

SOLAR PHOTOCHEMISTRY

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Summary

Fossil fuels are currently the primary source of energy that powers our modern civilization. As the world's population and energy demand continue to grow however, abundant and inexpensive fossil fuel supplies are dwindling. Use of fossil fuels is not sustainable. Once they are used there will be none left for future generations. We must therefore develop and expand other sources of energy, such as renewable energies, both to help our environment and to supply our energy needs.

Solar technologies could provide an adequate solution towards a sustainable future, as there is a general consensus that future energy supply will have to rely increasingly on renewable sources, of which the sun is regarded by many as the most important energy source. Sunlight conversion to chemical energy is widely recognized to provide a very important potential and its applications have been expanded during the last decade;

thermochemical applications are seen as the final and long-term goal of solar energy; electricity production is the intermediate goal and photochemical processes and applications are the short-term goal.

Solar photochemical processes in general, and photocatalytic applications to contaminants treatment in particular, have seen spectacular development in recent years due to their technological and environmental attractiveness. This development has led to reasonable expectations of technical and economical feasibility in the short term of specific industrial applications. Nevertheless, different engineering approaches (chemical, physical and biological) are still required to make solar photochemistry a significant segment of the chemical production industry.

The science base and strategic market information are available to identify and assess the most suitable photochemical processes to be commercially addressed using sunlight as the photon source.

The push for waste minimization and “green” technology will provide further openings for solar chemical processes. The continuing self-evaluation and environmental concern in the chemical industry will surely provide new opportunities for innovative solar technologies and processes. The important disadvantage of solar driven processes relative to artificial photon sources because of the intermittent nature of sunlight must be initially reduced by designing hybrid systems using solar and artificial photons. This disadvantage is less relevant in the case of processes which can be addressed in batch and in a discontinuous way, such as wastewater treatment, so in this chapter initial solar-only systems are clearly envisaged. Also, photosynthetic organisms to produce chemical substances are a very interesting possibility to expand the use of solar technology in the short term. In all these possible applications, efficient solar photochemical reactors that incorporate low cost methods for using sunlight as the photon source must be designed and developed to make possible the implementation and commercialization of the presently promising solar photochemical processes and technologies.

This chapter describes the main mechanisms and processes to combine sunlight and chemistry to produce useful chemical reactions, outlining the basic chemical and physical phenomena that are related with solar chemistry. The different approaches taken and progress made during the last two decades are presented. Also, some projections and highlights are provided with regard to the prospects of solar photochemistry commercialization, focusing on photocatalytic processes to the treatment of contaminated aqueous and gas effluents.

1. Solar Chemistry

The growth and development of solar chemical applications are of special importance, as solar chemistry is clearly a pathway towards the long-term goal of harnessing solar energy. The main objective of solar chemistry is to obtain, using the sun as primary energy source, fuels which could substitute the functions that are presently fulfilled by the fossil fuels. To achieve this final goal, these new fuels must have a high capacity of energy storage to make possible, throughout a chemical process, the storage of solar

energy at the places where it is abundant and at a competitive cost. Another important requirement is that fuels obtained from solar energy should be easily transported at ambient temperature, without thermal losses, avoiding the main drawback of solar energy that is the discontinuity in its availability.

Within the scope of Solar Chemistry, all the processes which use the solar radiation to achieve chemical reactions are included. In principle, any reaction or process requiring energy supply can be carried out by means of solar energy. These processes can be divided into two different groups depending on how the solar radiation is used: thermochemical, where the solar energy is converted into thermal energy thus provoking the reaction, and photochemical, where the solar photons are absorbed directly by the reactants or a catalyst, giving rise to the reaction.

In these two general groups, thermochemical and photochemical applications, both the objective and the technology are different. Thermochemistry drives chemical reactions by producing the thermal energy from the sun with the general objective to produce fuels or determine substances (energy carriers) to obtain the storage and transportation of the solar energy. Here, the investigation lines are normally characterized by thermochemical processes that need high-energy input with high density of solar flux (in the range of 10^6 W m^{-2}). This means that high concentration solar technology is necessary to drive these processes, such as central receivers systems or parabolic dishes. Some examples of these processes are: solar production of hydrogen, solar thermal, carbothermal, and electrothermal reduction of metal oxides, solar reforming of natural gas, solar thermochemical conversion of carbonaceous materials, solar heat pipes based on methane reforming and ammonia dissociation, etc.

In addition to the processes mentioned, there are other applications which fit under the thermochemical processes as they are based on the use of thermal energy from the sun, but their objective is different from the production of energy carriers. Some examples of these applications are: chemical commodities processing and manufacturing (such as metals, synthesis gas, ceramic substrates, carbon filaments, fullerenes, cement, etc.), solar recycling of sulfuric acid, etc. These processes generally are based on substances with an initial low energy and/or highly oxidized state, whose transformation to a high-energy form is possible by using solar energy. The requirements for the practical viability were already indicated [by Bolton], as follows:

- The photochemical reaction must be endothermic.
- The process must be cyclic.
- Side reactions that degrade the photochemical reactants must be absent.
- The reaction should use as much of the solar spectrum as possible.
- The quantum yield (moles of product/moles of absorbed photons) for the photochemical step should be near unity.
- The back reaction should be very slow to allow storage of the products but rapid when triggered to recover the energy content.
- The products of the photochemical reaction should be easy to store and transport.
- The reagents and container material should be inexpensive and non-toxic.
- The process should operate under aerobic conditions.

Current research and development efforts are addressed to make possible the successful fulfillment of all these requirements.

2. Artificial Solar Photochemical Processes

Roughly half of the sun's emitted energy is in the form of visible and ultraviolet light, with less than 5 percent of the energy reaching the Earth surface within the most powerful region of UV. The remaining half consist of near-infrared or infrared light, being this region of the spectrum normally not useful for promoting the electronic excitations needed to promote chemical reactions by breaking chemical bonds. Solar conversion systems based on electronic excitation have some wavelength threshold for excitation. For a molecule or semiconductor, light of longer wavelength than the threshold value is useless; shorter wavelengths, however, produce higher energy excited states.

Solar photochemical processes can be broadly defined as those which use the sun to drive specific chemical reactions by direct photochemistry (abiotic processes) or by photosynthetic organisms (biotic processes). The topic of this chapter is mainly focused on the abiotic processes and, therefore, it is addressed to describe and discuss artificial systems for the photochemical conversion of solar energy. The origins of photochemistry date back to the 18th and 19th centuries; at that time the sun was the only available light source and therefore, photochemistry was initially a full solar discipline. One specific characteristic of artificial solar photochemical processes is that the photons from the solar spectrum must be absorbed by some components of the reacting system, transferring their energy to the chemical system. Solar photons can be directly absorbed by reactants (direct photochemistry) and/or by a catalyst or sensitizer (photocatalytic processes). Some examples include: solar detoxification of contaminated water, soil and air, photocatalytic destruction of organic pollutants in gaseous emissions, solar photochemical synthesis of fine and bulk chemicals.

Other specific difference between thermochemistry and photochemistry is that the chemical storage of solar energy is uphill in the thermodynamic sense as opposed to photochemical processes the majority of which are downhill reactions. The efficiency of photochemical processes, also known as quantum yield, is defined as the ratio of the moles of final product obtained to the moles of photons absorbed by the photochemical system. In processes in which each photon initiates and concludes one chemical event, the quantum yield is 1. There are photochemical processes with a quantum yield lower than 1. An example of this last case is the TiO₂ photocatalytic processes; solar near-UV photon excites the catalyst (TiO₂ semiconductor particles) and generates an active electron-hole (e⁻/h⁺) pair that migrates to the particle surface and there starts the subsequent chemical reaction. However, most of the free electrons and holes generated by the incident photons are useless due to a recombination process within the catalyst particle and do not produce the desired chemical reaction. The consequence is a low quantum yield. Other times, such as in the case of free radical chain reactions, one photon can initiate a multiple chemical reaction and the quantum yield is greater than one. As a consequence, in solar photochemical processes, photons must be treated and considered like any other chemical reagent in the process, and their number must be considered a critical element in the overall chemical reaction.

Photochemical processes use the intrinsic energy of photons (i.e., wavelength) from the solar irradiation to provoke specific reactions. The energy of a photon is a function of its wavelength, according to Eq. (1), as follows:

$$E = \frac{hc}{\lambda} \quad (1)$$

where h is Planck's constant ($6.626 \cdot 10^{-34}$ J s), c is the speed of light and λ is the wavelength. As a consequence of this, photons with wavelengths higher than about 760 nm cannot significantly contribute to photochemical processes due to their low energy content. Roughly, about 4 to 5 percent of the sunlight at the earth's surface is in the near-UV region (wavelengths from 300 to 400 nm), about 45 percent is in the visible range (400 to 760 nm), and the rest is in the near-IR and IR regions. Solar photons from the visible and near-UV spectrum are energetic enough to be used in photochemical processes. Infrared photons are normally useless in photochemistry and can be considered as waste heat in chemical processes. Appendix 1 shows the distribution of extraterrestrial and terrestrial solar irradiance (direct normal and global) versus the wavelength spectrum. From these data, it can be calculated the available photon flux on earth surface at one-sun light intensities.

The principles of photochemistry are well understood and examples of a wide range of types of synthetic transformations are also well known. The problem is the identification of practical industrial applications in which the use of solar photons would be possible and economically feasible. In the current "State of the Art", artificial solar photochemical applications with reasonable expectations of being incorporated into industrial process are Solar Detoxification Processes, in which a strong oxidizing reaction is provoked to eliminate toxic compounds or by means of a catalyst, and Fine Chemical Synthesis Process, in which organic compounds with high added value are synthesized using sunlight. Other possible approach is to use solar photons as replacements for those from artificial sources; the goal in this case is to provide a cost-effective and energy-saving source of light to drive photochemical reactions when compared with the use of electric lamps.

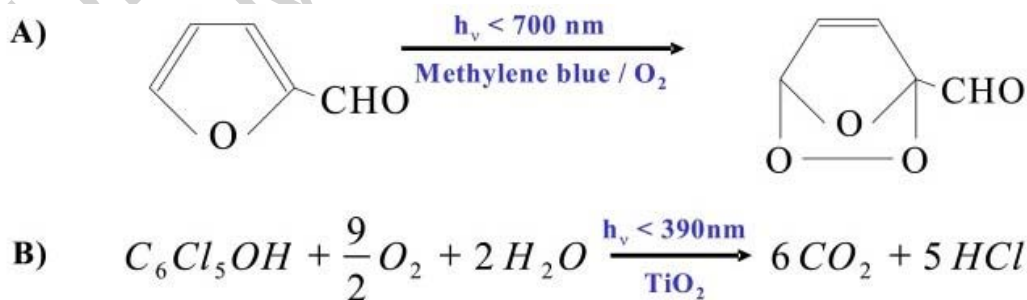


Figure 1. Examples of solar photochemical processes: a) Furfural photo-oxidation; b) pentachlorophenol photocatalytic mineralization

As an example, Figure 1 shows two examples of artificially driven photochemical processes; in the first case a molecule of furfural can be oxidized to an intermediate

endoperoxide (previous step to the production of an unsaturated lactone) in the presence of a sensitizer such as the methylene blue, oxygen and light with wavelength below 700 nm. In the second case, a molecule of pentachlorophenol (pesticide) can be mineralized to carbon dioxide if irradiated with light at wavelength lower than 390 nm being titanium dioxide present.

Another two interesting, but challenging, processes are the water splitting of water and the reduction of carbon dioxide to get secondary energy carriers which could be used in other secondary practical chemical reactions. However, up to date, none of these processes have been completely performed with the only use of solar radiation as energy source.

3. Biological Photosynthetic Processes

Photosynthetic organisms use biotic photochemical processes to produce high value chemical products (food production is considered out of the scope of this Chapter). Such photosynthetic organisms have developed the ability to carry out complex photochemistry processes using light in the solar spectrum, solving the problem of poor overlapping of the solar spectrum, which is one of the main inconveniences of artificial photochemical processes. The most known solar photoconversion reaction is photosynthesis, which convert water and carbon dioxide to glucose and oxygen using sunlight as energy source. This process has been the subject of intense study for decades due to its crucial importance to the life on earth. Photosynthetic plants have evolved to use the visible portion of solar spectrum where photons are most abundant and of adequate energy to drive the required chemical reactions. Other important fact is that plants are adapted to use low light intensity (less than one sun) and can integrate and store the available sunlight over long periods.

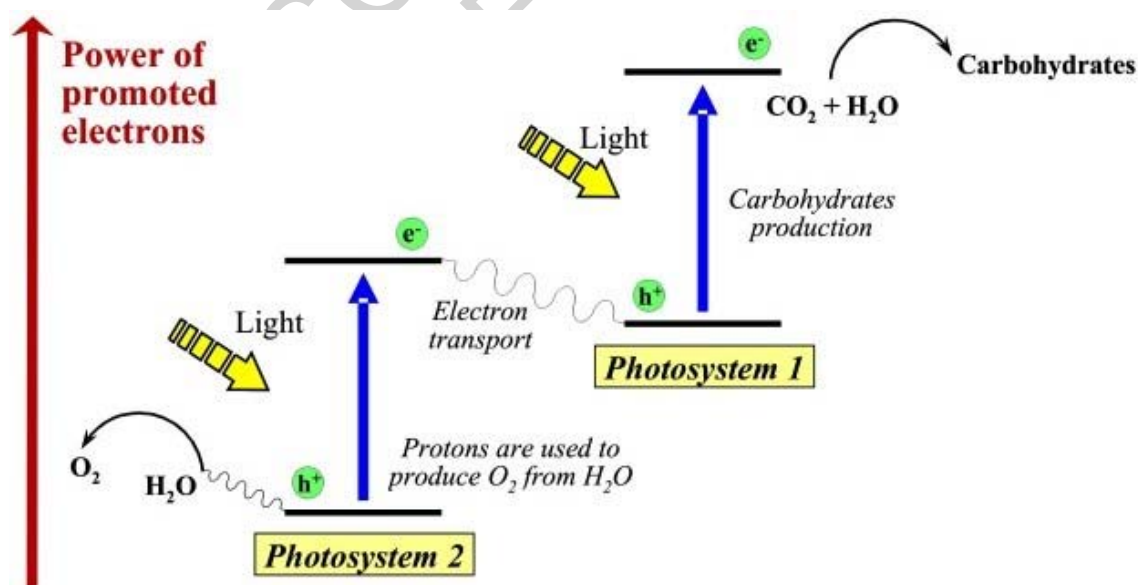
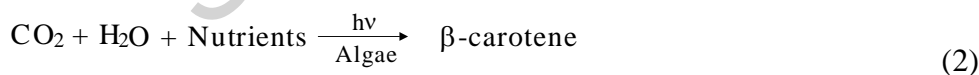


Figure 2. Simplified mechanism of natural photosynthesis

Natural photosynthesis has two main components, which are the light reactions and the carbon dioxide fixation. With regard to the light processes, there are also two major types of reactions, closely linked, usually called *Photosystem 1* and *Photosystem 2* (Figure 2). These two photosystems work together using the light as the necessary energy source to be able to use the carbon dioxide present in the air. The primary chemical result of light absorption is an excited-state electron transfer which drives both photosystems. In *Photosystem 2* water is split to form oxygen, releasing electrons that are transferred to the carbon dioxide together with protons. Finally, in *Photosystem 1* these excited electrons produced carbohydrates from water and carbon dioxide.

Industrial photosynthetic organisms are normally simple or complex plants that are grown, or derived from the waste of agricultural activity, for the purpose of producing a specific biomass from which a wide range of chemicals can be extracted. These are presently, the only photochemical processes using sunlight commercially practiced on a large scale. Plants absorb sunlight by means of chlorophyll's and other active pigments, which start the photochemical processes. These pigments, such as P-660, P-730, etc, are denoted by the light wavelengths at which they are active.

Presently, commercial photosynthetic organisms can convert simple feedstock's such as carbon dioxide, carbon monoxide/hydrogen (synthesis gas), and nitrogen into a wide array of natural chemical compounds with high value. One example is taxol, a potential anticancer drug obtained from the bark of the Pacific yew tree; other example is the own chlorophyll, with many applications in pharmaceutical and dietetic products. These and other products are obtained from biotic sources because of different reasons; most of the times, the chemical or biochemical compounds can be uniquely found at adequate concentrations in photosynthetic plants. Also, quite often, the extracted chemicals have complex molecular structures, which make them very difficult to produce by abiotic synthetic routes in the laboratory or their commercial production is less expensive when extracted from plant feedstock. This is the case, for example, of ethanol and organic and amino acids produced by fermentation of sugar and grain products, respectively. In addition to plants, photosynthetic microorganisms, including eukaryotic and prokaryotic strains, can also produce a wide variety of chemical products. One example of eukaryotic strains is that of microalgae, which can be also described as the most productive biochemical "factories" in the world. An industrial example of extracted chemicals is β -carotene, a natural food coloring pigment that also is the precursor of A vitamin.



Chlorophyll and anthocyanins are other useful colorant pigments, extracted from plants. Astaxanthin, a feed supplement for fish and shellfish, and w-3 fatty acids, used as supplementary feed in aquaculture and potential human food supplements with important activity in coronary heart disease prevention and reduction, can be additional examples. Prokaryotic strains are currently less commercially used. It has been found that some of these organisms can convert synthesis gas into biodegradable polymers, produce single cell protein and synthesize other high value chemicals. Photosynthetic

organisms have also been used to produce oxygen for aeration in sewage treatment plants and a specific photosynthetic bacterium has been reported to produce poly-3-hydroxyalkanoates from carbon monoxide and hydrogen.

It became clear that, as a result of the nature's demonstrated success with photosynthesis, a significant amount of R&D continues to be directed toward the development of an artificial industrial analog. The necessary technology for photobioreactors has much in common with solar reactor for photocatalytic applications. Factors such as large area, sunlight collection and transmission, light penetration, pH control, etc, are very similar in both technologies, so photosynthetic processes could provide an additional good pathway to the development of photochemical applications and their associated hardware.

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Biographical Sketches

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Sixto Malato Dipl. Chemistry (Chemical Engineering) by Facultad de Ciencias of University of Granada (1987). Master in Environmental Sciences by the Instituto de Investigaciones Ecológicas (Málaga, 1994). PhD in Chemical Engineering at the University of Almería (1997). 18 years of experience having worked at different sectors. His professional activities started in 1987 as Junior Researcher in Chem. Eng. Department of Univ. of Almería; in 1988 he joined the Production Department in an oil refinery (REPSOL S.A.) in Puertollano (Spain). Since 1990 he works at the Plataforma Solar de Almeria (PSA-CIEMAT) in all the EU R&D projects linked to the Solar Detoxification of water. Concretely, he has been involved in 11 EU, 13 National R&D Projects and 6 R&D Contracts (with Private Companies) related to the development of solar wastewater treatment technologies, and has been involved in the design and construction of all the experimental pilot plants for solar detoxification of industrial waste

water in Europe. He author of 1 book and co-author of 5 books as well as 21 chapters in others. He has also co-authored more than 80 publications in indexed international journals, 21 articles in technical journals and more than 140 contributions to 68 different International Congress and Symposiums and 4 patents. He has attended 31 Workshops and Conferences on Water Treatment and participated as a teacher in 17 courses on Advanced Wastewater Treatment. He has directed 4 PhD dissertations. The Jury's Grand Prix of "European Grand Prix for Innovation Awards" (Monaco, December 2004)

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