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PROSPECTS OF PHOTOSYNTHETIC ENERGY PRODUCTION*

by

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PROSPECTS OF PHOTOSYNTHETIC ENERGY PRODUCTION

It wasn't too long ago that serious consideration of direct solar energy conversion was limited to two economic and technological extremes, underdeveloped nations and highly developed spacecraft. The vast region in between -- the densely populated, industrialized world -- found it far more economical to use fossil fuels to meet virtually all their needs. Now, with the price of crude oil climbing to fantastic levels, solar energy conversion could become economically competitive (if not downright essential).

So far, the cheapest, largest, and most successful solar energy conversion system available is photosynthesis. It seems reasonable to take another look at this natural system that has provided man for eons with food, oxygen, and fuel.

One approach is to search for increased yield of combustibles (e.g., woody plants). Another, perhaps more exotic, approach might be to interfere with photosynthetic processes so that combustible gases are produced (e.g., hydrogen or methane).

The truth is that photosynthesis is not nearly as efficient as we'd like and that we still have a long way to go in our understanding of solar conversion in plants before this method of energy production can make a greater impact on a highly industrialized society. But, we must begin now if the promise of clean, inexpensive, and replenishable fuel supplied by photosynthesis is to be realized at some reasonable time in the future.

The purpose of this brief paper is to review the relevant aspects of photosynthesis, to evaluate prospects for expanded exploitation of natural solar conversion systems, and to suggest some avenues for needed research.

Mechanism and Efficiency of Plant Photosynthesis

In order to do photochemical work, light must be absorbed. Of several pigments used to this end in the plant kingdom, chlorophyll a is the most important and general. Its absorption spectrum, reveals two bands, one near 680 nm and one near 430 nm. Among the other, so-called accessory pigments, the yellow carotenoids are ubiquitous in plants. A leaf, because of its high pigment concentration, readily absorbs all wavelengths shorter than ~700 nm.

The chlorophyll molecules are densely packed in thin lamellae so that absorbed photons can "migrate" to trapping centers in the pigment array. In these centers, a special chlorophyll is excited by light, donating an electron to an associated acceptor molecule. In rapid, consecutive reactions, the electron (a reduced chemical moiety) and the hole (an oxidized chemical moiety) are processed into more stable forms, and the trapping center is restored to its photo-sensitive state. Photochemistry only occurs from the first excited singlet state of chlorophyll a (the red absorption band at ~700 nm), which represents about 1.8 volts. The chemical (midpoint) potentials of the oxidized and reduced products differ by ~1 volt, so that the energy efficiency of the primary photoacts is ~50%. But, as will be discussed, the overall efficiency of photosynthesis is much lower.

A chemical potential, well in excess of 1.2 volts, is required to (1) split water into oxygen and hydrogen (or its physical equivalent) and (2) generate

additional energy in the form of ATP. This work is performed by two photoacts, with the charge separations or "solar batteries" operating at different potential levels and connected in series. One photosystem produces a mild oxidant and a strong reductant on the level of the hydrogen electrode (an iron-containing enzyme, ferredoxin). The second photosystem produces a strong oxidant (a manganese-containing enzyme capable of liberating oxygen from water) and a mild reductant. The weak photooxidant of the first system reacts with the weak photoreductant of the second system, which closes the electron transport chain from water to ferredoxin. The ATP, generated by the photosystems, aids reduced ferredoxin to reduce CO_2 to sugar and to synthesize the multitude of products which constitute new plant material.

Rather independent of the nature of the ultimate product, be it plant material, (symbolised as $[\text{CH}_2\text{O}]$ in eq. 1), sugar, methane or hydrogen, the energy fixed in the overall process corresponds to 120 kcal per mole of O_2 evolved.

Since 2 photons are used per electron equivalent, it takes 8 quanta to produce an O_2 molecule. For average solar radiation ($\bar{\lambda}$ 550 nm), a mole of quanta represents ~ 50 kcal, and the "theoretical" light conversion efficiency, therefore $8 \times 50/120 = 30\%$. Because wavelengths longer than < 700 nm (about half of the solar emission) are not absorbed by chlorophyll, the best possible conversion of natural sunlight would be $\sim 15\%$. Although the quantum yields of the

photoacts approach unity and other steps also are quite efficient, the actually measured optima of plant growth are closer to 10%. (An efficiency of 10% of the average solar flux in the USA corresponds to ~70 kw/acre).

For many reasons, this optimal value seldom is realized in the field. Plants, like animals, must maintain themselves and do so by burning organic materials in respiratory processes. Thus, in dark and in very weak light, their energy balance is negative. On the other hand, the efficiency also drops in very strong light where the enzymic processing reactions cannot keep pace with the quantum influx. In most plants, photosynthesis "saturates" at intensities below that of full sunlight at noon.

In addition to light, plant growth requires water, CO_2 , and a variety of inorganic nutrients. The low concentration of CO_2 in the atmosphere (0.03%) generally limits the rate in strong light, and the availability of other ingredients, temperature levels, etc., often are suboptimal. Moreover, many land plants consume a significant fraction (up to one-half) of their "gross production" for their own maintenance, often in large, nonphotosynthetic, structures such as stems and roots. As a result, the total production of organic matter in the field seldom exceeds 2% of the solar radiation recieved. Typical values actually are 0.5-1.5% (3-10 kw/acre). In many crops, only part of this total production (e.g., only the seeds) are harvested.

Photosynthesis as a Source of Energy

Until the last century, contemporary photosynthesis, agriculture, and forestry filled nearly all of society's energy needs. Today it primarily fills our demand for food. Per capita, we use ~ 3000 kcal of food per day, corresponding to 0.15 kw. We use a much greater amount of energy ($\sim 70\times$) for all other purposes -- ~ 10 kw per person (of which ~ 2.5 kw is converted to electricity). Practically all of this non-food energy is derived from fossil fuel. (The 2.10^8 people in the U.S. use 70×10^{15} BTU, corresponding to ~ 2000 gw.)

At this moment, we wonder whether we have gone overboard, not only in thoughtlessly increasing our demands, but also neglecting renewable resources. Should we again consider using contemporary photosynthesis for broader energy purposes? A few figures reveal a considerable potential:

The sunlight falling on the U.S. is abundant, but dilute. It exceeds our total energy consumption 700-fold; e.g., if converted with 10% efficiency, only 1.5% of our land area would supply all our energy needs. On the other hand, this 1.5% amounts to 28 million acres -- a formidable area, corresponding to the entire state of Pennsylvania or about twice the area of all our highways.

Consider, however, that U.S. farmers and foresters already work a much larger area ($< 10\times$). More than 300 million acres in the U.S. are devoted to agriculture and forestry (1.5 acre per person). During a growing season of 5 months, these areas receive 24×10^{17} BTU of sunlight. A harvest, equivalent to $\leq 3\%$ of this sunlight, would equal the total energy consumption in the U.S. Actual above-ground harvests generally are below one-third of this amount.

We should consider, however, that conventional plant breeding aims for high yields of special products or parts of the plant, such as seeds, roots, sugar or stemwood. It is not unreasonable to expect considerable gains if, instead, genetic selection and other approaches were aimed at the most abundant production of combustible material -- in any form, as long as it can be harvested (and dried) conveniently. Proposals have been made to grow special crops in "energy plantations" with the sole purpose of combustion in electrical power plants. For 2% efficient conversion of light to combustibles and $\leq 40\%$ efficient conversion to electricity, a 1000-Mw power plant would require ≥ 250 square miles (1600 acres).

However, in view of the pressures for increased supplies of food and wood, this may not be too appealing. At least as a start, harvesting of combustible side products of already economically worthwhile crops seems to be closer at hand. It might not add a prohibitive expense to harvest the stalks along with the kernels.

In this respect, we should consider that the food on our table represents only a fraction of the total caloric harvest. It has been estimated that the major crops (corn, wheat, soybeans, etc.) leave $5 \cdot 10^8$ tons of stalks, stubble, and leaves, representing $4 \cdot 10^{15}$ BTU. In addition, we are quite careless with our soil, and we insist on eating a great deal of meat which requires up to 20 times more land area than the nutritional equivalent of vegetable food, notably soybeans. Some of this loss is readily retrievable as solid wastes from the farm animals, and urban, organic wastes already are being collected. These sources might relieve up to 10% of the total U.S. energy demand.

I should mention that burning of organic products (to generate steam for electricity) is not the only -- or necessarily the best -- approach. By pyrolysis or chemical reduction, organic materials can be converted into oil or gas. Methane (or ethanol) can be produced from wet materials, using biological fermentation. The above numbers and ideas may not be novel or dramatically promising (in terms of getting large amounts of energy on short notice), yet we can ill afford to neglect them forever.

Photolysis of Water as a Source of Energy

Recently, attention has been drawn to the possibility of using only that part of the photosynthesis apparatus which carries out the photolysis of water (Eq. 2)

Thermodynamically, this is feasible, since the potential of the primary reductant of photosynthesis ($[\text{e}^-]$ in Eq. 2) is below that of the hydrogen electrode.

If plants or algae could be made to carry out reaction (3) instead of CO_2 reduction, hydrogen, a clean, readily applicable fuel would be generated. Actually, it has been long known that many algae, under proper conditions, evolve some hydrogen when illuminated. Also, it is standard laboratory practice

to isolate chloroplasts from leaves which are no longer able to carry out CO_2 reduction (Eq. 1) but retain full capacity to split water, generate oxygen, and reduce low potential agents. These observations raise the tantalizing prospect of a 10% efficient solar generator of hydrogen at reasonable cost. In one conceivable scenario, algae are grown in the normal way, which can be done readily and cheaply; then their metabolism is tricked to produce H_2 rather than sugar.

Another approach is to move away from the living system. In this case, chloroplasts are isolated from green leaves and stabilized together with the hydrogenase (for instance, on a solid substrate) so that activity can be maintained for a long time outside the living cell.

Many gaps in our present knowledge of the system give these scenarios a somewhat futuristic flavor. For instance, bleeding off hydrogen would deprive the plant of its precious reducing power, and such a drastic derangement of the photosynthetic apparatus might imply a major feat of genetic manipulation. Hydrogenase, the enzyme which equilibrates hydrogen gas with metabolic redox agents (Eq. 3), although present in many algae, might not be coupled directly to the photosynthetic machinery. Outside the living cell, hydrogenases are strongly inhibited by oxygen, and, conversely, the photosynthetic photoact responsible for O_2 evolution is "turned off" under reducing conditions.

In the living system, such problems are solved by structural arrangements. The photosynthetic system consists of a two-dimensional array of functional units (assemblies of pigments, trapping centers, and processing enzymes)

arranged on a thin ($60 \text{ \AA}$) lamella, doubled as a flattened sac. The oxidized products of both photoacts are formed on the inside, and the reduced products are manufactured on the outside (apparently to prevent backreactions). Ideally, each photochemical reductant molecule in the array should be tightly associated with a compatible hydrogenase molecule. To arrange such a coupling artificially seems beyond the present art of molecular engineering.

A defeatist might enumerate many other unknowns and difficulties. Still, it seems realistic to predict that some day we will be able to accomplish this feat. It certainly would not hurt to try. The time table will depend on the amount of effort and the direction of research -- not only in photosynthesis, but also in genetic manipulation and stabilization of biological catalysis in vitro, areas showing considerable progress and promising radically new technologies. Photolysis of water may be one of these, but we should not count on it within the coming decade.