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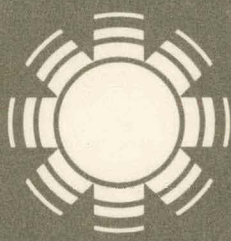
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Research Overview of Biological and Chemical Conversion Methods and Identification of Key Research Areas for SERI

Final Task Report



SERI

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SEPTEMBER 1978

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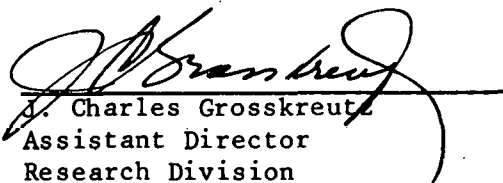
PREFACE

This research overview was compiled by the Biological and Chemical Conversion Branch in compliance with Contract EG-77-C-01-4042 for the Division of Solar Technology of the U.S. Department of Energy. Task 3302, of which this report is a part, was identified in the approved SERI FY78 Annual Operating Plan as a Research Division effort.

Approved for:
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ABSTRACT

This report is a qualitative overview of the current and future research areas of the Biological and Chemical Conversion Branch. Section I maps out the goals of the Branch and the general areas of Branch activities: Energy and Petrochemical Substitutes from Biomass, Thermochemical Conversion, and Photo-conversion. Section II discusses each of these three areas in some detail and is meant to be a general overview. Section III describes specific parts of the three major areas which have been selected, in the context of present Department of Energy sponsored research including the Fuels from Biomass and Office of Basic Energy Sciences programs, for initial SERI in-house research emphasis. Finally, Section IV outlines the Branch research efforts planned through FY79.

RESEARCH OVERVIEW OF BIOLOGICAL AND CHEMICAL CONVERSION METHODS
AND IDENTIFICATION OF KEY RESEARCH AREAS FOR SERI

I. INTRODUCTION--GOALS OF SERI AND THE
BIOLOGICAL AND CHEMICAL CONVERSION BRANCH

There is a broad range of actual or conceptual schemes whereby solar energy, as light or heat, can be converted biologically or chemically to fuels, electricity, or stored energy. These range from fully natural photosynthetic systems producing fuels to completely manmade chemical cycles for dissociating water or generating electricity.

There has been no single focal point in the Department of Energy (DOE) concerned with the full range of biological and chemical conversion of sunlight to fuels and electricity. Thus, programs in fuels from biomass, thermochemical hydrogen production, fuel-cell conversion of solar-derived fuels, and basic supporting research in photochemical conversion exist in separate branches or divisions of DOE.

Consistent with SERI's mandate "to provide significant support to DOE's solar energy program," the Biological and Chemical Conversion Branch has been formed within the Research Division to deal with this broad range of biological and chemical conversion processes. The Branch is assembling an interdisciplinary scientific staff to survey, assess, and conduct laboratory research in key areas.

Our initial choice of programs, as discussed in this report, is guided by ongoing programs in DOE and elsewhere, with emphasis on reviewing the existing National R&D program and on defining tasks

which support or supplement present DOE efforts.^{1,2} We believe that SERI can be particularly effective in bridging the gaps between fundamental research sponsored by the Office of Basic Energy Sciences (OBES) and technology development centered in the Fuels from Biomass (FFB) program.

SERI's major dedication as a performer of solar research will facilitate the Branch's ability to respond to both short and long-term research and to technical program direction, consulting, and assessment missions requested by DOE. The Branch will be a scientific and technical resource to SERI and DOE in its evolving areas of expertise. It will serve as a performer of innovative research, a reviewer of research programs, a technical monitor of selected DOE research contracts, and a technical director and manager of certain FFB program areas.

Notwithstanding the breadth of the solar conversion interests encompassed by the Biological and Chemical Conversion Branch, the goal of making major research contributions in specific areas requires that we be very selective in our initial staffing and research planning. The selection of these areas is the objective of our first task (Survey and Identify Research in Bio/Chemical Conversion, Task 3302). Activities under this task, to date, have led to the selection of several research areas as outlined below.

During the process of surveying research activities in solar biological and chemical conversion, we have categorized the general research areas within the purview of the Branch as shown in Table I. Section II discusses in detail the major subdivisions

¹Program summary, Fuels from Biomass Systems Branch, DST, January 1978.

²Program document, Division of Chemical Sciences, OBES, 1977.

of Table 1. Section III describes the selection of specific areas for initial in-house emphasis. Finally, Section IV summarizes anticipated activities and outlines, in broad terms, the next phase of Branch efforts in the development of an outstanding research capability in selected aspects of solar conversion.

TABLE 1
GENERAL RESEARCH AREAS WITHIN THE SCOPE OF THE
BIOLOGICAL AND CHEMICAL CONVERSION BRANCH

- A. Energy and Petrochemical Substitutes from Biomass
 - 1. Biomass Feedstock Supply and Production
 - 2. Conversion of Biomass to Heat, Fuels, Chemicals, and Electricity

- B. Thermochemical Conversion
 - 1. Thermochemical Conversion to Electricity
 - 2. Thermochemical Dissociation of Water to Hydrogen and Oxygen
 - 3. Reversible Thermochemical Reactions for Transport and Storage of Energy

- C. Photoconversion
 - 1. Photobiological Processes
 - 2. Photochemical Processes

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II. AN OVERVIEW OF BIOLOGICAL AND CHEMICAL CONVERSION PROCESSES

Parts of this report were written by each of the five senior scientists presently onboard in the Biological and Chemical Conversion Branch. Consequently, each of the research areas is discussed from the point of view of the individual staff member who will have primary responsibility in that area.

A. ENERGY AND PETROCHEMICAL SUBSTITUTES FROM BIOMASS

The processes involved in practical utilization of biomass as an energy source can be categorized under either production and supply or conversion schemes, as outlined in Table 2. Both aspects are represented by existing technologies, many of which were born of the very real energy crisis of World War II but were later abandoned in favor of much cheaper fossil fuels. Biomass energy is not merely a potential means of solar conversion; it is presently a commercial source, albeit on a relatively small scale (1-2% of U.S. energy use). The United States now obtains about one Quad from biomass, primarily as process heat for the wood industries.

Biomass residues produced in the United States have an energy content equivalent to more than 15% of the country's present annual energy requirements (Table 3). The growth of energy crops on marginal lands and improved forest management practices could supply, conservatively, another 10% to 15% of U.S. energy requirements. Such near-term biomass contributions are given in Table 4. However, research, development, and demonstration must be greatly accelerated if we are to realize this potential and keep pace with anticipated increases in energy needs. Systematic production schemes--from the collection of residues to the planting of "energy farms"--must be devised and brought online in

TABLE 2

OUTLINE OF BIOMASS ENERGY PROCESSES

Energy and Petrochemical Substitutes from Biomass

- A. Biomass Supply and Production
 - 1. Existing Biomass Resources
 - a. standing vegetation
 - b. agricultural residues
 - c. forestry residues
 - d. municipal/industrial cellulosic wastes
 - 2. Conceptual Biomass Resources
 - a. terrestrial biomass farms
 - b. aquatic biomass farms
 - c. hydrocarbon plant extractives
- B. Conversion of Biomass to Heat, Fuels, Chemicals, and Electricity
 - 1. Bioconversion Processes
 - a. anaerobic digestion to methane
 - b. microbial digestion to molecular hydrogen
 - c. hydrolysis of cellulose to sugars for fermentation to alcohols and chemicals
 - 2. Thermal Conversion Processes
 - a. combustion to heat and power
 - b. pyrolysis to gases, liquids, and char
 - c. gasification to low- and medium-Btu gases
 - d. liquefaction to light or heavy oils
 - e. densification to solid fuels
 - 3. Extraction Processes
 - production of latexes, oils, terpenes, waxes, and hydrocarbons by specific (exotic) green plant species
 - 4. Fuel-Cell Oxidation Processes
 - direct or multistep oxidation of biomass to generate electricity

TABLE 3
U.S. BIOMASS RESIDUES

<u>Category</u>	<u>Quads/Year</u>		<u>Estimated Cost \$/MBtu</u>
	<u>Produced</u>	<u>Easily Collectible</u>	
Dry Biomass Residues			
Municipal Waste	1.5	1.0	0-2
Agricultural	5.1	1.5	2-3
Forest	3.2	1.6	1-3
Wet Biomass Residues			
Sewage	0.2	0.1	2-5
Manures	3.4	0.4	2-5
Total	13.4	4.6	

Source: Benemann, J. R., "Biofuels: A Survey of Potential and Prospects," EPRI Report (in Press 1978).

the very near future. Similarly, a diversity of conversion technologies--biological, chemical, and thermal--must be developed so that various forms of biomass can be converted to usable energy quickly, cleanly, efficiently, and at low cost.

Biomass energy can be thought of as a particularly benevolent, long-range energy supply. Biomass is low in sulfur and relatively low in ash; it can be produced with a minimum disruption of our lands; and the combustion of biomass fuels, unlike coal, does not affect atmosphere CO₂ concentrations. Nevertheless, schemes or systems devised for biomass exploitation must be made compatible with natural ecological systems as well as the economic and technological systems which govern energy supply and demand.

TABLE 4

SOME POTENTIAL BIOMASS CONTRIBUTIONS
TO U.S. ENERGY SUPPLY BY 1990-2000

Energy Consumer	Product	Resource Base	Resource Available-Quads	Existing Technology	Developing or Required Technology
Paper & Lumber Companies	Heat, Power	Forest Residues & Cull	1.6/yr	Conventional Combustion	Fluid-Bed Combustion, Air & Oxygen Gasifiers for Retrofit
Municipalities	Power or Fuels	Solid Waste, Sewage	1.0/yr	Incinerators, Densification, Digestion	Gasification, Liquefaction
Homeowners, Space Heating Users	Heat	Wood, Biomass Residues	2/yr	Wood Stoves	Automatic Wood-Chip or Pellet Furnaces, DBF Commodity Market
Cars, Trucks	Alcohol Fuels	Agricultural Surplus, Wood, Waste	2/yr	Ethanol from Grain & Wood, Methanol from Biomass	Ethanol from Cellulose
Utilities	Electric Power, Heat	Land Improvement & Energy Farms	12-40/yr	Combustion	Wood-Gas Turbines
Food & Wood Processing	Process Energy, Gas, Solid Fuels	"Biomass Mines" of Stored Residues	10/yr	Densification Processes	Gasification

Biomass Supply and Production

The success of biomass exploitation as a solar energy resource is contingent initially upon the provision of a dedicated and assured supply of biomass feedstock. The feedstock resource base is distinctly divided into two categories, as indicated in Table 2. The first category is comprised of various forms of biomass which are now available by foraging, or through agriculture, or silviculture byproducts. Such activities can be developed in the near term. The extent of this near-term contribution, however, depends primarily upon competitive feedstock prices and the economics of available biomass conversion processes. A portion of this resource is now being used, and we expect its use will increase as advanced conversion technologies are developed.

The second resource category will be developed through energy farming per se. Energy farming is the purposeful production of biomass for use as an energy feedstock.

The extent of long-term contribution of terrestrial energy farming to national energy supplies will depend upon (1) the amount of land that can be devoted to this system and (2) the costs relative to competitive alternates. The first factor is intimately associated with the second. Before a landowner can be expected to dedicate land to biomass farming, he must be able to make a profit. In general, this is not true today. In the future, price increases for conventional energy forms, and increased biomass yields and decreased production costs through research, should enhance energy farming. Thus, an adequate R&D program is imperative if the concept is to evolve into a meaningful resource supply system.

Man's experience in agriculture and forestry will probably lead to terrestrial farming systems sooner than aquatic farming systems. The apparent opportunity presented by the expanse of the world's oceans, however, can be expected to continue to spur research interests in marine systems development. Algae pond and water hyacinth culture appear to be opportunities for fresh water systems. The development of practical aquatic farming systems is even more dependent upon research successes than is terrestrial farming.

The purposeful production of selected plant species which prefabricate natural hydrocarbon compounds occupies a special niche within the terrestrial energy farming concept. The potential of this system is exemplified by the guayule plant (Parthenium Argentatum Gray) which produces a number of high-value natural products which could be substituted for conventional feedstocks. These products include natural rubber, a variety of resins, a high-quality wax, an oilseed, as well as cellulosic biomass. A large number of arid land species have been designated as potential sources of prefabricated hydrocarbons. Their attraction is further enhanced by the potential for arid (low-value, marginal) land utilization.

Conversion of Biomass to Heat, Fuels, Chemicals, and Electricity

As shown in Figure 1, biomass occurs in both wet and dry forms, but most of it is relatively dry (<50% moisture). Due to energy requirements for processing, bioconversion (biological and biochemical processes) is usually used to convert wet forms of biomass; for example, manure to methane (by anaerobic digestion) and cellulose and sugars to alcohol (by fermentation). Thermal and chemical processes are used to convert dry forms to solid, liquid, and gaseous fuels as well as to chemical feedstocks. These two general areas, together with a limited number of special processes, are discussed in more detail below.

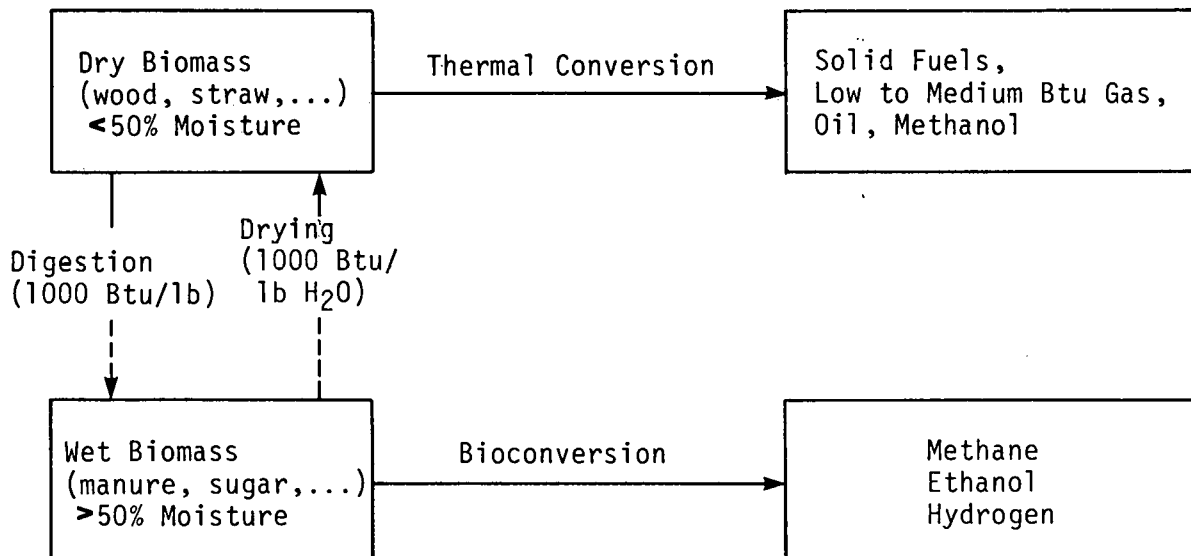


Figure 1. Natural Flow of Wet and Dry Biomass Through Bio- and Thermal Conversion Processes

Bioconversion Processes

The principal bioconversion routes are shown in Figure 2. A number of tests are in progress to convert feedlot manures into methane (biogas, Gobar gas, etc.).³ Other projects are attempting to do this on the small-farm scale and even at the household level.⁴ In addition, several groups are working on the microbial production of hydrogen.⁵ Biomass, in the form of sugar or starch,

³Program summary, Fuels from Biomass Systems Branch, DST, January 1978.

⁴Energy Recovery, Inc., Arvada, Colorado, "Fuels from Agricultural Wastes."

⁵Reeves, S. G., K. K. Rao, L. Rosa, and D. O. Hall, "Biocatalytic Production of Hydrogen," in Microbial Energy Conversion (H. G. Schlegel and J. A. Barnea, eds.), pp. 235-243, Erick Goltz, K. G. Gottingen, 1977.

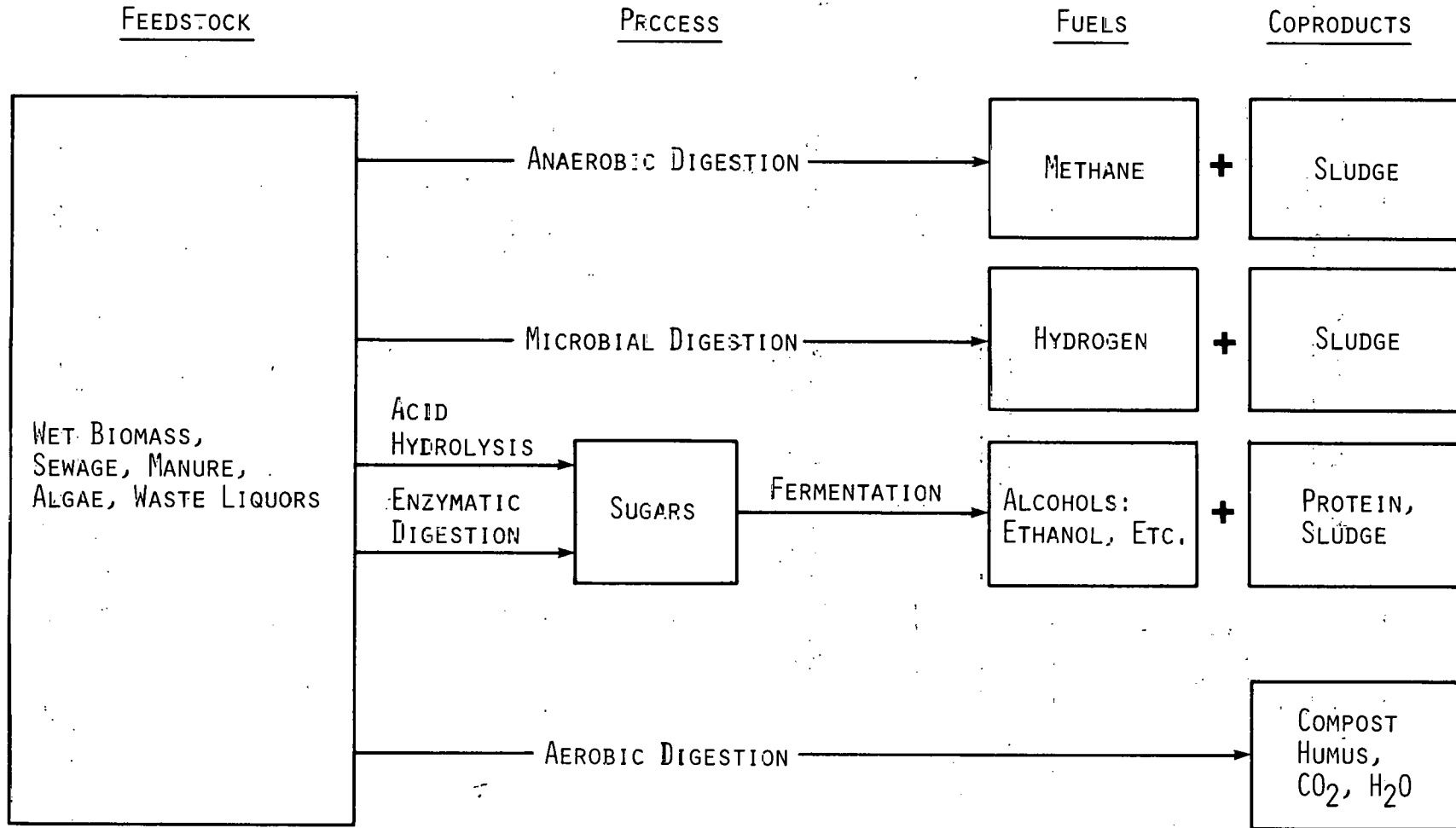


Figure 2. Bioconversion Processes

is relatively simple to ferment to alcohol. Cellulose, however, is more difficult to break down into its sugar components although acid hydrolysis of cellulose was a commercial process during World War II. Enzymatic hydrolysis is currently being investigated in several laboratories as is selective hydrolysis of cellulose with HCl gas. Experiments are also in progress to develop other microorganisms to produce alcohols directly from cellulose or to yield other products by fermentation and digestion.

Thermal Conversion Processes

The principal thermal conversion methods are shown in Figure 3. The simplest conversion process, of course, is combustion in stoves, furnaces, or power plants for heat and power. Processes are now being developed to dry and compress various biomass residues into pellets, briquettes, or cubes to make them more suitable for shipping and subsequent use as a fuel either for heat or gasification. By partial combustion with air, biomass can be converted primarily to a low-Btu gas suitable for use in gas- or oil-fired process heat boilers or for running stationary engines.

Combustion with oxygen produces a medium-Btu gas composed primarily of hydrogen and carbon monoxide; this gas can be burned in existing boilers for power generation or can form the basis for synthesis of methanol, ammonia, or gasoline. Indirect heating (pyrolysis) produces medium-Btu gases, liquids, and charcoal. Hydroliquefaction produces only oil from biomass.

Extraction

A number of plant species produce useful chemicals in vivo during photosynthesis, and these products can be extracted. For example, terpenes are produced by pine trees, and other useful hydrocarbons (e.g., waxes, oils, and latex) are produced by a variety of

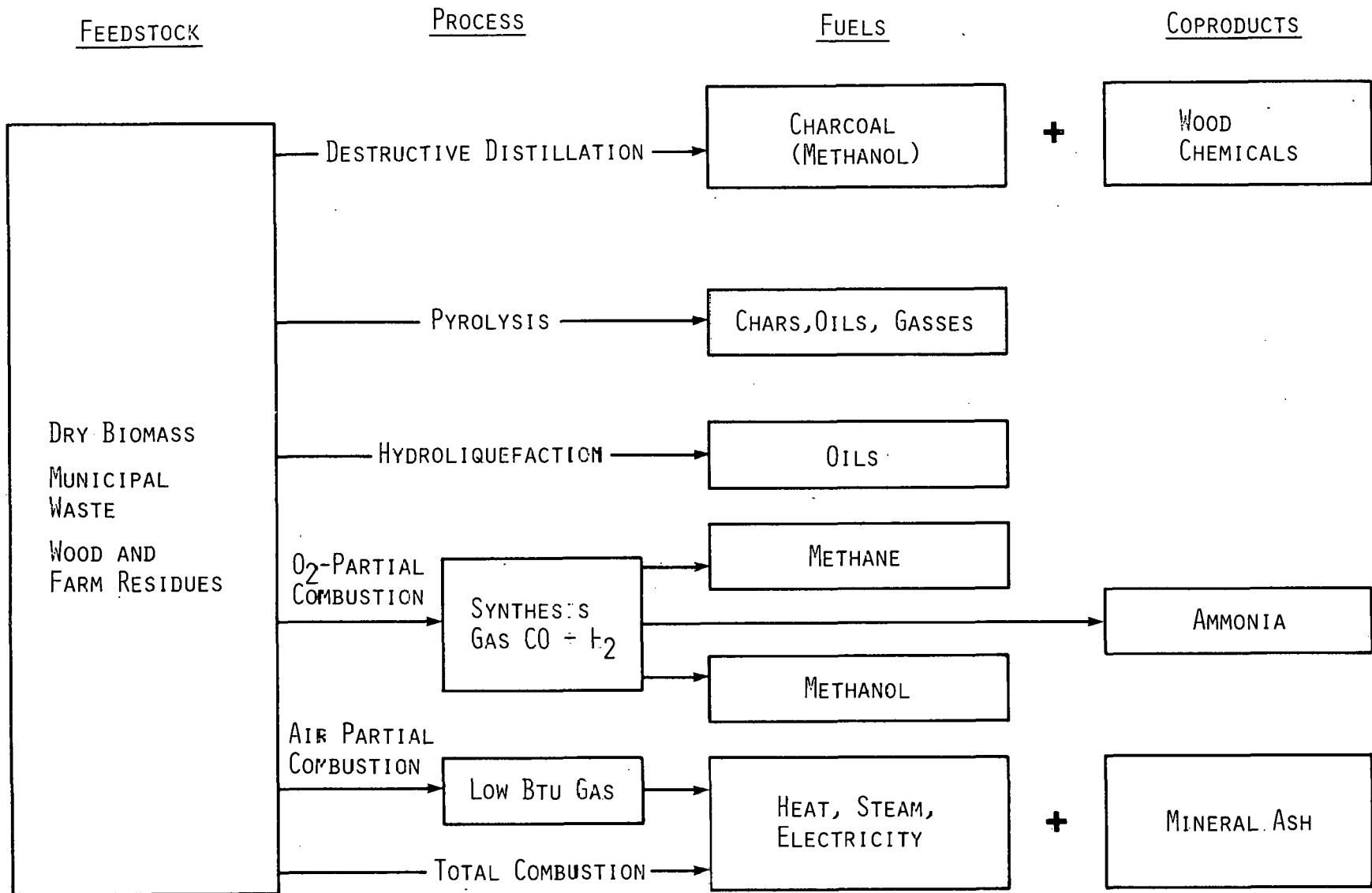


Figure 3. Thermal Conversion Processes

plants. In some cases, yields can be enhanced by chemical agents or by directed photosynthesis, as discussed below under "Photoconversion." One laboratory that is involved in this area is attempting to identify new species, enhance yields, and improve extraction techniques.⁶

Direct Fuel-Cell Oxidation of Biomass

Fuel-cell combustion is the most efficient way to convert the chemical energy of a fuel to electricity since it avoids the Carnot losses inherent in conventional combustion. A great deal of work is in progress on the fuel-cell combustion of fossil fuels.⁷ At present, no fuel cells are known to operate directly on biomass although a glucose/oxygen fuel cell has been demonstrated. Advanced fuel-cell research may make fuel cells a promising method for future biomass conversion.

B. THERMOCHEMICAL CONVERSION

Thermochemical conversion includes those chemical processes in which solar-derived heat is used to generate fuels, stored energy, or electricity. Since heat may be supplied from sources other than solar, principally via nuclear and fossil fuel sources, these conversion schemes are of general interest. The principal concerns at SERI naturally pertain to processes which are best suited to the utilization of solar heat or which involve hybrid systems with photochemical steps. An outline of thermochemical conversion processes is shown in Table 5.

⁶Nielsen, P. E. et al., Science, 198, 942 (1977).

⁷Abstracts, National Fuel Cell Seminar, June 21-23, 1977, Boston, Massachusetts.

TABLE 5
OUTLINE OF THERMOCHEMICAL SOLAR-CONVERSION PROCESSES

Thermochemical Conversion

1. Thermochemical Conversion to Electricity
 - a. LiI Cells
 - b. H₂O Cells
 - c. Sodium Heat Engines
 - d. Thermogalvanic Cells. Cyclic and Continuous

2. Thermochemical Dissociation of Water to Hydrogen and Oxygen
 - a. One step processes
 - b. Multistep processes
 - c. Zeolites

3. Reversible Thermochemical Reactions for Storage and Transport of Energy
 - a. Simple dissociations or rearrangements
 - b. Complex dissociations

Thermochemical Conversion to Electricity

All devices in which solar-thermal energy is converted directly to electricity through chemical reactions are included under this category. Examples are thermal batteries, electrochemical heat engines, and thermogalvanic cells. Table 5 lists four types of such devices.

In the LiI (lithium iodide) electrochemical heat engine,⁸ two LiI cells are operated in opposition. One cell is heated relative to

⁸Elliott, G. R. B., "Electricity Generation and Storage for Residences Using Li/I₂ Electrochemical Engines to Augment Photovoltaics," Report LA-UR-77-2330, Los Alamos Scientific Laboratory, 1977.

the other (e.g., 625°K vs. 298°K), resulting in a higher partial pressure of I₂ and a correspondingly higher cell voltage. Under these conditions, Li and I₂ combine in the high-temperature cell and LiI is dissociated in the low-temperature cell, resulting in net generation of electricity. Similar cells can be designed for higher temperature ranges. An analogous cycle has been suggested for electrolysis of water assisted by solar heat. The resulting H₂ either is used directly as a fuel, or is recombined with O₂ in a fuel cell at lower temperature, resulting in net conversion of heat to electricity.

A somewhat different mechanism for conversion of heat to electricity has been proposed in the so-called sodium heat engine.⁹ In this cell, hot sodium undergoes thermal ionization at an alumina membrane. Sodium ions (but not atoms) then migrate through the membrane to the cool side of the cell, and electrons flow through an exterior circuit to recombine with the Na⁺ ions. The cold sodium is reinjected to the hot side of the membrane so that continuous conversion of heat to electricity results.

A third example is the so-called thermal battery or thermally regenerative galvanic cell. Both cyclic and continuous cells have been proposed in which a thermally driven chemical reaction provides the chemical potential for conversion to electricity.

Presumably, many additional systems could be identified as candidates for the thermochemical conversion of solar heat, over a wide range of temperatures, to electricity.

⁹Cole, Terry, "Sodium Heat Engines," Report ALO/3701-76/1, Ford Motor Co., 1976.

Thermochemical Dissociation of Water to Hydrogen and Oxygen

A variety of thermal processes has been proposed to dissociate water. Among these are single-step dissociations involving direct, but partial, decomposition of water at quite high temperatures; intermediate-temperature cycles involving several steps; and low-temperature processes in complex environments such as molten salts.

Much of the work to date was spawned by the prospect of using nuclear-generated heat to drive the cycles. However, arguments have been made¹⁰ that solar heat is better suited for isothermal decompositions near the maximum available temperature, as many thermochemical cycles require, than are power plants in which heat is supplied at several temperatures. High-temperature solar heat can also be used to produce other fuels and chemicals and in chemical processing of ores, etc.

Reversible Thermochemical Reactions for Transport and Storage of Energy

This category encompasses the storage of energy through breaking of chemical bonds by thermally driven, reversible reactions. A great variety of chemical systems is being studied or proposed which, for the most part, require catalysts to reverse the reactions and release the stored energy. In the transport application, such systems have been termed "chemical heat pipes." In the storage mode, such devices exceed the capabilities of ordinary phase-change systems in the amount and quality of heat that can be stored.

¹⁰Bowman, M. G., "Thermochemical Production of Hydrogen from Water," Report LA-UP77-1337, Los Alamos Scientific Laboratory, 1977.

C. PHOTOCONVERSION

"Photoconversion" includes those biological and chemical conversion processes which are initiated by electronic excitation of photoreceptor molecules. Photoelectrochemistry incorporates aspects of both physical chemistry and solid-state physics and is also included under photoconversion since chemical processes are involved. Photoconversion is distinct from both thermal and thermochemical conversion in that an increase in kinetic energy does not necessarily accompany light absorption. As defined here, photoconversion differs from photovoltaic conversion in that processes other than those associated with solid-state ensembles of atoms and molecules are involved. For our purposes, we divide photoconversion into two general areas: "Photobiological Processes" and "Photochemical Processes." A detailed outline of these areas is shown in Tables 6 and 7.

Photobiological Processes

Photobiological processes encompass both photosynthetic and nonphotosynthetic processes as discussed in the following paragraphs and outlined in Table 6.

Modified Photosynthesis

In green plants, the maximum theoretical conversion efficiency of sunlight to stored chemical energy in the form of organic material is in the neighborhood of 10%.¹¹ Typical field observations range from 0.1% to 2% averaged over the period of a year, but during short periods of time, efficiencies of 4% have been reported for

¹¹Bolton, J. R., Proceedings of the Fourth International Congress on Photosynthesis, pp. 621-634, 1977.

TABLE 6
PHOTOBIOLOGICAL PROCESSES

- A. Modified Photosynthetic Processes
 - 1. Directed Photosynthesis (whole organisms)
 - a. Environmental modifications
 - Batch and continuous cultures
 - Immobilized cultures
 - b. Genetic Modifications
 - Selected organisms
 - Recombinant organisms
 - 2. Engineered Photosynthesis (extracted components)
 - a. Immobilized systems
 - b. Hybrid systems
- B. Nonphotosynthetic Processes
 - 1. Visual pigments and analogs
 - 2. Photomorphogenic systems

certain land plants and 4% to 5% for algae.¹² These lower efficiencies are primarily due to losses resulting from nonoptimal physical, metabolic, and environmental conditions.

Several options are available for the use of photosynthetic processes as intermediary steps in solar energy conversion. The first two, conversion of residues or energy farm crops and improved production techniques, were discussed previously in Section II.A.

¹²Seibert, M., J. S. Connolly, T. A. Milne, and T. B. Reed, AICHE Symposium Series (1978 in press).

A third option is to circumvent the low photosynthetic conversion efficiencies observed in the field by modifying the organism, the conditions to which the organism is exposed, or the processes of normal photosynthesis (e.g., physical extraction and chemical manipulation of the normal photosynthetic apparatus). We call this approach "Modified Photosynthesis."

Modified Photosynthesis can be further subdivided into two functional categories: "Directed Photosynthesis," which deals with modifications involving the whole organism and "Engineered Photosynthesis," which is concerned with modifications involving extracted components of the photosynthetic apparatus.

Directed Photosynthesis is a general term intended to describe research and development aimed at manipulating the physiology of plants including algae and photosynthetic bacteria so that they produce hydrogen, fixed nitrogen, or perhaps electricity rather than carbohydrates. The approach involves either modification of the environment to which currently available organisms are exposed or genetic modification of the organisms themselves. A number of groups in Japan, England, U.S.S.R., and the United States (funded primarily through NSF) are working in this area, investigating particularly the biochemistry of hydrogenase and nitrogenase enzymes. It has been established that blue-green algae use these enzymes to evolve hydrogen when the organisms are adapted to unusual environmental conditions such as an anaerobic atmosphere and nitrogen starvation. Recent work, including two DOE-supported projects which are listed in the FFB Program summary under "Biophotolysis," has emphasized the use of batch or continuous cultures. However, one commercially supported study has demonstrated an immobilized, multiorganism system which has produced hydrogen at a conversion efficiency of about 1% for several days. Since aerobic conditions inhibit the function of these enzymes, a major technical problem in devising large,

commercial algae ponds to produce hydrogen is the inhibitive effect of oxygen generated by the algae during photosynthesis. To circumvent this problem, NSF-supported investigators are attempting to select mutant organisms which have an oxygen-tolerant enzyme so that hydrogen can be generated in the presence of oxygen.

Engineered Photosynthesis involves research and development designed to produce electricity and, ultimately, fuels using extracted photosynthetic components (e.g., photosynthetic molecular complexes as in Figure 4 or photosynthetic membranes) immobilized either on artificial membranes or in other ways. A number of research groups have attempted to produce electricity by incorporating isolated chlorophyll into artificial membranes in modified photogalvanic-type photoelectrochemical cells. Results of these experiments have been disappointing in that observed conversion efficiencies were substantially below 0.1%. However, one group has immobilized isolated, intact thylakoid membranes from pea leaves on an electrode in a photoelectrochemical cell; conversion efficiencies of around 2.5% using a filtered ($\lambda > 630$ nm) incandescent light source were reported.¹³

Under Engineered Photosynthesis, we also include hybrid systems which combine the use of whole organisms, extracted biological components, and/or synthetic chemical systems for the production of electricity, fuels, or stored chemical energy. To our knowledge, little work has been reported in this area with the exception of hydrogen production although other possibilities have been discussed, such as in vitro CO₂ reduction and nitrogen

¹³Allen, M. J., "Direct Conversion of Radiant into Electrical Energy Using Plant Systems," in Living Systems as Energy Converters (R. Buvet, M. J. Allen, and J. P. Massue, eds.), Elsevier/North-Holland Biomedical Press, New York, 1977.

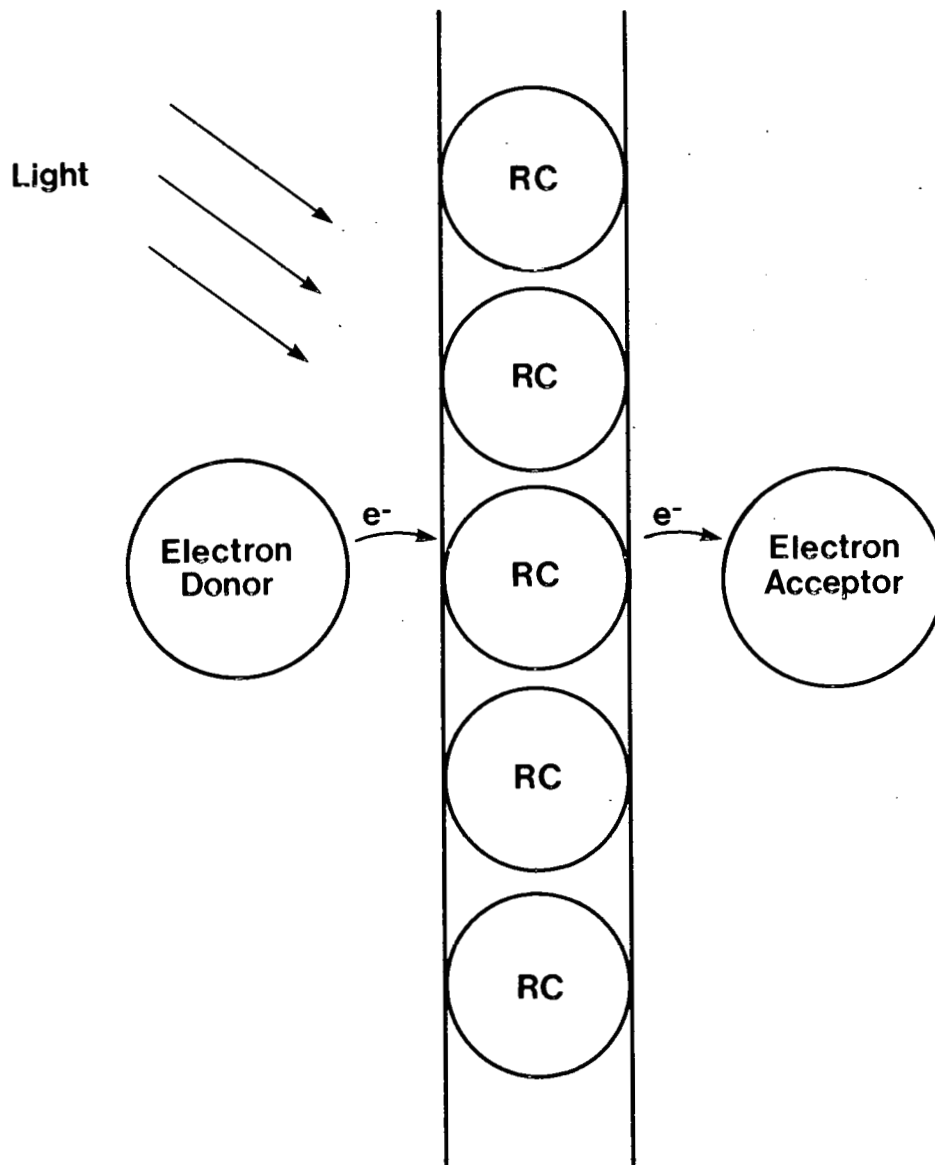


Figure 4. Incorporation of Biological or Model Reaction Centers (RC) into a Membrane or Monolayer

The membrane is immersed in an aqueous solution and separates electron donor and electron acceptor reagents.

fixation systems incorporated into photoelectrochemical or photobiological schemes.

Nonphotosynthetic Processes

A number of nonphotosynthetic biological photoreceptors have been identified including visual pigments, phytochrome, flavins, and bacteriorhodopsin. Of these, bacteriorhodopsin, or the "purple membrane" system from Halobacterium halobium, has been suggested as a potential candidate for applications in solar energy conversion since the system can "pump" protons across a membrane in the presence of visible light.

Photochemical Processes

Of the many schemes proposed for conversion and storage of solar energy, photochemical processes are perhaps the most fundamental. Photochemistry involves alteration of chemical bonds by quantized absorption of light in the ultraviolet to near-infrared region of the electromagnetic spectrum. In the context of solar energy conversion, the practical wavelength limits of interest are roughly 300 to 1,200 nm, corresponding to about 4.1 to 1.0 eV/photon, respectively. Since these energies are in the same range as those of chemical bonds, photochemical processes offer the possibility of achieving extremely high conversion efficiencies.

However, of all proposed solar conversion schemes, those involving photochemical processes are probably the furthest from commercial application. As a result, a facile breakdown of the elements of the many photochemical approaches is not possible in terms of starting materials, techniques, or end products. For the most part, research is progressing along disciplinary lines, and current work is reviewed briefly in this context in the Appendix.

A somewhat oversimplified view of the area is shown in Table 7, in which photochemical processes are categorized according to systems, reaction types, and function (i.e., conversion or storage). Evidently, chemical reactions can be carried out in either homogeneous or heterogeneous media; but we are mostly concerned with processes in the liquid phase, owing to considerations of reaction rates, material transport, ease of handling, etc. Moreover, we wish to focus a great deal of attention on aqueous systems because of the (presumed) availability of water for either distributed or central conversion units. In this context, "homogeneous" generally refers to liquid solutions, as opposed to solid or gaseous mixtures.

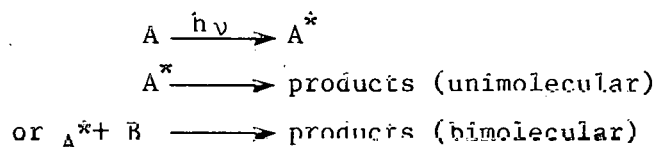
TABLE 7
PHOTOCHEMICAL PROCESSES

- A. Homogeneous Systems
 - 1. Photosensitized or direct photochemical reactions
 - a. Conversion
 - Photoredox (electricity, fuels)
 - Synthesis (fuels, chemicals)
 - b. Storage
 - Isomerization
 - Dissociation
 - Synthesis
- B. Heterogeneous Systems
 - 1. Photosensitized Reactions
 - a. Model systems for conversion to electricity or fuels
 - Artificial and extracted membranes
 - Monolayer and multilayer assemblies
 - Polymer micelles
 - b. Photoelectrochemical Cells
 - Photovoltaic mode (electricity)
 - Photoelectrolytic mode (fuels, e.g., H₂)
 - 2. Direct Photochemical Reactions

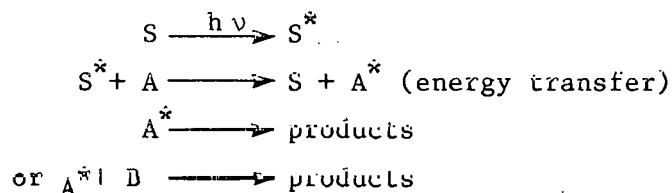
"Heterogeneous" refers to suspensions or immersions of insoluble materials (either liquids or solids), probably in water; examples are artificial membranes and the electrodes of a photoelectrochemical cell, respectively.

The two principal types of photochemical reactions are "direct" and "photosensitized." In a direct photochemical process, at least one of the reactants must absorb the incident light directly, and it is consumed in the subsequent chemical reaction which captures the light energy. In a photosensitized process, on the other hand, a sensitizer transfers the absorbed energy to another reactant and is not itself involved (except perhaps reversibly) in the ensuing chemical reaction. Schematic examples of these processes are:

Direct:



Sensitized:



where A and B are reactants, S is a sensitizer, and A* and S* represent excited electronic states. It is thus possible to sensitize a chemical reaction to wavelengths which might otherwise be inaccessible.

In homogeneous media, we are concerned with both conversion and storage processes initiated by either photosensitized or direct reactions. Conversion to electricity or fuels, notably hydrogen,

can be effected by photoredox reactions, i.e., photoinitiated oxidation-reduction reactions. Synthesis reactions leading to formation of new chemical bonds, in the form of fuels or chemical feedstocks, can also be carried out in homogeneous systems by either mechanism. The distinction between synthesis and storage reactions is not well defined, but in this connection is considered to involve the stability of the reaction products in a specific system. For example, a conversion system could generate unstable products which are consumed online in a fuel cell. In contrast, a storage system might use the same photochemical reaction but with separation of the products for consumption on demand. In this sense, unimolecular processes, such as isomerization or dissociation, are particularly amenable to incorporation into energy-storage schemes in which the primary photochemical reactions simultaneously convert the absorbed solar energy to another form and store it for future use.¹⁴

In heterogeneous systems the picture is somewhat different. As indicated in Table 7, sensitized reactions afford more possibilities for solar energy conversion in mixed-phase systems than do direct photochemical processes. The latter are not excluded, of course, but heterogeneous media do not appear to offer any distinct advantage for scale-up or commercialization of photochemical reactions in which the light absorbing species are consumed. Heterogeneous systems probably are more suitable for photosensitized processes in which, for example, the sensitizer is held fixed and the mixture of reactants and products is flowed through a reaction zone, e.g., a solar panel.

¹⁴Jones, G., II, T. E. Reinhardt, and W. R. Bergmark, Solar Energy, 20, 241-248, 1978.

Two broad examples of photosensitized reactions in heterogeneous media are model systems for conversion to electricity or fuels and photoelectrochemical cells. Model systems include, but are not limited to, the biomimetic systems discussed in Section III.C. under "Photobiological Processes." The biomimetic approach involves design of molecular assemblies which mimic the primary photophysical and photochemical processes of certain photobiological systems. One of the most important of these processes is photosynthetic charge separation following, on the picosecond to nanosecond time scale, absorption of light. Membranes appear to be desirable in order to stabilize this charge-separation state in preparation for useful forward reactions and to inhibit wasteful recombination steps (see Fig. 4). Thus, research on this type of model system necessarily includes studies of various membranes, including those extracted from biological systems, as well as polymer micelles, vesicles, and assemblies of molecular monolayers and multilayers.

Model systems and photoelectrochemical cells are discussed in more detail in Section III and in the outline of current research in the Appendix.

III. AREAS FOR INITIAL BRANCH RESEARCH PLANNING

In this section, we have selected several major research areas as subjects for detailed research planning and implementation. The topics are discussed as they appear in the categories of Table 1.

A. ENERGY AND PETROCHEMICAL SUBSTITUTES FROM BIOMASS

Biomass Supply and Production

The topics selected for initial Branch research in the area of feedstock supply/production were suggested both by the need to develop near-term applications for biomass, utilizing the existing resource base, and the need to initiate long-term research programs to assure the provision of an expanded feedstock supply for the future through the development and practice of energy farming methods.

The previous and current FFB program has adequately defined the availability and utility of agricultural and forestry residues within the conterminous United States. That program, however, has devoted little effort toward characterizing the largest of the near-term resources; namely, standing vegetation. SERI, therefore, has opted to devote immediate attention to the task of defining the nature and utility of this widely distributed resource which consists essentially of low-value standing forests. The Mid-South Biomass Program being initiated by SERI at the request of DOE will in all probability become a component of this effort.

In regard to developing long-term feedstock supplies through the process of energy farming, the major research requirements have already been accommodated within the current and planned DOE/FFB program. SERI has decided, therefore, that its major mission in

this regard should be to assist FFB in planning, directing, and coordinating the technical aspects of that program. Topics selected for immediate attention include:

1. Technical direction and management of the pilot silvicultural biomass farm program, including the Savannah River Project and five regional plantations.
2. Energy species selection, evaluation, and development, involving planning, directing, and monitoring a structured regional-based research program.
3. Planning and directing an arid-land hydrocarbon ("exotic") species program, devoted to the selection and development of plant species which prefabricate hydrocarbon compounds.
4. Systems analyses of integrated energy farming systems, including combined wood fiber/energy farms, combined species energy farms, and cash crop biomass farming by the private farmer.

Conversion Processes

Because of the nature of our present patterns of fuel consumption, production of liquid fuels and high-quality SNG has high priority as does the production of equivalent petrochemical replacements. The major obstacle to general adoption of biomass-based technology is economic.

Conversion processes for biomass can be grouped according to similarity in processing technology as follows:

1. Gasification, high-temperature pyrolysis, partial oxidation and combustion processes. That is, those processes producing primarily direct heat or gaseous fuel. Some common denominators are reaction kinetics

and reactor design, similarity to coal conversion, certain plant design parameters, and downstream derivative processes such as methanation and methanol and ammonia production.

2. Hydrolysis, extraction, and similar integrated liquid fuel or petrochemical replacement processes.
3. Anaerobic digestion.
4. Low-temperature pyrolysis and liquefaction processes, or those thermal processes producing directly a mixture of liquids requiring further separation or conversion to useful fuels or products.
5. Hydrogenation and reduction processes.

The major emphasis of the biomass conversion research and development program will be a comprehensive screening of the above technology by group to establish present economics, energy efficiencies, economy of scale, weakness in the process, and opportunities for innovation which could have significant impact. Maximum use of the literature and DOE FFB project results along with selected use of industrially oriented process engineering subcontractors will be made. This information plus the strong and growing technical capability of SERI's Biological and Chemical Conversion Branch should allow us to reach the following objectives:

1. Orient the relatively new Branch staff in the bioconversion art from an industrial and economic perspective.
2. Provide a unified, independent analysis of the various developing options.
3. Help identify specific areas for in-depth research on meaningful problems and in an organized framework of technology development needs.

4. Establish the necessary perspectives to guide us in expanding our internal capabilities.
5. Select the one or two best technologies offering a good opportunity for early commercialization on which we can concentrate our resources.
6. Provide the perspectives necessary to establish a broad and sound long-range basic research program in biomass conversion and other technologies.

Other research efforts will follow leads previously developed, specifically in the areas of advanced research and development on gasification techniques and hydrocarbon fuels from exotic plants.

Opportunities in some of these process areas are discussed below:

1. Gasification, High-Temperature Pyrolysis, Partial Oxidation and Combustion Processes

DOE FFB has funded numerous programs in this area. In addition, this biomass conversion technology is closely related to coal conversion technology. Potential products are: low- and medium-Btu fuel gas, syn-gas, methanol, ammonia, and methanation to SNG. Specific tasks are related to detailed process review, process economic modeling, and identification of areas for rewarding innovative research. Included are fundamental studies on gasification kinetics and fluid bed reaction kinetics. This work is of moderately high priority.

2. Hydrolysis and Extraction

Woody biomass is comprised of three major fractions: hexosans, principally cellulose (45-50%); lignin (20-30%); and pentosans, principally xylan (7-25%). Other

components usually comprise 3% to 6%, dry weight basis. Various hydrolysis processes have been or are now practiced commercially throughout the world. With the exception, perhaps, of several major hydrolysis plants operating in the Soviet Union, these processes recover only a portion of one or another of the major components.

For example, the German (Udic-Rheinlan and Scholler-Tornesch) processes and Japanese (Noguchi-Chisso and Hokkaido) processes have been used to produce fermentable sugars which in turn were used to produce fodder yeast and alcohol. Several producers throughout the world currently operate major plants to produce furfural from birch chips, sugarcane bagasse, and other agricultural waste materials. In the United States, the West Vaco Company is currently producing development quantities of a nonsulfonated lignin resin. With the possible exception of the Soviet installations, there are no known operators of fully integrated biomass hydrolysis plants.

The use of biomass components at their highest value, commensurate with the optimum price-market volume relation, should greatly improve the process economics of an integrated biomass hydrolysis facility. This should enhance the viability of liquid fuels from biomass. By comparison, furfural plants recover only about 10% by weight of the dry base biomass as final product yet are operated profitably at many world locations. Plant size is, of course, scaled to market demand, which is quite small compared to the market for liquid fuels. Current world furfural price is about 37¢/lb. At 15¢ to 20¢/lb, furfural and its derivatives

could displace many petrochemicals, thus greatly increasing the market for pentosan derivatives.

Lignin is generally considered a waste product and valued at fuel value (13,000 Btu/lb). However, with minor processing, lignin could be converted to phenolic resins which can be formulated to displace similar petrochemical products valued at 30¢/lb or more. At 15¢ to 20¢/lb of lignin, sufficient incentive should exist for uses at current petroleum prices. Most work by the forest products researchers on lignin utilization has been with the sulfonated lignin from pulp manufacture. This interferes with the development of many applications.

Cellulose hydrolysis processes are receiving major attention and a significant portion of DOE funding. Perhaps the greatest technical and economic obstacles to this route are overall cost, relatively large quantity of enzymes required, the necessity for elaborate and expensive substrate preparation, and the long retention time required. Experimental evidence suggests that removal of the lignin and pentosans can significantly reduce these problems. A number of investigators are considering several such schemes. Our experience on similar industrial scale processes should be of significant benefit.

There is a significant opportunity to review all pertinent technology and to assess a number of conceptual, integrated processing schemes. This work is of high priority.

3. Anaerobic Digestion

DOE FFB has funded several projects including demonstration-scale facilities. This technology will be reviewed. Variables limiting its acceptance will be identified. Areas offering significant opportunity for improvement will be identified, and recommendations will be made. This work is of medium priority.

4. Low-Temperature Pyrolysis and Liquefaction Processes

These processes produce a mix of oil and water soluble products. Tasks include process review and process economic modeling to identify areas having significant improvement potential. This work has a low priority.

5. Hydrogenation and Reduction Processes

These processes produce a high yield of liquid hydrocarbons. They are generally operated at high pressure and temperature. There may be some application of certain coal liquefaction technology. The processes will be reviewed for areas offering significant improvement potential. This work will be of lower priority.

B. THERMOCHEMICAL CONVERSION

The Branch will follow developments in this area through literature reviews, meetings, and professional contacts. We have special interest in low-temperature electrochemical heat engines and in thermochemical cycles to dissociate water. However, in view of the work already underway in these areas (even though not solar-supported), in-house research is not contemplated in FY78 or

FY79. Depending on the particular suitability of solar sources in driving these processes, cooperative research may be undertaken in the future.

The Thermal Conversion Branch at SERI has an overlapping interest in the chemistry of chemical storage systems. Cooperative research efforts in thermochemical dissociation, and fuels and chemicals, involving also the Systems Analysis and Materials Branches, may well take place in the future.

C. PHOTOCONVERSION

Photobiological Processes

Our rationale for investigating Modified Photosynthesis as a potential solar energy conversion technology is based on the knowledge that the light-driven reactions in photosynthesis associated with primary charge separation and electron transport have high-quantum yields, whereas the dark reactions associated with CO₂-fixation and normal cellular metabolism are relatively inefficient. Thus, if one could "short-circuit" the dark reactions, energy-conversion efficiencies much higher than those observed for plants grown under field conditions might be realized. For example, calculations show that the efficiency of conversion of incident solar radiation to charge-separation (i.e., redox) or chemical potential energy can be as high as 31% in photosynthetic bacteria and 25% in green plants at the level of the subnanosecond acceptor and as high as 19% in both organisms at the level of the "classical" acceptor. The former figures suggest an upper theoretical limit for the production of electricity using these organisms and the latter, a limit for the production of storable fuels. In a practical system, though, 18% would probably be a reasonable upper limit for energy conversion. Even if these high efficiencies prove to be unattainable in practical devices,

one should be able to produce hydrogen or generate electricity with the same 4% to 5% conversion efficiencies observed for the production of biomass in algae. This alone would be of practical advantage because the energy thus produced would be in a more convenient form than biomass.

Recent progress in characterizing the primary photosynthetic apparatus in both bacteria and green plants has demonstrated that the dark reactions can indeed be short-circuited by physically separating the cellular components in which they function from those containing the light-driven reactions. In addition, energy flow in various whole organisms can be diverted from the normal dark-reaction pathways by modifying the environment to which the organisms are exposed and perhaps by genetically modifying the organisms themselves. Both hydrogen and electric current production have already been reported in the 0.5% to 2.5% conversion efficiency range. Thus, Modified Photosynthesis is a technically promising area for future in-house research. Moreover, many aspects are not adequately funded at the present time because the field is young and the technology new. Finally, there are also potential economic advantages in this area since the biological raw materials for commercial solar-driven devices would probably be inexpensive compared, for example, to the raw materials needed for photovoltaic devices.

Of the photoreceptors identified as being associated with nonphotosynthetic processes, bacteriorhodopsin (the purple membrane of H. halobium) is one with interesting potential for solar conversion because it alone is used by its host organism to provide large amounts of energy to drive metabolic processes. Unfortunately, much less is known about purple membrane systems than about photosynthesis at this point. Also the percentage of the solar spectrum over which bacteriorhodopsin absorbs is less than that of chlorophyll. Consequently, this aspect of

photobiological processes will not be discussed further in this report. However, as more basic information becomes available in the future, research in this area will be reexamined.

With nonphotosynthetic processes eliminated as a major thrust area, at least in the near term, the remainder of this discussion will deal with specific aspects of Modified Photosynthesis which will be examined over the coming months. Elements of both functional categories of Modified Photosynthesis (see Table 6) will be addressed.

Under the category, Directed Photosynthesis, in-house research in environmental modifications to batch or continuous cultures of blue-green algae will not be undertaken during the foreseeable future. Work of this type is presently funded under the FFB "biophotolysis" program, and SERI will assume a project management role in this area. On the other hand, DOE is not presently funding research in other aspects of Directed Photosynthesis, such as hydrogen production from immobilized or genetically altered green algae or photosynthetic bacteria. These areas appear to be both fertile and relatively unexplored. Immobilization of whole organisms has been demonstrated, and additional research might lead to ways of stabilizing algae for extended periods of time under ambient temperatures. Such organisms, when exposed to an anaerobic environment, might well generate hydrogen for much longer periods than have been presently demonstrated. However, the identification of genetically modified organisms, selected for their ability to produce hydrogen in the presence of oxygen or conditionally when oxygen is excluded, would simplify the construction of commercial, hydrogen-evolving algae ponds. Genetically selected photosynthetic bacteria might also be used to produce hydrogen from organic substrates in waste water. In-house research in these areas will be examined in Section IV of this program definition task.

Engineered Photosynthesis is also an area that has been investigated to some extent but covers much virgin territory. On the chemical side, recent emphasis has been placed on the "biomimetic" approach, i.e., incorporating isolated chlorophylls in artificial membranes and generating electricity by placing a high-potential redox reagent (electron donor) on one side of the membrane and a low-potential reagent (electron acceptor) on the other; electrodes placed on either side of the membrane provide a path for photogenerated electrons to flow through the external circuit. Such systems are intended to mimic the natural primary photosynthetic apparatus (hence the term, "biomimetic"), but in practice have proved to be quite inefficient because it has not yet been possible to incorporate all of the recently discovered details of the primary photophysics and photochemistry of photosynthesis. In contrast, we propose to consider stabilization of extracted components of the photosynthetic apparatus, including reaction-center complexes and membrane fractions of both higher plant and bacterial systems, on artificial membranes or on the electrodes of a photoelectrochemical cell. As mentioned before, thylakoid membranes have been used to produce electricity in this manner, and the technology should be investigated further.

The second aspect of Engineered Photosynthesis which we shall address specifically is the hybrid system approach, which is also a new field of solar energy research. Multiorganism, hydrogen-generating systems were mentioned in Section II.C., in which both protons and reducing power are generated by algae while photosynthetic bacteria provide large amounts of hydrogenase. One could carry this concept a step further and replace the immobilized organisms with a cell-free biological system. This

possibility has in fact been reported in an immobilized two-stage system.¹⁵

Probably one of the more speculative areas in this aspect of solar energy conversion involves the construction of an in vitro system to mimic the plant's ability to reduce CO₂ to the level of carbohydrate (e.g., sugars). An immobilized photosynthetic electron-transport apparatus or a synthetic photochemical apparatus could generate the necessary reducing power. This energy could be coupled via enzyme or catalytic systems to produce carbon compounds. One approach might build on a recent report of ketoacid formation from CO₂, an inorganic reductant, and an alkyl-mercaptan catalyst.¹⁶

Research in hybrid systems, of course, will have considerable overlap with various aspects of photochemical conversion. The Biological and Chemical Conversion Branch is in a technical position to initiate research projects in both areas and will institute cooperative interdisciplinary programs when the support of multiple areas is required.

Photochemical Processes

Research in this area is complex and is still in its formative stages with respect to applications to solar energy conversion. In addition, there are few truly interdisciplinary groups working in the field. One of the missions of the Biological and Chemical Conversion Branch will be to establish such a group and to explore

¹⁵Egan, B. Z. and C. D. Scott, presented at the Symposium on Biotechnology in Energy Production and Conservation, May 10-12, 1978, Gatlinburg, Tennessee.

¹⁶Nakajima, T., Y. Yobushita, and I. Tobushi, Nature, 256, 60, 1975.

the many gaps which exist between fundamental research, both basic and applied, and commercial utilization.

The specific interests of the Branch in the area of photochemical conversion and storage of solar energy are (1) model systems, (2) photochemical synthesis, (3) photochemical storage, and (4) photoelectrochemistry. In all four areas, in-house research efforts will be closely coordinated with research in photobiological processes as well as with programs sponsored by various divisions within DOE.

Our approach to studies of model systems for photochemical conversion of solar energy will involve many aspects of physics and physical chemistry, as discussed in the Appendix. Thus, optimum spectroscopic, photophysical, photochemical, and electrochemical properties of such systems will be examined both theoretically and experimentally. Consideration will be given to other properties such as chemical stability and toxicity, and the potential for long-term applications will be kept foremost in mind.

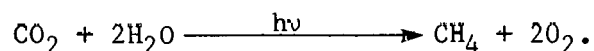
Initial emphasis will be placed on synthesis and characterization of organometallic compounds, not only because they occur in natural biological photoreceptors (e.g., chlorophylls), but also because several molecules of this general class have been demonstrated to sensitize photodissociation of water.¹⁷ In addition, organometallics are amenable to alterations of their molecular structure to enhance specific properties such as optimal absorption characteristics, redox potentials, solubility, and stability.

¹⁷Mann, K. R. et al., J. Amer. Chem. Soc., 99, 5525, 1977;
Lehn, J. M. and J. P. Sauvage, Nouv. J. Chimie, 1, 449, 1977;
Fong, F. K. et al., J. Amer. Chem. Soc., 99, 5802, 1977.

Studies of model systems will also include experiments with a variety of molecular ensembles: membranes, micelles, vesicles, and monolayer and multilayer assemblies. As pointed out earlier, physical separation of initial photoproducts (i.e., those formed on the picosecond to nanosecond time scale) appears to be essential to promote useful forward reactions and to inhibit wasteful recombination processes. However, careful examination of homogeneous as well as heterogeneous systems will be required.

The goal of our initial research in this area will be to identify optimal molecular properties--chemical and physical--for photochemical generation of fuels, most probably hydrogen. Thus, monolayer assemblies of model "reaction centers" such as indicated in Figure 4, or perhaps suspensions of polymer micelles or membrane vesicles as shown in Figure 5, might be scaled-up for photochemical generation of hydrogen from water, either in small distributed systems or in large central systems.

Photochemical synthesis involves new ways to convert the sun's energy into useful products using readily available materials as reactants. In principle, one would like to be able to reverse, photochemically, the combustion of methane; i.e.,



In practice, this reaction is not achievable using direct solar radiation since light in the far ultraviolet ($\lambda < 150$ nm) would be required. However, solar-induced photochemical reduction of CO_2 to methane may be possible via a reaction mechanism involving absorption (simultaneous or sequential) or eight visible photons ($\lambda > 600$ nm) which induce an equal number of electron-transfer steps. Synthesis of new compounds with the molecular architecture required to stabilize the intermediate species will be exceedingly difficult; but once understood, photocatalytic reduction of CO_2 to

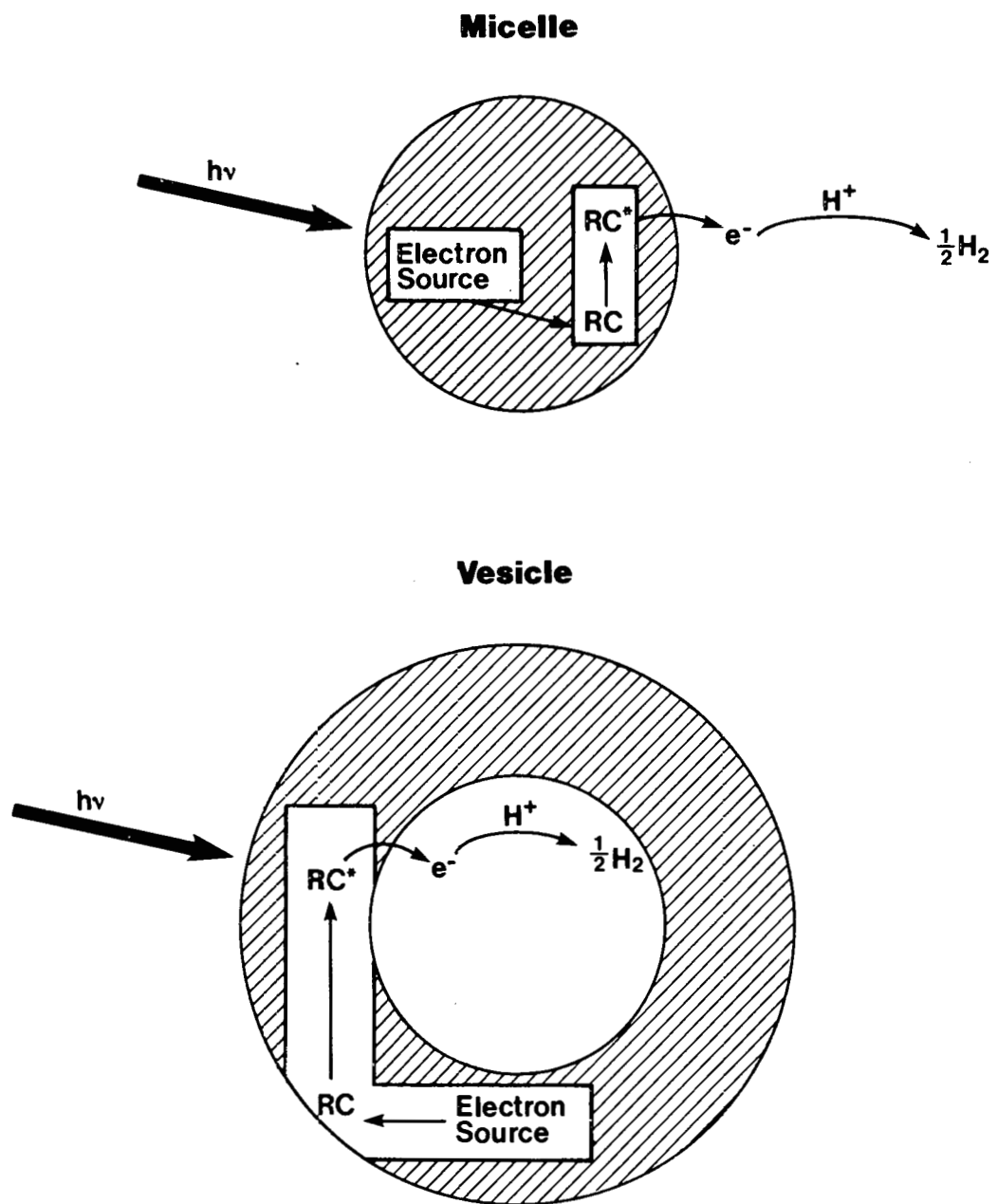


Figure 5. Incorporation of a Model Photochemical Reaction Center into a Micelle or Vesicle

other products (e.g., formic acid, formaldehyde, or methanol) as well as fixation of atmospheric nitrogen (e.g., to hydroxylamine, hydrazine, or ammonia) should be possible. Our long-term goal will be to demonstrate and characterize these reactions in the laboratory pursuing, in turn, photochemical redox reactions involving 2-, 4-, 6-, and 8-electron transfer processes.

For the near term, we shall concentrate on reactions with lower energy barriers than those mentioned above, and which can be carried out via single-photon processes. These reactions must be capable of utilizing available sunlight to produce any of a variety of fuels or chemical feedstocks. Research in this area, therefore, will be highly exploratory, and consideration will be given to a great variety of starting materials and products. Our initial emphasis, however, will be on organic compounds which will utilize the high-energy end of the solar spectrum, either by direct photochemical or photosensitized reactions.

In the photochemical storage area, research will focus on compounds which, either by direct or sensitized exposure to light in the 400 to 600 nm region, will undergo transformation to higher energy forms (e.g., isomers). The most efficient way to utilize this stored energy would most likely be catalytic reversal to the original form accompanied by release of heat.¹⁸ The overall process is depicted schematically in Figure 6. Here again, such processes could be used in either central or distributed systems. With a judicious choice of molecular systems, it may be possible to adapt or retrofit existing thermal collectors for photochemical conversion of solar energy.

¹⁸Jones, G., II et al., op. cit.

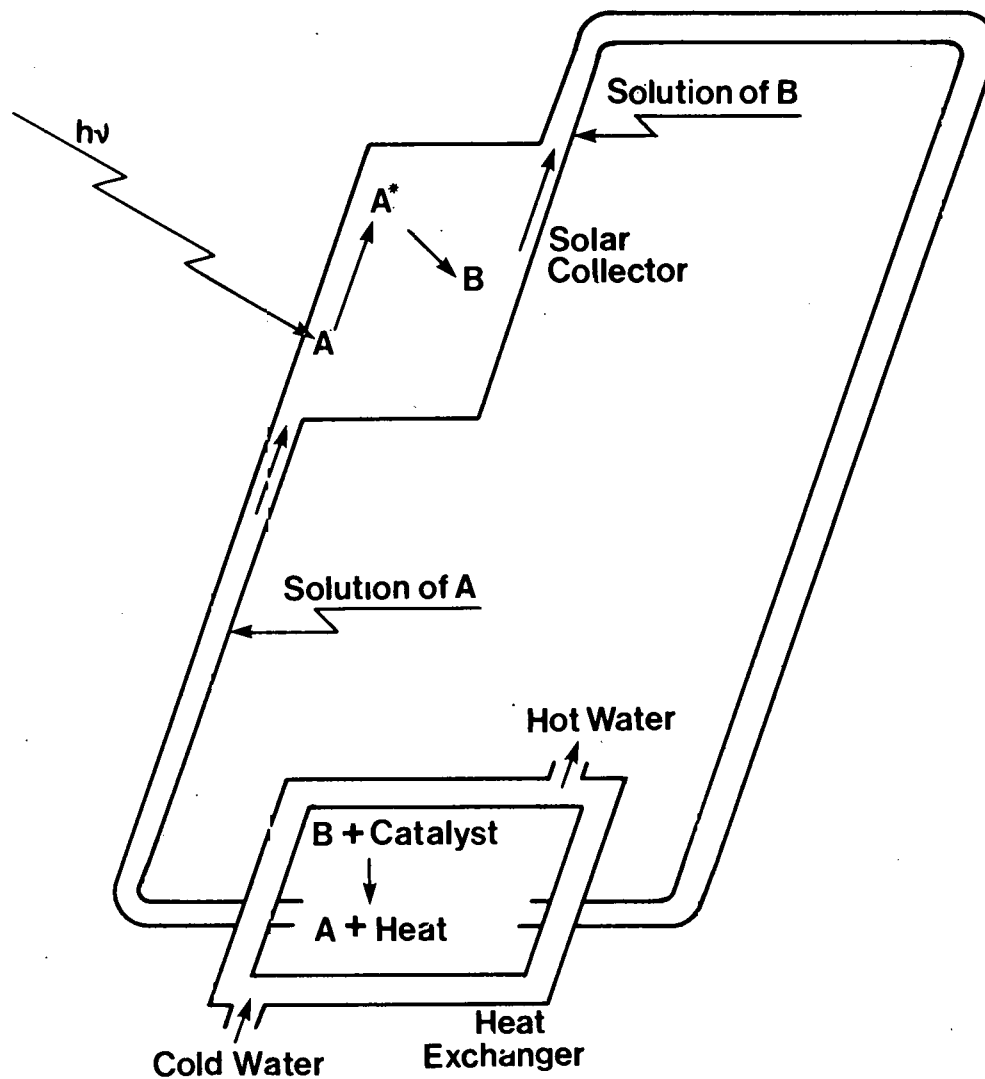


Figure 6. Schematic Diagram of Photochemical Solar Collector System

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IV. SUMMARY AND PLANS FOR FY78-FY79 RESEARCH

In the preceding discussion, we have identified two major areas for in-house research:

1. The supply and production of biomass and its conversion by biological and thermal means.
2. Photoconversion, specifically photobiological and photochemical processes for production of electricity, fuels, and chemicals.

We were guided in the choice of specifics in these areas by the technical considerations discussed previously and by the following factors:

- The nature of ongoing programs in the Fuels from Biomass (FFB) program, in the Office of Basic Energy Sciences (OBES) and elsewhere in DOE.
- The state-of-the-art in solar biological and chemical conversion research as perceived in our scientific review to date.
- The tie-in with proposed technical management of FFB programs by the Branch.
- The objective that in-house research at SERI bridge the region between the very fundamental orientation of OBES programs and the applied orientation of efforts supported by Energy Technology.
- The promotion of interaction between the Biological and Chemical Conversion Branch and other Branches at SERI, particularly Materials, Thermal Conversion, Resource, Photovoltaics, Storage, and Institutional and Environmental Assessment.

During this fiscal year, Branch manpower and laboratory resources will be approximately evenly split between work in the two major research areas listed above. In accordance with the Annual Operating Plan, senior staff members will devote their time to the following subtasks:

- Detailed research-task planning supported by: (1) in-depth literature reviews, (2) monitoring of ongoing research worldwide, (3) visits to other research laboratories, (4) attendance at major scientific meetings, and (5) consultation at SERI with selected experts.
- Performance of specific in-house and subcontracted research programs.

In FY79, increasing emphasis will be placed on the Clean Fuels from Biomass Program. Specifics of planned research and subcontracting activity are given in the following sections.

A. ENERGY AND PETROCHEMICAL SUBSTITUTES FROM BIOMASS

The following task descriptions represent the proposed Branch involvement in the Clean Fuels from Biomass Program in the SERI FY79 AOP.

Biomass Supply and Production Tasks

The current DOE/FFB program concerning biomass supply, procurement, and production is multifaceted and complex, involving both near-term (existing resources) and long-term (energy farming) applications. It is proposed that the FFB Branch assign major planning and technical management responsibilities to SERI in those program areas where SERI's expertise and overall mission can be most responsive to program needs, i.e., areas involving systems and resource base analysis and/or field production research. It

is intended that field production research would be conducted wholly by subcontractors selected and directed by SERI with FFB approval and that resource base/systems analyses would be conducted by SERI staff and selected subcontractors.

The proposed SERI task in biomass production addresses the following topics:

1. Evaluation of Standing Biomass Resources for Near-Term Use

The resource base available for near-term use consists of various agricultural/forestry residues and standing biomass. The former have been extensively inventoried and evaluated by the FFB Branch. The standing biomass resource, consisting primarily of nonmerchantable or low-value timber and other woody species, offers considerably more near-term use potential than residues, but has not been suitably identified, quantified, or characterized. The proposed analyses would be conducted at the state level by separate SERI subcontractors within the respective states chosen for analyses.

Certain research efforts to be associated with the Mid-South Regional Biomass Program being structured by SERI will be folded in with this effort.

2. Energy Farming--Long-Term Research Program

Energy farming is not expected to contribute to near-term energy supplies. A long-term program, however, is required to develop this concept for future applications. This program is a prominent feature of the FFB plans. SERI proposes that it be assigned

technical management/research responsibilities in the following areas:

a. Energy Species Evaluation and Development

Species screening, field management, and improvement research on both herbaceous and woody species are required at a regional level. SERI would plan and manage a long-term (10-15 years) coordinated field research program. The field research would be conducted by SERI subcontractors or by the USDA/FS. The research program already requested of SERI by FFB on "exotic," arid-land/hydrocarbon species would be made a component of this task.

b. Pilot Silvicultural Biomass Farm (PSBF)

Proof-of-Concept Experiment

A PSBF of 1,000 acres is currently being planned by FFB for a site at the Savannah River Plant (SRP) in South Carolina. SERI proposes that DOE assign management responsibilities to SERI for this long-term proof-of-concept experiment, including both the operation of the pilot plantation and its associated research studies. The associated research studies of the SRP project would be coordinated with the program described in (a) above. The SRP site could, in fact, be designated as one of the regional research sites required for that program. The PSBF operation as well as the associated research studies would be conducted by SERI subcontractors or the USFS.

c. Regional PSBF Program

FFB is currently planning to issue an RFP for five regional PSBFs to be installed and operated by private industry. SERI proposes to perform technical management, support, and coordination for this program. Private industrial contractors selected on a regional basis would carry out the program.

d. Integrated Energy Farming Systems Analyses

Systems analyses are needed in three areas to amplify the potential of the energy farming concept. The proposed analyses would be conducted by SERI, combining expertise in the Bio/Chemical Conversion, Systems Analysis, Energy Resource Assessment, Economics and Market Analysis, Policy Analysis, and Institutional and Environmental Assessment Branches. The proposed analyses are:

- Combined Wood Fiber/Energy Farms . . . largely associated with the needs of the wood products industry and the potential utilization of energy farming practices to serve both the energy and fiber needs of that industry.

- Mixed Species Energy Farms . . . analyses of combinations consisting of both woody and herbaceous, annual, and perennial species--and the logistics and economics of combined crop management and harvesting operations.

- Cash Crop Biomass Farming . . . analysis of the potential competitiveness of cash-crop biomass farming by the private farmer, to identify the extent to which biomass might compete economically with food and fiber crops in the future as biomass yields are increased through research.

Biomass Conversion Tasks

The proposed SERI task in conversion addresses the following topics:

1. Gasification, High-Temperature Pyrolysis, Partial Oxidation and Combustion
 - a. Complete the review of literature, related DOE contract study results, and other available process data. Complete and publish SERI translation of GENGAS, the definitive Swedish book on gasification by the Swedish Academy of Engineering.
 - b. Prepare economic and process computer models of one or more of the leading gasification processes.
 - c. Using the model, evaluate the effect of scale, biomass costs, raw material moisture, operating conditions, and other independent variables on energy efficiency, yields, production costs, and other important dependent variables. Identify specific areas of inefficiency or high-capital investment or other areas for potential improvement.
 - d. Hold a gasifier workshop and form a gasification working group. Develop a critique on the design and reliability of key process steps. Identify any problem areas requiring special attention.

- e. Conduct a fundamental, in-house study of thermal conversion mechanisms for biomass.
 - f. Using the technical survey and modeling (a, b, and c above) plus comparable data on coal gasification, determine the circumstances which make biomass based gasification competitive to coal gasification.
 - g. Prepare a comprehensive summary report on biomass gasification. Report to include summary of gasification processes, economic models, discussion of reaction kinetics, and recommendations for further research and development.
 - h. Complete monitoring of contract on testing of the Hesselman Swedish gasifier.
2. Hydrolysis, Extraction, and Other Wet Processing
- a. Compile a comprehensive review of the literature and review current DOE FFB and other program activities related to hydrolysis, etc.
 - b. Prepare conceptual process flow sheets on integrated xylan/cellulose/lignin conversion processes.
 - c. Identify potential problems and opportunities for innovative research, i.e., glucose fuel cell, separation technology, large fermentation reactor design, etc.
 - d. Prepare models on selected state-of-the-art process configurations. Using sensitivity methods, determine areas of opportunity for creative research.

- e. Conduct appropriate extraction studies on exotic hydrocarbon producing plant species.
- f. Prepare comprehensive summary report on hydrolysis, extractive, and other wet conversion processes.

3. Anaerobic Digestion

Initial activities limited to a technical survey of the state-of-the-art, plus selected exploratory work on targets of opportunity, i.e., anaerobic digestion of preconditioned substrate, anaerobic digestion in modified atmosphere, etc.

4. Low-Temperature Pyrolysis

We have recently completed a joint study on the pyrolysis of densified biomass in cooperation with Professor Antal of Princeton University and are continuing an analysis of the results.

5. Hydrogenation and Reduction

No specific efforts planned.

B. THERMOCHEMICAL CONVERSION

Though thermochemical and electrochemical conversion processes are of major interest to the Branch, limitations imposed by staffing, laboratory, and equipment requirements dictate that major experiment activities in this area be deferred until FY80. Activities in solar thermoelectric conversion are being planned by the Systems Analysis and Materials Branches.

C. PHOTOCONVERSION

Photobiological Processes

To date, the photobiological group consists of a photobiologist, a biochemist, and a microbiologist, all of whom have had extensive research experience investigating various photosynthetic processes in a number of different organisms. Specific expertise covers the primary processes, the oxidizing and reducing sides of photosynthetic electron transport, photophosphorylation, photosynthetic hydrogen production, the enzymology of hydrogenase and nitrogenase, and the genetics of photosynthetic organisms. This experience is essential in designing the in-house photobiological research program described briefly below.

Photobiological research will emphasize modified photosynthetic processes and will be classified under two categories. The first category includes fundamental research (though mission-oriented) and will seek to understand more clearly the normal photosynthetic and related processes, including energy transfer mechanisms, structure and function of macromolecular components, and the biochemistry of secondary energy storage including the hydrogenase (hydrogen production) and nitrogenase (nitrogen fixation) systems. The second category will encompass that work designed to apply the above-gained knowledge in coupling biologically generated chemical potential or reducing power to complementary biological and chemical systems to produce useful energy.

Characterization of Fundamental Processes

Specific activities in this area will emphasize the identification of stable, highly active systems (cellular and molecular) which can be used to produce hydrogen; electricity; and, ultimately, other forms of energy directly.

Survey of Organisms for Increased Hydrogenase and Nitrogenase Activities. Presently available laboratory organisms evolve hydrogen under special environmental conditions at rather low rates.¹⁹ This survey will seek to identify strains with high hydrogenase and/or nitrogenase activities. Both enzymes can be associated with hydrogen evolution. Initial emphasis will be placed on photosynthetic bacteria (both freshwater and marine organisms) because they are the simplest organisms known to contain the two enzymes and evolve hydrogen. Superior isolates will aid in understanding the process of hydrogen evolution and the relationship between hydrogenase and nitrogenase metabolism. In addition, they may be applicable in whole-cell hydrogen evolving systems and could supply highly active enzyme for use in in vitro systems.

Protection of Hydrogenase and Nitrogenase from O₂ Inactivation. Nitrogenase, and to a lesser extent hydrogenase, activities are sensitive to oxygen inactivation in whole cells. Attempts to select algal mutants with an oxygen-tolerant hydrogenase for use in practical hydrogen evolving systems have had minimal success. Photosynthetic bacteria are ideally suited genetically and physiologically to test for the mutability of hydrogenase to oxygen resistance. The feasibility of this genetic approach will be investigated. An alternative solution to the oxygen problem would be to conditionally exclude oxygen from the working system²⁰ and would be the subject of future research.

¹⁹Mitsui, A. et al. (eds.), Biological Solar Energy Conversion, Academic Press, New York, Section I, 1977.

²⁰P. Weaver, personal communication.

Genetic Derepression of Hydrogenase or Nitrogenase Synthesis.

Organisms which produce large amounts of hydrogenase or nitrogenase (e.g., constitutive strains) would be beneficial in order to promote maximal activity without undue restrictions in controlling the medium and culture conditions. Such organisms could be isolated using known selection techniques and would additionally serve as a source of large quantities of enzyme for in vitro studies or applications.

Preparation of Stabilized Hydrogenase. The development of organisms with highly active, oxygen-tolerant hydrogenase has been discussed above. The enzyme will be isolated using standard techniques and tested for stability and activity outside of the host organism. Hopefully, improved in vivo characteristics will carry over to the extracted enzyme. Further stabilization of the enzyme under in vitro conditions will be attempted using unique immobilization techniques²¹ to be developed under subcontract.

Preparation of Stable, Highly Active Bacterial Reaction Centers and Photosystem I. Isolated bacterial reaction centers are reputed to be very stable over a period of months.²² Reaction center-enriched Photosystem I particles (from algae and higher plant chloroplasts) may well display similar properties.²³ Preparations from various sources will be isolated by means of detergent and solvent extraction and subsequent chromatographic separation. The physical and physiological properties of such preparation will be characterized and the stability of the particles examined under both aerobic and anaerobic conditions for

²¹Klabanov, A. H., N. O. Kaplan, and M. D. Kamen, Proc. Nat. Acad. Sci., U.S.A. (in press).

²²P. L. Dutton, personal communication.

²³S. Lien, personal communication.

biological and photochemical degradation. Improved stabilization by means of chemical modification or immobilization will be explored. The reaction center complex is the specific component of the photosynthetic apparatus which converts light energy into chemical potential. Thus, stable preparations are central to any applications involving in vitro biological solar energy conversion systems including coupling to the stabilized hydrogenase mentioned above.

Application of Fundamental Processes

The second area of investigation, coupling of biologically generated chemical potential to complementary systems for the production of useful energy, will grow in future years as indicated in the previous section (Characterization of Fundamental Processes). Initially, however, we shall attempt to couple reaction center complexes to the electrodes of an electrochemical cell.

In the past, investigators have tried to couple chemical potential produced during reaction center photochemistry to electrode systems in hopes of producing an electric current. Results have been encouraging with thylakoid membranes oriented onto the working electrode of a "photogalvanic type" photoelectrochemical cell.²⁴ Dried reaction center electrodes have proven unsuccessful. We shall orient monolayers of bacterial reaction centers and Photosystem I particles onto electrodes and fabricate photoelectrochemical cells using a dye system to couple the working and the counter electrodes. Such a system would act as a

²⁴Allen, M. J., "Direct Conversion of Radiant into Electrical Energy Using Plant Systems," in Living Systems as Energy Converters (R. Buvet, M. J. Allen, and J. P. Massue, eds.), Elsevier/North-Holland Biomedical Press, New York, 1977.

biological liquid junction cell. This approach holds promise for increased efficiency since the active biological complex contains a minimum of extraneous membrane and proteinaceous material which only serves to increase the internal resistance of the cell and to decrease the stability of the biological material. The production of electricity does not require water splitting capability since the same electrons would be recycled (analogous to cyclic electron transport in the intact organism).

Future work with in vitro systems will attempt to couple reaction centers to hydrogenase (hydrogen production) and perhaps nitrogenase (nitrogen fixation) or chemical systems to reduce carbon.

Photochemical Model Systems

Initial research will focus in two areas: photosensitizers and photocatalysts. The former will include porphyrins (and structurally related chlorins and bacteriochlorins), and the latter will concentrate on binuclear organometallics.

The requirements for model photosensitizers include both facile electron transfer following absorption of light and subsequent charge-stabilization. A recent hypothesis²⁵ of the primary photophysical processes in bacterial photosynthesis involves fission of singlet excitation energy into two triplets in the bacteriochlorophyll (BChl) "special pair," followed by electron transfer to yield a $BChl^+ \dots BChl^-$ ion-pair. This is possible because: (a) the energy of two triplets is thought to be slightly

²⁵Connolly, J. S., Abstracts, First International Conference on the Photochemical Conversion and Storage of Solar Energy, London, Ontario, August 24-28, 1976.

less than the energy of an excited singlet dimer,²⁶ and (b) the absolute sum of the oxidation and reduction potentials of BChl is in turn less than the energy of two triplets.²⁷ The hypothesis further requires that the triplet energy of bacteriopheophytin (the recipient of electron transfer from the presumed ion-pair)²⁷ be greater than that of BChl.

Accordingly, a search will be made for the absolute triplet energies of these pigments using direct (i.e., phosphorescence spectroscopy) and indirect (energy transfer) techniques. The former will involve detection of emission in the near-infrared (1-2 μm), which is a notoriously difficult region of the spectrum for emission studies, owing to limited availability of suitable detectors with high sensitivity. Energy transfer studies can be conducted using the method of laser flash photolysis²⁶ by selectively exciting the pigment of interest and observing the kinetics, on the nanosecond to microsecond time scale, of subsequent energy transfer to added reagents.

Charge stabilization will be investigated using porphyrin-like compounds as photochemically active sites bound to polymer micelles or membrane vesicles. This work will involve synthesis of surfactants of the porphyrins, as well as of the electron donors and acceptors, in order to effect specific orientation of the various constituents. An additional requirement is high local concentrations of the light-harvesting and electron donor and acceptor species at or near the surfaces of the respective assemblies.

²⁶Connolly, J. S., D. S. Gorman, and G. R. Seely, Ann. N.Y. Acad. Sci., 206, 649, 1973.

²⁷Fajer, J. et al., Proc. Nat. Acad. Sci. U.S.A., 72, 4956, 1975.

Kinetics and quantum efficiencies of light-induced charge separation will be determined by standard photochemical techniques, including absorption and fluorescence spectrophotometry, flash photolysis, determination of action spectra, and actinometry.

Our interest in solar photocatalysis stems from the necessity to carry out sequential multielectron transfer steps. For example, evolution of hydrogen or oxygen from water, fixation of atmospheric nitrogen to ammonia, and reduction of carbon dioxide to methane are, respectively, 2-, 4-, 6-, and 8-electron transfer reactions. Thus, it will be necessary to stabilize intermediate redox states so that stepwise oxidation and reduction reactions can occur at the relatively low intensities typical of solar radiation conditions.

Initial efforts will concentrate on synthesis and characterization of binuclear organometallic compounds such as cofacial diporphyrins²⁸ and bisfulvalene dimetals.²⁹ Both classes of compounds offer the potential of charge stabilization in the form of mixed valence intermediates, but initial efforts will concentrate on the latter.

In any case, commencement of experimental work will have to await completion of the SERI interim laboratory facilities, currently scheduled for late 1978.

²⁸Chang, C. K., J. Heterocyclic Chem., 14, 1285, 1977.

²⁹Smart, J. C. and C. J. Curtis, Inorg. Chem., 16, 1788, 1977.

APPENDIX

CURRENT RESEARCH IN PHOTOCHEMICAL APPROACHES
TO SOLAR ENERGY CONVERSION

CURRENT RESEARCH IN PHOTOCHEMICAL APPROACHES
TO SOLAR ENERGY CONVERSION

As noted in the text (Section II), much of the current research in the area of photochemical conversion of solar energy is progressing along disciplinary lines. Hence, a discussion in this context provides a convenient framework for examining the spectrum of photochemical conversion schemes and for assessing the state-of-the-art. In the following paragraphs, the nonbiological side of photoconversion is discussed from the standpoint of chemical physics, physical chemistry, organic chemistry, inorganic chemistry, and biochemistry, as outlined in Table A-1. One must bear in mind, however, that the borderlines of these fields are far from distinct and that certain categorizations will necessarily be somewhat arbitrary.

At the risk of some oversimplification, chemical physics, in the context of photoconversion, is divided into solid-state physics and spectroscopy. The former includes photovoltaic conversion in which separation of electrons and holes is induced by quantized absorption of light in atomic and molecular ensembles, such as semiconductors. In general, neither a change of state nor a transition across phase boundaries is involved; hence, conversion of light to electricity in the solid state is considered to be more of a physical than a chemical phenomenon and is included in the mission of SERI's Photovoltaics Branch. However, if such a material (semiconductor, heterojunction, or p-n junction) is immersed as an electrode in a conducting solution for the purpose of generating electricity or a chemical product, the term "photoelectrochemistry" is generally used. This area is at the interface of solid-state physics and physical chemistry and is discussed below under the latter category.

TABLE A-1
OUTLINE OF PHOTOCHEMICAL APPROACHES TO
CONVERSION AND STORAGE OF SOLAR ENERGY

Photochemistry

- A. Chemical Physics
 - 1. Solid State
 - 2. Spectroscopy and Photophysics
- B. Physical Chemistry
 - 1. Kinetics
 - 2. Thermodynamics
 - 3. Electrochemistry
 - a. Photoelectrochemical cells
 - b. Photogalvanic cells
- C. Organic Chemistry
 - 1. Isomerization
 - 2. Dissociation
 - 3. Synthesis
- D. Inorganic Chemistry
 - 1. Photoredox Reactions
 - 2. Mixed Organic-Inorganic Systems
 - 3. Organometallic Compounds
 - a. Chlorophylls and porphyrins
 - b. Transition-metal complexes
 - c. Metallocenes
- E. Biochemistry (isolated macromolecules)
 - 1. Visual pigments
 - 2. Bacteriorhodopsin
 - 3. Cytochromes
 - 4. Photosynthetic Reaction Centers
 - 5. Hybrid Systems

Spectroscopy includes a variety of theoretical and experimental methods as well as studies of unimolecular processes of excited states which do not involve the making or breaking of chemical bonds (i.e., photophysical processes). Studies of electronic excitation spectroscopy involve calculations and measurements of the light-absorbing properties of molecules, absorption wavelengths (i.e., photon energies), and transition probabilities (absorption and emission strengths), as well as the fates and lifetimes of excited electronic states.

Other physical techniques of particular relevance to photoconversion include electronic emission spectroscopy and magnetic resonance spectroscopy. The former is implicitly included with electronic excitation spectroscopy. Of the latter category, electron spin resonance (ESR), nuclear magnetic resonance (NMR), and electron-nuclear double resonance techniques (ENDOR) have proved to be invaluable tools in aiding our understanding of the precise molecular architecture of the photoreceptor complexes involved in photosynthesis as well as in less complicated photoconversion processes.

Knowledge of these spectroscopic and photophysical properties is of fundamental importance to the understanding of a variety of photoconversion mechanisms, biological as well as chemical, and hence to the design and fabrication of new devices and systems.

The majority of current programs are supported by OBES in DOE, with lesser support being provided by the basic research offices of the Department of Defense and by the National Science Foundation.

In the area of physical chemistry, we are concerned primarily with kinetics and electrochemistry. We also include thermodynamics since considerations of equilibrium and the energetics of reaction mechanisms necessarily underlie any physicochemical approach.

Within the area of kinetics are included pulse-relaxation techniques such as flash photolysis and laser excitation. Both techniques overlap significantly with electronic excitation spectroscopy and provide valuable insight into such primary photophysical and photochemical events as energy and electron-transfer, bond dissociation, isomerization, and energy-dissipation processes. Events can be studied by such methods on time scales ranging from picoseconds to tens, or even thousands, of seconds.

Electrochemistry involves both generation of electric current by controlled chemical reactions and reverse processes. Electrochemical reactions can occur in the electrode, the electrolyte, or both. Thus, by immersing a photovoltaic device (e.g., semiconductor) as an electrode in a conducting solution and making appropriate connections through a counter-electrode to complete an electric circuit, one can construct a photoelectrochemical cell.

Such a device can be operated in either of two modes: the photovoltaic (photoregenerative) mode, in which incident light induces a flow of electric current, or the photoelectrolytic mode, in which incident light, perhaps with the assistance of an external voltage source, causes chemical reactions to occur--reduction at the anode and oxidation at the cathode. Thus, photoelectrolysis of water has been demonstrated to produce both hydrogen and oxygen. In either mode, the actinic light is absorbed at one of the electrodes; hence, both types of systems are examples of photosensitized, heterogeneous reactions. The distinction is that operation in the photoelectrolytic mode requires either irreversible reactions at the electrodes or physical separation of the products. In the photovoltaic mode, reversible redox reactions must occur at the electrodes so that an electric current can be passed through the external circuit.

A photogalvanic cell is analogous to a photoelectrochemical cell operating in the photovoltaic mode. In this case also, the electrolyte undergoes reversible redox reactions at each electrode; however, the actinic light is absorbed in the electrolyte, and the electrodes are passive. Hence, a photogalvanic cell is categorized as a homogeneous photoredox system. The anode and cathode must be distinguished, either by using a different electrolyte in each compartment, or in such a way that only one compartment is illuminated. In either case, a current flows in the light and ceases when both electrode compartments are in the dark.

Research in these areas is sponsored by the same agencies mentioned previously, with DOE taking the lead role. In addition to OBES, two current projects in the photoelectrolysis area are being supported under the auspices of the FFB Program.

Thus far we have discussed methods and techniques without specifying the nature of the systems to be investigated. There are broad distinctions among organic, inorganic, and biochemical systems which lend themselves to specific types of photoconversion processes.

Organic compounds are being studied by a number of research groups for possible energy-storage applications. Mechanisms include isomerization, dissociation, and synthesis. The purpose is to store the energy of electromagnetic radiation in chemical (covalent) bonds for subsequent recovery, usually in the form of heat. Another function of organic compounds is to act as photosensitizers. Of particular interest in this application is the goal of synthesizing molecules with specific properties for optimum utilization of the solar spectrum.

Another attractive mechanism for chemical conversion of solar energy involves photo-induced oxidation and reduction (photoredox) of inorganic compounds. The underlying principle is the shift in redox equilibrium following absorption of light. Electron transfer, i.e., oxidation of an electron donor and reduction of an acceptor species, is induced from an excited electronic state of one of the reactants. Subsequent dark reactions can then be utilized, for example, to induce an electric current (in a photogalvanic cell) or to generate hydrogen. In mixed organic-inorganic systems, a photoredox mechanism might be used for chemical synthesis or other chemical processes leading to the storage of light-induced chemical energy for consumption on demand.

Organometallic compounds are another important class of molecular systems being studied quite actively for solar applications. The chlorophylls (magnesium-porphyrin complexes) are examples of organometallic molecules used in nature to convert light into chemical energy. In addition to chlorophylls and porphyrins, active research is being pursued by a number of groups throughout the world using organic complexes of transition metal ions. Of particular interest are heterocyclic (e.g., substituted pyridines) complexes of ruthenium and rhodium. The electronic energy levels of the organic skeleton interact with those of the metal ion in such a way as to shift the absorption spectrum well into the visible region and, at the same time, promote useful redox reactions. Metallocenes offer the prospect of acting as intermediates in sequential electron-transfer processes. The photochemistry of these compounds, especially in the context of solar energy conversion, is virgin territory. It is expected that the Branch will undertake a pioneering role in this new area.

Chlorophylls and transition metal coordination compounds have been incorporated into model systems using artificial membranes, mono- and multilayer assemblies, and polymer micelles. As noted previously, electron transport across a membranous structure appears to be necessary to promote useful forward reactions (e.g., reduction of protons to hydrogen gas) and to inhibit energy-wasteful recombination processes. This is one of the most active research areas in the photochemical approach to solar energy conversion, with about a half dozen research groups throughout the world exploring various approaches.

Finally, we turn to biochemical systems. Physical studies of in vitro photoprocesses in biological molecules are at the interface of photochemistry and photobiology. What is involved is a detailed understanding of light-induced processes in relatively high molecular weight molecules and molecular ensembles. The visual pigment (rhodopsin) and its bacterial analog (the purple membrane of Halobacterium halobium), cytochromes, and extracted photosynthetic reaction centers are a few examples of biochemical systems of current and potential interest. Research in this area is interwoven with studies of hybrid systems, both photosynthetic and nonphotosynthetic, as discussed previously under "Photobiological Processes."

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