

Photochemical Conversion and Storage of Solar Energy

Charles Kallal

University of Georgia, Athens, GA 30602

Rising prices and sporadic shortages of fossil fuels in the 1970's provided the impetus for the present worldwide effort to develop alternative sources of energy. The exploitation of solar energy as an especially attractive option, since this resource is abundant, non-pollutantly drawn, and exchange provided by the difference in flow power per unit area¹ and international availability of solar radiation,² however, some method of storage must be provided in order that energy can be stored when it is plentiful for use when other times when demand exceeds supply.

Nature furnished a photochemical solution to the problem of energy storage with the process of photosynthesis in green plants. Through its complex series of steps, carbon dioxide and water are converted photochemically to oxygen and a convertible carbohydrate. The challenges facing the photochemist to be devise an artificial (e.g., non-molecular) cycle which accomplishes the same task, namely, the production of a storable fuel from readily available and inexpensive raw materials (3-11).



Figure 1. Scheme for conversion and storage of solar energy.

The essential components of such a cycle are outlined in Figure 1. Sunshine drives a photochemical reaction in which a portion of the incident photon energy is converted to and stored as the increased free energy of the photo-product¹. The reactant(s) need not be converted directly by the light absorption process if a photocatalyst is present. Restoration of the system to its original state occurs with the release of the stored energy in the form of either heat or electricity. Ideally, the restorative step is negligibly slow at ambient temperature and proceeds rapidly upon heating or the addition of a catalyst. This feature ensures that energy can be stored for extended periods and will be released only when desired.

In the present article, I consider the use of inorganic photochemical reactions for the conversion and storage of solar energy.¹ The primary emphasis is on reactions occurring in homogeneous solution.² Rather than attempting to catalog all of the systems examined to date, I will focus upon the principles and general strategies that have emerged from this work. I begin with a brief description of the important characteristics of the sun as a radiation source and then summarize the practical criteria for a photochemical energy storage cycle. This is followed by an overview of the thermodynamic and kinetic limitations associated with the conversion of radiant energy into chemical storage. Several examples of energy-

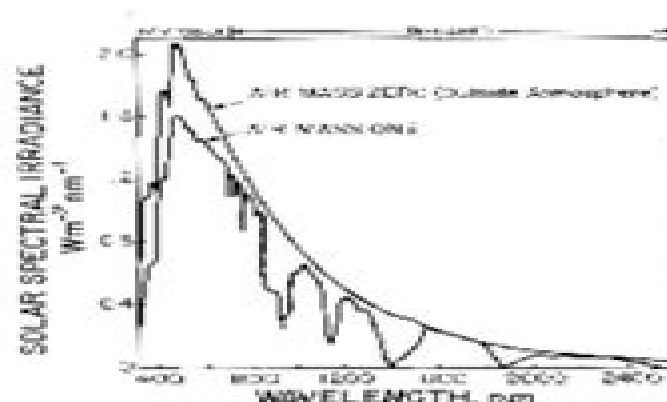


Figure 2. Solar spectral distribution outside the Earth's atmosphere for various air masses of incidence on the Earth's surface (reference 1).

storage photochemical reactions are also presented. The final section summarizes concepts underlying the progress and progress in this frontier area.

Characteristics of Solar Radiation

The sun is a sphere of intensely hot gaseous matter lying at an average distance of 1.5×10^8 km from the Earth. Its temperature varies from approximately 6000°K at the surface to $>10^6$ °K in the interior regions. These extremely high temperatures result from a series of nuclear reactions, the end result of which is the fusion of four protons to form an alpha particle (helium nucleus). This process liberates energy which ultimately is radiated into space (12).

Scientists approximate the Earth with the spectral distribution shown in Figure 2. This spectrum is modified in the atmosphere by scattering and absorption processes, the importance of which depends upon the pathlength of the light beam through the atmosphere, and λ . A parameter, specific pathlength in terms of the air mass, AM , this parameter is defined by the relation $AM = 1/\cos \theta$, where θ denotes the angle between the incident beam and the Earth's surface (considered to be a plane).³ As seen in Figure 2, the spectrum with through the atmosphere varies when the sun is directly overhead at this position, $\theta = 0^\circ$, and $AM = 1$. For $\theta = 30^\circ$, $AM = 2$ and the pathlength doubles.

The spectral distribution of solar radiation when $AM = 1$ is shown in Figure 2. This is shown in Figure 2. Inasmuch as we are interested in practical applications of solar energy, only those photons having wavelengths in the range 200-2500 nm need be considered. The short wavelength cutoff results from absorption by O₃, N₂, O₂, N₂, and O₂, while absorption by water vapor and carbon dioxide is vital when the long wave length limit. About half of the solar spectrum lies in the ultraviolet and visible regions, while the remaining half falls in the infrared. The energy equivalent of an electron volt of photon

¹ Discussions of photochemical energy storage in primarily organic systems can be found in references 1-35.

² The article by Whiggson in this issue provides a thorough discussion of heterogeneous photochemical processes.

³ Because of the curvature of the earth's surface, this expression is less satisfactory at very small angles of θ .

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Table of Contents Photochemical Conversion And Storage Of Solar Energy 198

1. Understanding the eBook Photochemical Conversion And Storage Of Solar Energy 198
 - The Rise of Digital Reading Photochemical Conversion And Storage Of Solar Energy 198
 - Advantages of eBooks Over Traditional Books
2. Identifying Photochemical Conversion And Storage Of Solar Energy 198
 - Exploring Different Genres
 - Considering Fiction vs. Non-Fiction
 - Determining Your Reading Goals
3. Choosing the Right eBook Platform
 - Popular eBook Platforms
 - Features to Look for in an Photochemical Conversion And Storage Of Solar Energy 198
 - User-Friendly Interface

4. Exploring eBook Recommendations from Photochemical Conversion And Storage Of Solar Energy 198
 - Personalized Recommendations
 - Photochemical Conversion And Storage Of Solar Energy 198 User Reviews and Ratings
 - Photochemical Conversion And Storage Of Solar Energy 198 and Bestseller Lists
5. Accessing Photochemical Conversion And Storage Of Solar Energy 198 Free and Paid eBooks
 - Photochemical Conversion And Storage Of Solar Energy 198 Public Domain eBooks
 - Photochemical Conversion And Storage Of Solar Energy 198 eBook Subscription Services
 - Photochemical Conversion And Storage Of Solar Energy 198 Budget-Friendly Options
6. Navigating Photochemical Conversion And Storage Of Solar Energy 198 eBook Formats
 - ePub, PDF, MOBI, and More
 - Photochemical Conversion And Storage Of Solar Energy 198 Compatibility with Devices
 - Photochemical Conversion And Storage Of Solar Energy 198 Enhanced eBook Features
7. Enhancing Your Reading Experience
 - Adjustable Fonts and Text Sizes of Photochemical Conversion And Storage Of Solar Energy 198
 - Highlighting and Note-Taking Photochemical Conversion And Storage Of Solar Energy 198
 - Interactive Elements Photochemical Conversion And Storage Of Solar Energy 198
8. Staying Engaged with Photochemical Conversion And Storage Of Solar Energy 198
 - Joining Online Reading Communities
 - Participating in Virtual Book Clubs
 - Following Authors and Publishers Photochemical Conversion And Storage Of Solar Energy 198
9. Balancing eBooks and Physical Books Photochemical Conversion And Storage Of Solar Energy 198
 - Benefits of a Digital Library
 - Creating a Diverse Reading Collection Photochemical Conversion And Storage Of Solar Energy 198
10. Overcoming Reading Challenges
 - Dealing with Digital Eye Strain
 - Minimizing Distractions
 - Managing Screen Time
11. Cultivating a Reading Routine Photochemical Conversion And Storage Of Solar Energy 198
 - Setting Reading Goals Photochemical Conversion And Storage Of Solar Energy 198
 - Carving Out Dedicated Reading Time

12. Sourcing Reliable Information of Photochemical Conversion And Storage Of Solar Energy 198
 - Fact-Checking eBook Content of Photochemical Conversion And Storage Of Solar Energy 198
 - Distinguishing Credible Sources
13. Promoting Lifelong Learning
 - Utilizing eBooks for Skill Development
 - Exploring Educational eBooks
14. Embracing eBook Trends
 - Integration of Multimedia Elements
 - Interactive and Gamified eBooks

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