the hydrogen is evolved and how the oxygen is evolved, and put the two processes together conceptually and, ultimately, synthetically.

The right side of Fig. 5 shows that the oxygen comes from the water, and the water molecule has only one oxygen atom in it, while the oxygen molecule has two. A total of four electrons is involved in converting two molecules of water into a molecule of oxygen and four hydrogen atoms. In order to generate oxygen molecules from the water molecules it is necessary to bring two oxygens together and remove four electrons. It is known that manganese is involved in this part of the system (*17*), but a single manganese ion by itself seems unable to remove four electrons. However, it appeared to me that if two manganese atoms, each of which would have oxidation number changes from 2+, to 3+, to 4+, were put together in the same complex, there would be a source of the required electrons without the necessity of generating free oxygen atoms or hydroxyl radicals. This process could be performed entirely in the double manganese complex. Thus arose the notion of a binuclear manganese complex, which contains two water molecules and which could be used in the quantum conversion process (*18*). The light, sensitized or direct, could induce a ligand-to-metal charge transfer, thus generating reduced metal ions and virtual hydrogen peroxide on the way to molecular oxygen. The reduced metal ions could then be the source of electrons for another quantum act, giving rise to molecular hydrogen. This was the theoretical basis on which the next experiment was performed. The idea was that we needed two manganese atoms in one complex. Could we find a system which could generate oxygen or hydrogen in separate quantum acts?

The structure of the dimanganese complex which we used is shown in Fig. 6 (*19*). It turns out that, if this molecule is irradiated in a suitable aqueous solution, oxygen is indeed given off. Figure 7 shows oxygen evolution by this binuclear manganese compound, when the light is turned on. We thus have a system which will generate oxygen when the light is turned on (*20*).

The overall scheme representing the light action on the binuclear manganese catalyst which generates oxygen and reduced catalysts is shown as reaction 1 in scheme 1. The reduced catalyst can move to the place where the hydrogen-liberating enzyme exists (presumably near ferredoxin) and another quantum act could then move the electron into an acceptor (the ferredoxin) and reoxidize the catalyst (reaction 2). The reduced ferredoxin plus protons with either one of the hydrogen-liberating enzymes, hydrogenase or nitrogenase, would then liberate hydrogen and recover the oxidized ferredoxin (*21*) (reaction 3).

$$\tfrac{1}{2}\,H_2O \xrightarrow[{[cat]_{ox}}]{h\nu_{(2)}} \tfrac{1}{4}\,O_2\uparrow + \underset{[cat]_{red}}{[H]} \qquad (1)$$

$$\underset{[cat]_{red}}{[H]} + Fd^{3+} \xrightarrow{h\nu_{(1)}} Fd^{2+} + [cat]_{ox} \qquad (2)$$

$$2\,Fd^{2+} + 2\,H^{+} \xrightarrow[\text{(ii) hydrogenase}]{\text{(i) nitrogenase or}} H_2\uparrow + 2\,Fd^{3+} \qquad (3)$$

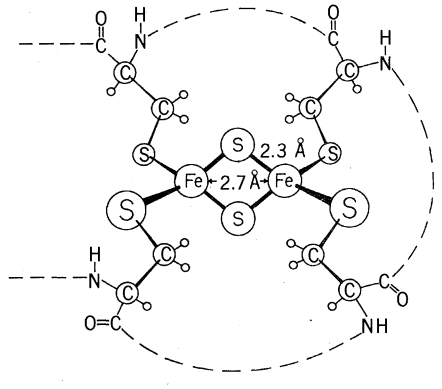

Fig. 8. Proposed structure of plant ferredoxin and hydrogenase, showing the suggested $Fe_2S_2(CyS^-)_4$ center of green plant Fd and for hydrogenase.

What I have shown you so far is some experimental evidence for the first reaction only. We have produced a reduced catalyst, whose structure is still unknown, and we are, of course, actively pursuing its elucidation. We are also in the process of deciding how to achieve the second step. For this purpose we have had to examine the structure of green plant ferredoxin and of the hydrogen-liberating enzymes. It appears that these two substances have certain elements of structure in common, if they are not identical. Both their functional groups are iron atoms completely coordinated by sulfur atoms of various kinds. The bacterial ferredoxin contains the unit of four iron atoms and four sulfur atoms, arranged at the alternate corners of a distorted cube, the entire cube being supported or contained in a polypeptide framework by the four mercaptide sulfur atoms of cysteine molecules in the peptide chain (*22*). A somewhat simpler structure, consisting of two iron, two sulfur, and four cysteine mercaptides, is suggested for both plant ferredoxin and hydrogenase (Fig. 8) (*23*). The binuclear iron center contains each iron, tetrahedrally surrounded by four sulfur atoms, two of which are sulfide bridges between the two iron atoms. The remaining four are mercaptides, from a presumed surround of peptide. This latter structure (Fig. 8) has simple analogs that can be synthesized. By tying all the mercaptides together into a macrocyclic structure it should be possible to add two electrons to such a system of iron and sulfur atoms without causing the separation of the iron and sulfur atoms. The reduced complex, with the two sulfur atoms so close together, could provide the centers for the addition of protons and the ejection of molecular hydrogen, and thus return to the oxidized form.

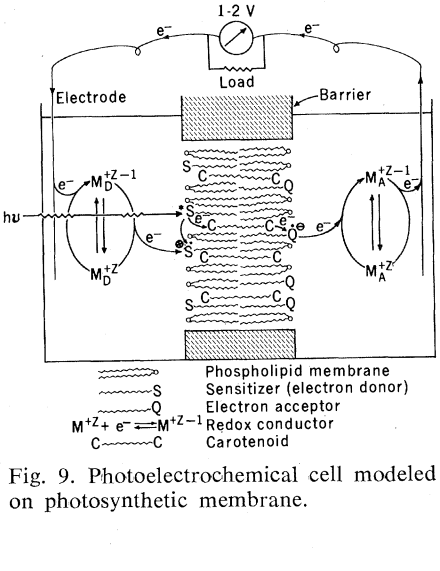

Fig. 9. Photoelectrochemical cell modeled on photosynthetic membrane.

If we can succeed in this construction we will then have available the components of a totally synthetic system that sensitizes the photochemical decomposition of water into hydrogen and oxygen in two different places. There are various methods of engineering this process, and I am not much concerned about that problem. Once the two separate reactions are achieved as two separate reactions, the construction of the system will go forward. At present, we have demonstrated the first half of this synthetic system, and we are on the road to elucidating the second part.

## Photoelectric Membrane

Another type of notion has evolved from an examination of the nature of the primary quantum conversion act in the green plant. As was shown earlier, the primary quantum conversion apparatus in some ways simulates a solid state device in which impinging light separates charge—positive and negative, electrons and holes. We have used this concept for the last 15 years, trying to learn if and how such a system might work in the green plant (*20*). In the last couple of years we have found that it is possible to demonstrate that the intact chloroplasts of the green plant, when light of the proper wavelength is shone on them, do indeed behave as though there were "conduction electrons" developed by incident light (*24*). We were able to demonstrate a Hall effect in illuminated chloroplasts. By placing the chloroplasts in a magnetic field and shining the light on them, two different carriers are evolved, one positive and one negative, having different lifetimes and moving in opposite directions in the magnetic field.

This result encouraged us to design sensitized systems for separating charge, using various dyestuffs whose photoactivity resembles that of chlorophyll (*25*, *26*). Figure 5 shows some of the details of such two quantum processes. Instead of allowing the evolution of oxygen, and hydrogen, or carbohydrate, it may be possible with this quantum conversion system to take the holes and electrons off as current, across a suitable device. The device I am about to propose is an example (*18*). I have seen the designs of other such devices (*27*). It is a photoelectrochemical cell (*25*) modeled on the photosynthetic membrane itself, which incorporates the idea of photoelectron transfer, generating voltage and a current (Fig. 9) (*28*). There is a sensitizer (S) on one side of the synthetic membrane which, upon the absorption of a quantum, transfers its excited electron (by tunneling 10 to 20 Å) to a carotenoid (C) which resembles a wire inside the membrane. The electron delocalized in the carotenoid travels through the membrane and is captured by an electron acceptor (Q) on the other side, which then goes through the cycle of a dyestuff ($M_A$) to deliver the electrons to the electrode. Similarly, the hole remaining ($S^+$) is fed an electron from another pair of dyestuffs ($M_D$) at a different potential. The dyestuffs are electroactive on the electrodes, thus generating a voltage and a current which can be taken off, and dependent on incident light which transfers the electron from one side of the membrane to the other. Components of such systems have been made, for example, in which the bilipid membrane has a donor system on one side and an acceptor on the other, without the conductor, only two lipid layers thick (about 60 Å). The idea of a conductor is to produce various conducting channels through a thicker membrane which will allow only the excited electron to pass through but be thick enough to be stable (*29*).

This kind of a totally synthetic system which emulates and stimulates in some ways the chloroplast membrane activity of the green plant may very well, in the more distant future, be another means of capturing the energy of the sun and producing electricity directly from it.

## Summary

Photosynthesis, both natural and as a model process, can be examined for its potential as a possible annually renewable resource for both material and energy. The conversion of carbohydrate from cane, beets, and other sources through fermentation alcohol to hydrocarbon may soon again become economic in the light of increasing costs of recovery of hydrocarbon from fossil sources and improved fermentation technology. Even the direct photosynthetic production of hydrocarbon from known sources (for example, *Hevea*) or newly bred ones seems possible. Finally, more distantly, synthetic systems constructed on the basis of growing knowledge of the photosynthetic processes, may produce both fuel and power.

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