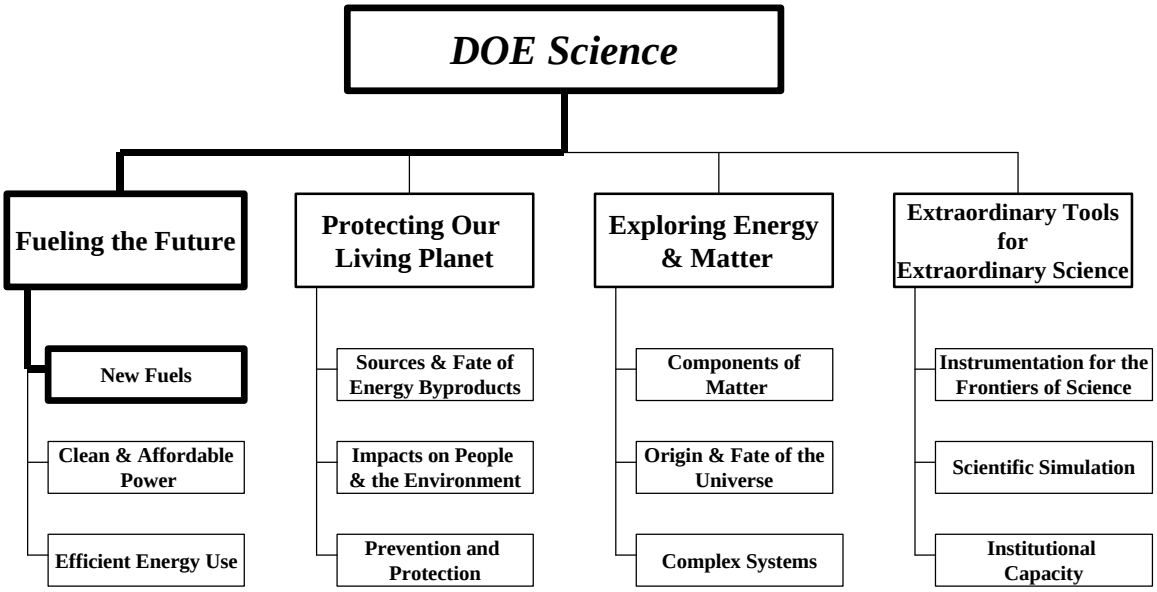
Chapter 2
New Fuels

Scientific Challenge: ***To understand the geological, chemical, biological, and physical processes for clean and affordable domestic fuels.***



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Most of the goods and services we use in our everyday lives depend for their production on our energy system, which is powered predominantly by fuels. Fuels enable our standard of living, from heating and cooling our homes to growing and preparing food, to transporting us near and far, to manufacturing a plethora of goods. Wood fuels have been used for hundreds of thousands of years. Coal has been mined since the thirteenth century. Oil began to be burned for energy early in the nineteenth century; later in that century, the age of electricity dawned. In the 1950s advanced alloy steels, welding techniques, and large-scale compressors allowed efficient pipeline transport of natural gas, greatly expanding its role in the energy system. All of these fuels are used today to produce energy for human consumption.

Fuel use, however, often has negative consequences, including local and regional pollutants and greenhouse gases; moreover, considerations of energy security prompt the United States to expand the role of domestic fuels. The challenge of the coming decades is to produce the energy needed by the nation while minimizing or eliminating the impact of fuel use on the environment—reducing or removing sulfur and nitrogen compounds, fine particulates, and (perhaps hardest of all) carbon from the fuel or carbon dioxide from the atmosphere.

Developing clean fuels necessitates a wide range of scientific endeavors: geologic investigation of new fossil reserves; biology, genetic engineering, and materials science to develop renewable sources; materials, engineering and chemistry to develop more acceptable energy options; chemistry to remove pollutants from fuels and convert them to other useful products; and mathematics to model and control such processes. In addition, science provides the means to advance our understanding of the effects of energy extraction from fuels and the means to measure, model, and deal with its impacts.

Solar Energy Conversion

Description, Objectives, and Research Performers

The research effort in photochemical energy conversion ranges from the photophysics associated with direct conversion of solar energy to electricity to the photochemical conversion of solar radiation to fuels and specialty chemicals. Related to the photochemistry program but using different techniques is the radiation chemistry research program. A major goal is to obtain molecular level information on chemical reactivity in solution, reactive transient intermediates, the kinetics and mechanisms of chemical reactions and processes at the solid/liquid interface. This research is conducted at national laboratories and universities.

Research Challenges and Opportunities

The program challenges are to understand, at the molecular level, fundamental processes that capture and convert solar energy. Solar photochemical energy conversion offers an attractive alternative to solid state, semiconductor photovoltaic solar cells. Fundamental concepts of light-induced charge separation at the molecular level may be applied to photodriven endothermic reactions for the conversion of light energy to chemical energy. Industrially significant chemicals such as alcohols may be produced from carbon dioxide, or hydrogen from water, or ammonia from atmospheric nitrogen. In addition, photochemistry presents opportunities for altering chemical reaction pathways so that high volume industrial intermediates and specialty

chemicals and fuels can be produced by less polluting processes. In both industrial and specialty chemicals commercial production using solar energy may result in lower financial cost with reduced environmental impact. In regard to global warming, photochemical reduction of CO_2 poses scientific challenges that deserve serious attention. The radiation chemistry research program provides information on intermediates in solution, at liquid/solid interfaces relevant to solar photochemical energy conversion, environmental waste management and remediation, as well as nuclear energy production and catalysis.

Research Activities

The program explores the fundamental concepts associated with understanding photosynthesis focuses on the light-induced charge separation at the molecular level. This understanding is germane to photodriven endothermic reactions for converting light energy to chemical energy. The program encompasses several broad areas, including organic and inorganic photochemistry, electron and energy transfer in homogeneous and heterogeneous media, photocatalysis, and photoelectrochemistry and, hence, examines fundamental issues of chemical reactivity in solution. This research includes biomimicry, or artificial photosynthesis. Naturally occurring photosynthetic reaction centers and antenna systems are studied as models of biomimetic/photocatalytic assemblies that can carry out efficient photoinduced charge separation. Research activities include the spectroscopic investigation of photosynthetic systems at short times following the absorption of light to determine the nature of the excited electronic states involved in the energy conversion process. The radiation chemistry research provides information on transients in solution and intermediates at liquid/solid interfaces for resolving important issues in solar photochemical energy conversion, environmental waste management and remediation, and intermediates relevant to nuclear energy production.

Major research efforts include inorganic photochemistry and electron transfer at Brookhaven National Laboratory; photoelectrochemistry at the National Renewable Energy Laboratory; and photosynthesis at Argonne and the Ames Laboratory. The radiation chemistry program is centered around specialized facilities at the Notre Dame Radiation Laboratory, Argonne National Laboratory, and Brookhaven National Laboratory. The Notre Dame Laboratory serves as the primary user facility for radiation chemistry in the United States.

Accomplishments

- Understanding of the conformational arrangement necessary for initiating charge separation and electron transfer has provided a new basis for development of biomimetic molecules for photosynthesis. A liquid molecule was recently discovered that spontaneously self-organizes into highly ordered ribbon-like crystals, a state known to be important for photoconversion because of the importance of crystallinity in semiconductor films. The electrical conductivity of the film increased sevenfold during the spontaneous transformation.

- Molecular models that duplicate key parameters of the light-energy conversion apparatus of photosynthesis, including charge separation, have been achieved. Supramolecular structures for light harvesting, such as pentameric porphyrin arrays and starburst dendrimers, were obtained and multimetal complexes that feature chromophoric and

catalytic sites were designed and synthesized. Long-lived charge separation has been achieved in a variety of microheterogeneous environments, such as zeolites, layered oxide assemblies, and ordered polymers.

- Theoretical studies on semiconductor nanoclusters successfully predicted their size-dependent optical properties—important for selecting semiconductors to make quantum dots with more efficient optical transitions or as better single electron devices. To make smaller, faster, cheaper components, scientists are investigating nano-scale fabrication techniques. Nanocrystalline semiconductor quantum dots have been exploited for their large surface area and size-dependent absorption characteristics.

- Studies of translationally excited atoms were a staple of the early program in radiation chemistry as it related to nuclear technologies. F. Sherwood Rowland was supported to study such systems, especially hot chlorine atoms. He recognized that photolysis offered an easier path to hot chlorine atom formation, that fluorocarbons were convenient sources and serendipity led him to recognize the impact of chlorine atoms upon the ozone layer, a discovery that resulted in the Nobel Prize in Chemistry in 1995.

- Improvements in the knowledge of behavior of condensed matter physics have been applied to develop photovoltaic solar cells that convert sunlight into electricity with 30% efficiency—far more than the 10-20% efficiencies of earlier devices.

- Paradigm studies of Ruthenium bipyridal complexes have demonstrated the feasibility of photovoltaic, photogalvanic, and chemical photoconversion processes based on this and other inorganic and organic molecular sensitizer systems.

Plant and Microbial Research

Description, Objectives, and Research Performers

The program supports mechanistic research on fundamental biological processes related to capture, transformation, storage, and utilization of energy. Research focuses on the microbiologically driven carbon exchange between the oceans and atmosphere and the exchange between the atmosphere and the terrestrial biosphere and soils. These exchanges have been absorbing much of the anthropogenic carbon released to the atmosphere. Genomic DNA sequences will be determined for microbes capable of transforming sunlight and waste products into methane and hydrogen at room temperature and room pressure, offering the promise of new energy sources. This research is conducted primarily at universities. A Memorandum of Understanding signed in 1987 established a three-agency plant science partnership (DOE, NSF, and USDA) that jointly solicits and reviews proposals for multi-institutional research coordinating group awards and interdisciplinary research training group awards. In addition, there is an internationally recognized group at the Plant Research Laboratory at Michigan State University, which studies many areas of plant science and uses Arabidopsis as a model plant system. The Complex Carbohydrate Research Center at the University of Georgia provides services and instrumentation for the structural analysis of carbohydrates derived from microbial sources.

Research Challenges and Opportunities

The research focuses on plants and non-medical microorganisms to form a broad scientific foundation for support of the Department of Energy's challenges in energy production, environmental management, and energy conservation. Almost all aspects of energy are immersed in the web of life on earth. Plants, which are a major component of that web of life, can represent an energy demand in terms of producing food and other products, an energy source in terms of biomass or plant-based fuels and chemicals, or a biological filter and digester in terms of exposure to the waste and byproducts of different energy production systems that are released into the air, water and soil. Microbes are also used extensively in various energy-related activities ranging from tertiary oil recovery to the production of alcohol fuels. In nature, microbes have evolved very complex and diverse metabolic and physiological capabilities. The study and understanding of these capacities will permit their full exploitation in an energy context.

Fundamental research in plants and microbes increases our opportunities to understand how carbon moves through the ecosystem and provides concepts on means to impact man's activities, because plants and microbes provide the main route for living system to convert carbon dioxide into higher chemicals. Each of these areas have the potential to be commercially applied, resulting in major economic and societal impacts, such as the formation of a new generation of bio-based industries and a major impact on the nation's production and use of energy-expensive chemicals and fuels.

Research Activities

The focus of research on plants includes photosynthetic mechanisms and bioenergetics in algae, higher plants, and photosynthetic bacteria; control mechanisms that regulate plant growth and development; fundamental aspects of gene structure, function, and expression; plant cell wall structure, function and synthesis; and mechanisms of transport across membranes. Research supported in these areas seeks to define and understand the biological mechanisms that effectively transduce light energy into chemical energy, to identify the biochemical pathways and genetic regulatory mechanisms that can lead the efficient biosynthesis of potential fuels and petroleum-replacing compounds, and to elucidate the capacity of plants to remediate contaminated environments by transporting and detoxifying toxic substances.

The research focus in the microbiological sciences includes the degradation of biopolymers such as lignin and cellulose; anaerobic fermentations; genetic regulation of microbial growth and development; thermophily (e.g., bacterial growth under high temperature); and other phenomena with the potential to impact biological energy production, conversion, and conservation. Organisms and processes that offer unique possibilities for research at the interface of biology and the physical, earth, and engineering sciences are also studied.

Accomplishments

- The composition and structure of pore proteins can now be altered to change the size of the pore, the selectivity of the pore for letting different molecules pass through, and the pore's ability to open and close. Among the potential products of this research are

chemical triggers or molecular switches that can be used to create new sensors to detect harmful chemicals or viruses.

- A chemical in the walls of cells destined to become embryos has been shown to make other nearby cells change their development so that they too are fated to become embryos. This simple cell-to-cell communication shows how a cell can differentiate according to its precise location within the whole plant.

- The DNA sequences of several energy-related microbes have been or are being determined to provide information needed to develop new or improved energy sources that minimize pollution. The microbes being characterized include *Archaeoglobus fulgidus* (which contribute to oil well souring), *Thermotoga maritima* (which may be used in energy generation from biomass), *Methanobacterium thermoautotrophicum* (a methane producer), and *Carboxydothermus hydrogenoformans* (a hydrogen producer).

- Research on fatty acid desaturases and hydroxylases has deciphered the mechanism that controls the introduction of double bonds or hydroxyl groups at specific sites between pairs of carbon atoms in long-chain fatty acids. Identification of the active sites for these enzymes enables the synthesis of new enzymes with specific properties.

- The complete metabolic pathway leading to the bacterial biosynthesis of methane was resolved. The biochemistry of this process was very unusual, involving previously undiscovered cofactors, one-carbon carriers, and enzymes. The novelty of the biochemistry of methanogenesis prompted investigations into the relationship of these bacteria to other known bacteria. These studies concluded that archeabacteria represent a different kingdom of life, a kingdom that was the likely progenitor of both eucaryotes and true bacteria.

- Dr. Paul D. Boyer shared the 1997 Nobel Prize in Chemistry for "elucidation of the enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP)." The energy captured from photosynthesis or released from respiration is converted into the central molecule, ATP, where it is used to maintain cells and synthesize cellular components, as well as for energy-requiring processes such as movement. Dr. Boyer's work, which was sponsored by the Office of Science, examined the detailed chemical reactions involved in the synthesis of ATP and the roles played by specific parts of the ATP synthase molecule.

Geosciences

Description, Objectives, and Research Performers

Geosciences research aims to build the long-term fundamental knowledge base underlying energy technologies of the future. These future energy technologies will involve exploration, enrichment, production, conversion and consumption of energy and mineral resources and generation of technological wastes. Energy and mineral utilization will also require a better understanding of natural processes that will help to minimize anthropogenic perturbations of earth systems. Ultimately, geosciences research impacts control of industrial processes to

improve efficiency and reduce pollution, to increase energy supplies, and to lower cost and increase the effectiveness of environmental remediation at polluted sites. Advances in geophysical imaging are improving the basis for characterizing the distributions of material properties, including layering, mineralogy, lithology, geometry, fracture density, porosity, fluid distribution and type, and composition of the lithosphere. Geophysical methods are achieving higher resolution and greater penetration. This research is conducted at national laboratories, and in industry and universities.

Research Challenges and Opportunities

Research in geosciences focuses on geophysical and geochemical understanding for advancing choices among current and emerging energy and environmental technologies. Fundamental understanding of mineral-fluid interactions will provide a better foundation for oil, gas, and geothermal resource recovery, and for control of energy byproducts and contaminants in groundwater flow. New fundamental physico-chemical property information on rocks, minerals, and geologic fluids will aid in resource recovery and contaminant assessment and monitoring. Extending the applicability of isotopic tracer and geophysical characterization methods will enable evaluation of natural and human-perturbed processes in the geologic environment. The goal is to increase fundamental knowledge of the processes that transport, concentrate, emplace, and modify energy and mineral resources and their byproducts. A major challenge of geosciences research is to develop improved analytical tools for better characterizing earth materials and systems. This is particularly important because earth systems are inherently heterogeneous, multicomponent and multiphase mechano-physico-chemical environments.

Research Activities

Basic research in geosciences includes geophysical and geochemical properties of rocks and minerals (dry, unsaturated, and saturated) determined in the laboratory or in the field (in situ), by direct or indirect techniques. The research is applicable on many spatial and temporal scales of geologic processes. This includes the interrelationships among constituents and their dynamic properties (physical, chemical, and mechanical) and the role of fluid flow as a cause and/or effect. Research is being conducted on fluid transport processes and dynamics (including advanced numerical analyses) and reaction-transport-mechanical properties of fluid-rock systems from the laboratory to the basinal scale. These studies are advancing the understanding of physical transport processes in porous and fractured rocks, leading to predictive capabilities. Research on the physical controls and effects of the dynamic evolution of geologic structures on a local or regional scale are taking advantage of recent developments in geophysical characterization and computational analyses.

Accomplishments

- Novel non-linear inverse modeling has been developed to relate 3-D electromagnetic fields to subsurface fluid distributions and flow. Such non-invasive characterization and monitoring of contaminant fluids in the subsurface remains one of the highest priorities in remediation technology and has implications for resource recovery as well. For example, 3-D images of a salt-water injection test have shown the shape of the salt-water body and locations of maximum permeability through which the salt water has migrated.

- Innovative experimental methods have been developed to evaluate the effects of density-driven and diffusion-driven fluid flow, which is essential for analyzing multiphase flow in geologic systems.

- A new approach to describing the scaling behavior of fault slip-rates during earthquakes has been developed based on analysis of how earth materials respond to stress-state instability across a fault.

- High-resolution mass spectrometry has been developed and is being used to investigate the transport processes, mechanisms, and pathways of heavy metal contaminants, including uranium- and thorium-series isotopes. Scientists can now calculate the residence times of heavy metals in seawater, and better understand the processes by which they are extracted by precipitating sediment.

- Improvements in laboratory, analytical, and numerical modeling have contributed to a better understanding of the origins and evolution of fracture and fault systems under three-dimensional stress-states; these improved models better reflect natural processes and are better able to characterize potential interactions among fractures and faults.

Materials Chemistry

Description, Objectives, and Research Performers

Basic research in materials chemistry includes the synthesis and characterization of complex, multicomponent materials with improved properties through new combinations of atoms and new degrees of complexity. The program emphasizes biomolecular and organic materials research and the self-assembly of structures on a nanoscale to take advantage of the huge number of biomolecular materials and processes. The aim is a fundamental understanding of the behavior of novel materials and structures.

This research is conducted predominantly at national laboratories and universities. Some of the centers of excellence in materials chemistry are (1) the Centers for Advanced Materials in Biomolecular Materials, for Advanced Materials in Polymers and Composites, and for Advanced Materials in Surface Science and Catalysis at Lawrence Berkeley National Laboratory; (2) the Chemical-Materials Collaborating Access Team (ChemMatCARS) for studying surface science at the University of Chicago; (3) a concentration of expertise on Chemical-Vapor Deposition at Sandia National Laboratories (to understand the interplay of chemical reactions and fluid dynamics, develop computer codes to model such processes, and transfer this technology to industry; (4) a concentration of expertise on polymeric superconductors at Argonne National Laboratory; (5) a very strong research group on the synthesis and characterization of inorganic materials at Ames Laboratory; (6) a very strong effort in Biomimetic Materials at Pacific Northwest National Laboratory.

Research Challenges and Opportunities

Materials chemistry provides the primary support for fundamental research in surface science, polymers and organic materials, and for new inorganic materials. The surface science is

important for energy in the understanding which can bear on catalysis as well as surface interactions which lead to degradation and corrosion of surfaces including photovoltaic devices, batteries and fuel cells. New techniques for fabrication of nanocrystals such as the use of inverse micelles may have a big influence on the development of arrays of tunable photoabsorption materials for conversion of sunlight into stored energy. Similarly, the development of synthetic membranes may have uses for separations and for energy storage. Research on solid electrolytes is already paying off in new rechargeable batteries which can be recharged many more times than existing commercial cells. Research on polymers may lead to lightweight structural materials that can be used for automobiles and thereby provide substantial savings in gas mileage, and reduce corrosion. It should be noted that Saturn cars use polymeric door panels which are flexible and bounce back after deformation.

State-of-the-art experimental tools are becoming more available: synchrotron x-ray sources, new and upgraded neutron sources, high magnetic fields, and high pressures. There will be an increase emphasis on nanoscale structures and the way these structures behave chemically. We may see new techniques to develop materials using DNA-type templates. In addition, there will be increased multi-investigator efforts to bring appropriate talent to bear on increasingly more difficult problems.

Research Activities

This program is the primary support in the nation for research in polymers, organic materials, biomaterials, surface science, and new inorganic materials, all of which are important in applications such as fuel cells, batteries, membranes, catalysis, electrochemistry, and photoabsorption. Activities include investigations of low-dimensional structures of self-assembled monolayers, micelles, polymeric conductors, organic superconductors and magnets, complex fluids, colloids, biomolecular materials clusters and nanocrystals, and interfacial phenomena. The research employs a wide variety of experimental techniques to characterize these materials, including x-ray and neutron spectroscopies, scanning-tunneling and atomic force microscopies, nuclear magnetic resonance (NMR), and x-ray and neutron reflectometry. The activity also supports the development of new experimental techniques such as double rotation NMR, neutron reflectometry, atomic force microscopy of liquids, and zero field NMR using SQUID detection.

Accomplishments

- A combinatorial chemistry system has been devised for optimization of physical and chemical properties in which the chemical composition of a material can be changed, with each composition located at a point on a grid. The performance of each composition is then tested and the optimized composition can be selected easily and rapidly. This is one of the important new methodologies to reduce the time and costs associated with producing effective, marketable, and competitive new substances.

- Scientists have discovered a broad class of designed organic molecules that self-organize at three hierarchical levels into functional supramolecular materials. The basis for the synthesis of this new class of films is a pencil shaped organic molecule termed a "rodcoil," so named because one-half of the molecule is rigid and the other half is

flexible. This property could make the films useful for everything from anti-icing coatings on airplane wings to anti-bloodclot linings for artificial blood vessels.

- A wide range of experimental and theoretical techniques has been developed and used to investigate the fundamental science of Chemical Vapor Deposition (CVD). The complex chemistry and the complex fluid flow were modeled, experimental detection of reactive gas phase species including molecular beam radical-surface studies was achieved, state-of-the-art CVD reactors were developed, and extensive models easily adapted to specific systems were generated and tested. A new facility at Sandia, established as a result of these fundamental studies, aids CVD reactor manufacturers design better instrumentation.

- Over the past 10 years, new techniques in high resolution nuclear magnetic resonance (NMR) have been developed and applied to scientific problems. Included in a long list of such techniques are: Laser-Polarized Xenon NMR and MRI signal enhancement, making possible sensitive study of structure and dynamics of molecules in solution, on surfaces, and in live tissue; double-rotation NMR, making possible analysis of quadrupole nuclei; zero-field NMR, making possible, when coupled with hyperpolarized Xe, brain and cardiac MRI in the absence of a magnet; and multiple quantum NMR.

- Synthesis and characterization of the first room temperature molecular polymer-based magnet was achieved. This achievement increased the critical temperature of molecular magnets from 19K to ~400K. This result has spawned a new wave of research in this area with a new class of molecular inorganic magnetic materials.

Portfolio Summary

This portfolio area, “New Fuels,” encompasses research from many programs and supporting activities that crosscut the research topics covered above. The table below summarizes specific programs that strongly support or moderately support New Fuels, including solar energy conversion, plant and microbial research, geosciences, and materials chemistry. The funding totals for these areas are an analytic tool reflecting the highly crosscutting, leveraged aspects and implications for individual research areas within DOE’s science portfolio. **Because research areas may appear in multiple chapters, there will be significant instances of multiple counting, and the chapter totals will not sum to the overall science budget.** Additional details on these research areas are presented in the Research Summary Matrix and the corresponding Research Summary Profiles.

Strongly Supportive RSPs (Combined Budget: $165.90 Million)
Applied Mathematics
Chemical Energy and Chemical Engineering
Climate Change Technology Initiative (CCTI)
Energy Biosciences
Geosciences
Materials Chemistry
Microbial Genomics
Photochemistry and Radiation Research

Moderately Supportive RSPs (Combined Budget: $761.18 Million)
Advanced Computing Software and Collaboratory Tools
Catalysis and Chemical Transformations
Cleanup Research
Computer Science to Enable Scientific Computing
Environmental and Molecular Sciences Laboratory (EMSL)
Experimental Program to Stimulate Competitive Research (EPSCoR)
General Purpose Plant & Equipment (GPP/GPE)
High Performance Computer Networks
Laboratory Technology Research and Advanced Energy Projects
Multiprogram Energy Lab Facilities Support (MELFS)
Neutron and Light Sources Facilities
Science Education Support
Separations and Analysis
Small Business Innovation Research (SBIR) Program
Small Business Technology Transfer (STTR) Program

NOTE: Please see Appendix A for more information on the budgets, the research performers, and other related information for each Research Summary.