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Solar Photochemistry-Twenty Years of Progress, What's Been Accomplished, and Where Does It Lead?

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SOLAR PHOTOCHEMISTRY-TWENTY YEARS OF PROGRESS, WHAT'S BEEN ACCOMPLISHED, AND WHERE DOES IT LEAD?

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ABSTRACT

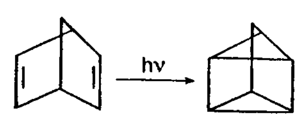
It has been more than 20 years since the first oil embargo. That event created an awareness of the need for alternative sources of energy and renewed interest in combining sunlight and chemistry to produce the chemicals and materials required by industry. This paper will review approaches that have been taken, progress that has been made, and give some projections for the near and longer term prospects for commercialization of solar photochemistry.

INTRODUCTION

The dramatic increases in the cost of oil beginning in 1974 focussed attention on the need to develop alternative sources of energy. It has long been recognized that the sunlight falling on the earth's surface is more than adequate to supply all the energy that human activity requires. The challenge is to collect and convert this dilute and intermittent energy to forms that are convenient and economical or to use the photons in place of those from lamps. The subject of this paper is the use of sunlight as a photon source for photochemical reactions. As a consequence, work on thermal and thermal catalytic reactions such as pyrolysis, and reforming are not covered. Solar photochemistry is broadly defined to include chemical production by both direct photochemistry (abiotic) and via photosynthetic organisms.

From the outset it was recognized that direct conversion of light to chemical energy held promise for the production of fuels, chemical feedstocks, and for the storage of solar energy. Production of chemicals by reactions that are uphill in the thermodynamic sense can utilize solar energy and store it in forms that can be used in a variety of ways. A wide range of chemical transformations that illustrate the concept have been proposed [1,2,3,4]. A few representative examples are given in Table 1.

Table 1. Representative Chemical Reactions That Can Store Solar Energy

	ΔH (kJ/mol)	ΔG (kJ/mol)
$CO_2(g) = CO(g) + 1/2O_2(g)$	286	237
$CO_2(g) + 2H_2O(g) = CH_3OH(l) + 3/2O_2(g)$	727	703
$H_2O(l) = H_2(g) + 1/2O_2(g)$	286	237
$CO_2(g) + H_2O(l) = 1/6C_6H_{12}O_6(s) + O_2(g)$	467	480
	110	-

These processes generally start with substances in low energy, highly oxidized forms. An exception is the last example which is a valence isomerization reaction. The requirements for viable processes were outlined by Bolton [5], as follows (with some modification by the author):

1. The photochemical reaction must be endergonic
2. The process must be cyclic (for energy storage this must be the case, for carbon based fuels recycle of CO_2 would reduce greenhouse gases)

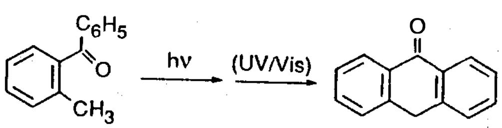
3. Side reactions that degrade the photochemical reactants must be absent
4. The reaction should use as much of the solar spectrum as possible
5. The quantum yield (moles product/mole of photons absorbed) for the photochemical step should be near unity
6. The back reaction should be very slow to allow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

The key feature is that the reactions would raise the energy content of the chemicals using solar energy. It was recognized from the outset that this approach is in the realm of long-term research and development.

A second pathway for the use of sunlight in photochemistry is to use solar photons as replacements for those from artificial sources such as arc lamps, fluorescent lamps, and lasers that are powered by electricity . The goal in this case is to provide a cost effective and energy conserving source of light to drive photochemical reactions that produce useful products.

The latter approach can build on the well developed understanding of organic and inorganic photochemistry [6,7]. Photochemical reactions can be used to carry out a wide range of chemical syntheses ranging from the simple to the complex. For example, (some chemical reactions are shown in schematic, unbalanced form):

$$Mo(CO)_6 + C_5H_5N \xrightarrow{hv,\ solvent} Mo(CO)_5(C_5H_5N) + CO$$



Processes of this type can start with more complex compounds than would fuel producing or energy storage reactions and convert them to substances where the photochemical step adds to the value to the chemical products. The principles of photochemistry are well understood and examples of a wide range of types of synthetic transformations known. Therefore the problem becomes one of identifying applications where using solar photons is possible and makes economic sense.

The third path for using sunlight in chemical production is to utilize photosynthetic organisms to produce high value chemical products. A wide range of chemicals are available from the biomass produced by simple or complex plants [8].

The processes of interest to us in this article are photochemical hence they require that some component of the reacting system be capable of absorbing a photon in the solar spectrum. Normally, each photon can initiate at most one chemical event hence the efficiency or quantum yield defined as moles product/moles photons absorbed can be at most one. The exception is if the photon initiated event starts a free radical chain reaction, in which case the quantum yield based on moles of product formed per mole of photons absorbed can be greater than one. Because photons can be treated like any other chemical reagent in the process, their number is a critical element in the consideration of solar photochemistry. The distribution of the number of photons in the solar spectrum is given in Figure 1. It can be seen that the flux is below a millimole/m^2sec in any given wavelength band at one-sun light intensities. In general the wavelengths above about 800 nm are less likely to contribute to photochemistry and that portion of the solar spectrum must be dealt with as waste heat in a chemical process.

REVIEW OF PROGRESS

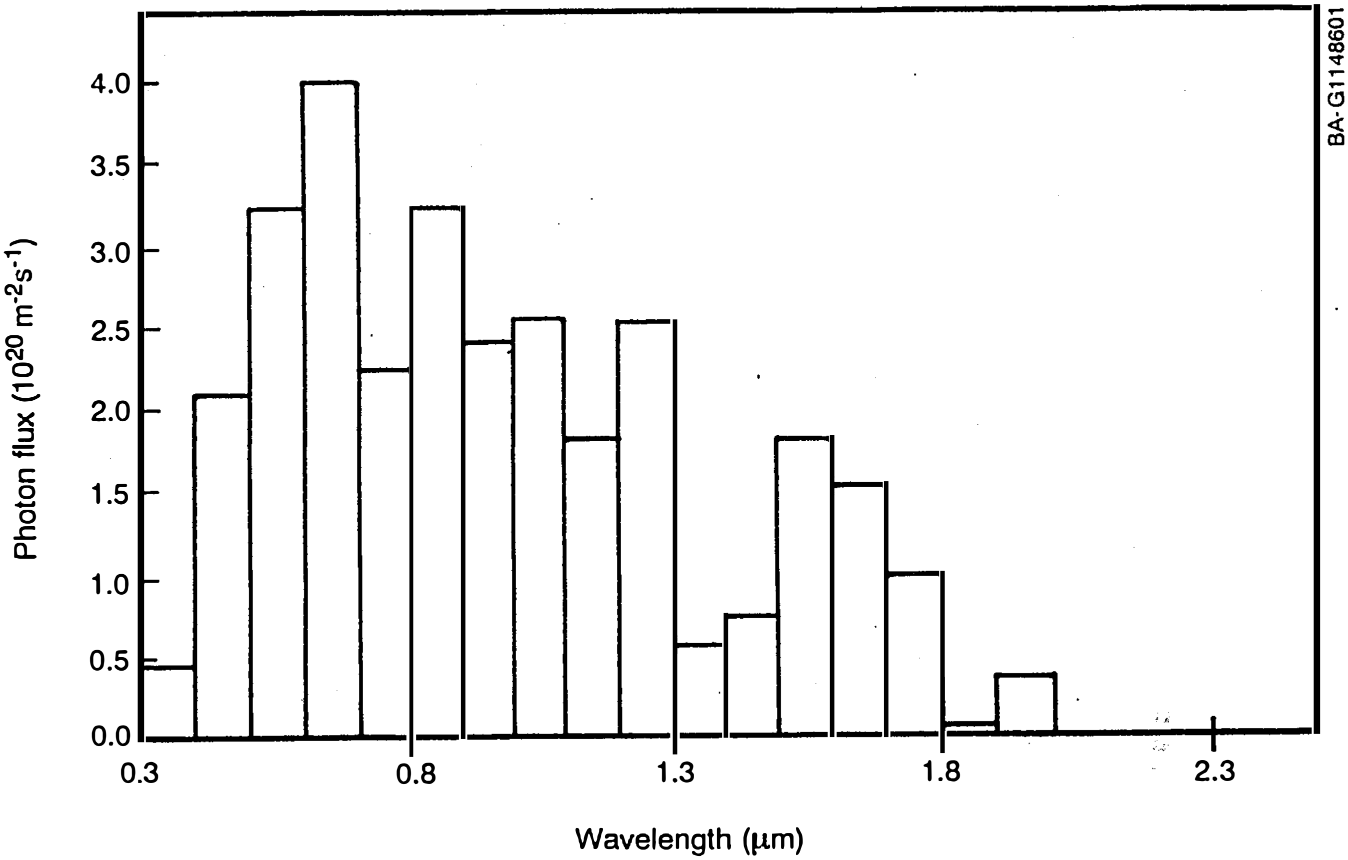
Endergonic Photochemical Reactions

The archetypal uphill, endergonic, solar photoconversion reaction is photosynthesis, converting water and carbon dioxide to glucose and oxygen using sunlight as the energy source, which is shown above. This process has been the subject of intense study for decades because of its key importance to life on earth. A high level of understanding has unfolded [9]. Photosynthetic plants have evolved to use the visible portion of the solar spectrum where photons are most abundant and of adequate energy to carry out the chemistry required. Plants use light with wavelengths shorter than about 700 nm, are adapted to use less than one sun of light intensity, and integrate available sunlight over long times [5]. To do this they have evolved a photosynthetic reaction center to absorb the light and store its energy long enough to carry out the chemistry. To generate enough reducing potential the process requires the absorption of two photons. The complex reaction center structure functions to collect light and separate the positive and negative charges (oxidized and reduced sites) formed when the photons are absorbed so they can be held long enough for the complex chemical transformations to occur.

Because of nature's demonstrated success with photosynthesis a significant amount of R&D continues to be directed toward an artificial analog. A defining feature of this approach is understanding the mechanisms of electron transfer and developing methods to separate charge [10,11]. The concept can be illustrated in a schematic way as follows for a chemical structure that includes a photosensitizer, P; a linking component, L; and a quencher, Q. In this example the excited state P^* plays the role of electron donor [11]:

$$\text{P-L-Q} + hv \rightarrow {}^*\text{P-L-Q} \quad \text{(excitation)}$$
$$^*\text{P-L-Q} \rightarrow \text{P-L-Q}^* \quad \text{(energy transfer)}$$
$$^*\text{P-L-Q} \rightarrow \text{P}^+\text{-L-Q}^- \quad \text{(electron transfer)}$$

Figure 1. Available Number of Photons as a Function of Wavelength in Air Mass 1 Solar Spectrum [12]



The objective is to minimize the loss of energy gained in the excitation step by preserving the oxidizing and reducing power by separating the charges in the electron transfer step so that it can be used to produce chemical products. The energy can be lost either by emitting light, or by radiationless pathways that convert the energy to heat. Research in this area of solar photochemistry is moving on two fronts, unlocking the mechanism of photosynthesis and developing artificial analogs.

Another approach that is being taken to carrying out uphill conversions is based on using semiconductors as photocatalysts or as electrodes in photoelectrochemical cells. In this approach charge separation is accomplished by the delocalization of holes and electrons in the valence and conduction bands of an electronically excited semiconductor material [13,14]. The major emphasis has been on developing a solar process for splitting water into hydrogen and oxygen for which the equation and thermodynamics are given above. Modification of semiconductors to improve the oxidation and reduction kinetics by deposition of catalytic sites on the surface, to prevent photocorrosion (self oxidation and dissolution of the semiconductor), and to improve the overlap of the absorption spectrum with the solar spectrum have been the subject of basic R&D [15,16].

The use of photosynthetic plants to produce chemicals (food and fiber production is not included in the scope of this discussion) is an example of solar photochemistry and the only one that is practiced commercially on a large scale. A wide range of chemicals can be extracted from biomass grown for that purpose or that is derived from the waste of agricultural activity. This is possible because photosynthetic organisms produce a very wide range of chemicals that are necessary for their maintenance and growth [8]. Many of these natural products have high value, for example: taxol, a potential anticancer drug, from the bark of the Pacific yew tree and β-carotene from microalgae. Often the chemicals extracted from plants have complex molecular structures which make them very difficult to produce by abiotic synthetic routes in the laboratory. Other compounds may be produced from plant matter when that is a less expensive feedstock than other potential sources, for example ethanol and organic and amino acids produced by fermentation of sugar or grain products.

Exergonic Photochemical Reactions

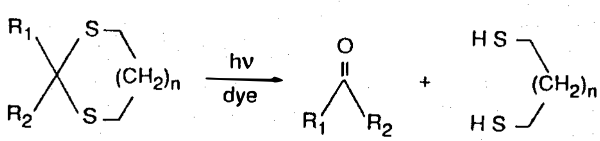
Another application of solar photochemistry is to carry out reactions that are thermodynamically downhill. Much work has been done on developing chemical processes that can use sunlight directly. The use of semiconductors as photocatalysts for oxidation of organic compounds has been studied as a means of producing oxygenated products and carrying out other useful organic syntheses. Reactions done for synthetic purposes have usually been accomplished in either the gas phase or in organic solvents [13,17]. Many semiconductors have been studied, but titanium dioxide has been found to be the most effective. Examples include:

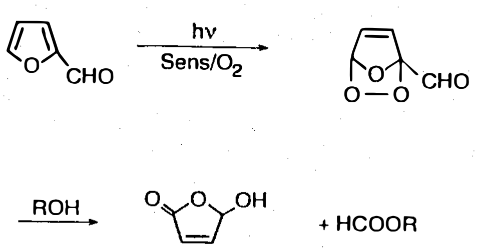
$$H_2NCH_2CH_2CH_2CH_2CH_2NH_2 \xrightarrow{TiO_2/Pt,hv} C_5H_{10}NH + NH_3$$

$$(C_6H_5)_2C{=}CH_2 + O_2 \xrightarrow{TiO_2,hv} (C_6H_5)_2C{=}O + H_2C{=}O$$

Photocatalytic oxidation using titanium dioxide has been developed more extensively for the purpose of complete oxidation of low levels of organic compounds in air or water. This has resulted in evaluation of the technology for use in environmental remediation and treatment of process waste streams [13,18]. The photocatalytic reactions in which the semiconductor is titanium dioxide use only the near UV portion of the solar spectrum. The general topic of using solar energy to destroy hazardous chemicals has been reviewed elsewhere [19].

To increase the use of the solar spectrum other approaches have been investigated. Among the most promising are dye sensitized reactions which have been explored for both synthetic and waste destruction purposes. In these processes a dye, which absorbs in the visible region of the solar spectrum, is used to capture the light. The electronically excited state of the dye then transfers its energy to a molecule that is to be involved in the chemical reaction, examples include[20,21]:





Dye sensitized oxidations have also been used to remove organic contaminants from water by a solar process and for solar water disinfection [22,23]

Direct solar photochemistry for synthetic purposes is limited to some extent because the majority of organic compounds are colorless and either do not absorb in the solar spectrum or have absorption bands that overlap only in the near UV portion of the spectrum. This may remove sunlight from consideration as a light source in some applications or can limit its use to cases where the low use of the solar spectrum can be offset by the cost of photons from other sources. Many inorganic compounds are colored and have a rich photochemistry but they are relatively less important commercially than organic compounds [6].

This has been a brief overview of a large body of work that has been done to apply the energy available from the sun in photochemical processes. Next we shall make an assessment of where one might look for successful solar driven photochemical processes.

SOLAR PHOTOCHEMISTRY - WHERE TO NEXT?

Since we are looking for commercial applications of solar energy for the photochemical production of chemicals, it is instructive to look at the way the chemical industry views its products. Commercial chemicals are categorized as commodity, fine, or specialty chemicals where the defining features are outlined in Table 2 [24,25]. Industrial applications of photochemistry have been covered in prior reviews [26,27] as has the application of solar energy to industrial processes [28].

In terms of energy usage, the production of the top 50 commodity chemicals consumes about 5 quads (1Quad = 1.05 exaJoule) of energy per year[29]. That data has not been assembled for specialty or fine chemicals. The market price for all of the top 50 commodity chemicals was under $1.00/lb (1 lb = 0.454 kg) in 1992 while some fine chemicals have costs in excess of hundreds of dollars per pound. Another way to look at chemical production and price is a plot of price versus production level, which is shown for a random sampling of chemicals in Figure 2 [30]. A log log plot is necessary because of the very wide range of prices and production levels.

Superimposed on the graph in Figure 2 is the cost estimated for solar photons having wavelengths below 415 nm as supplied using currently available parabolic troughs or one sun collectors [31]. The band covers both technologies at a good solar site (e.g. Albuquerque, NM). The upper line is for near UV from a concentrator and the lower line is for photons from a non-concentrating system. Photons at longer wavelengths will be lower in cost on a per mole basis because they are more abundant (see Figure 1). The upper limit is comparable to the cost of photons in the same wavelength range from efficient fluorescent and low pressure mercury arc lamps [31].

Table 2. Categories of Chemical Products

Characteristics	**Commodity Chemicals**	**Fine Chemicals**	**Specialty Chemicals**
Product life cycle	Long (>30 years)	Moderate	Short (<10 years)
Product slate	Narrow	Very broad	Very broad
Product volumes	>>10,000 tons per year	<10,000 tons per year	Variable
Product price	<$5.00 per kg	>$10 per kg	Variable
Product differentiation	Nonexistent	Low	Very High
Service differentiation	Low	Average	High
Value added	Small	High	Moderate/high
R&D focus	Process improvement	Process development	Product development
Capital intensity	Low	Moderate	High

Based on this information one can in broad terms rule out using solar photochemistry to produce many kinds of chemicals, mainly commodities, based on economics alone, without considering whether a photochemical process exists or not. In the foreseeable future, defined by the time domain of long term research (<25-30 years), it is unlikely that any commodity chemicals will be produced by a solar photochemical process. There are a number of reasons which lead to this conclusion:

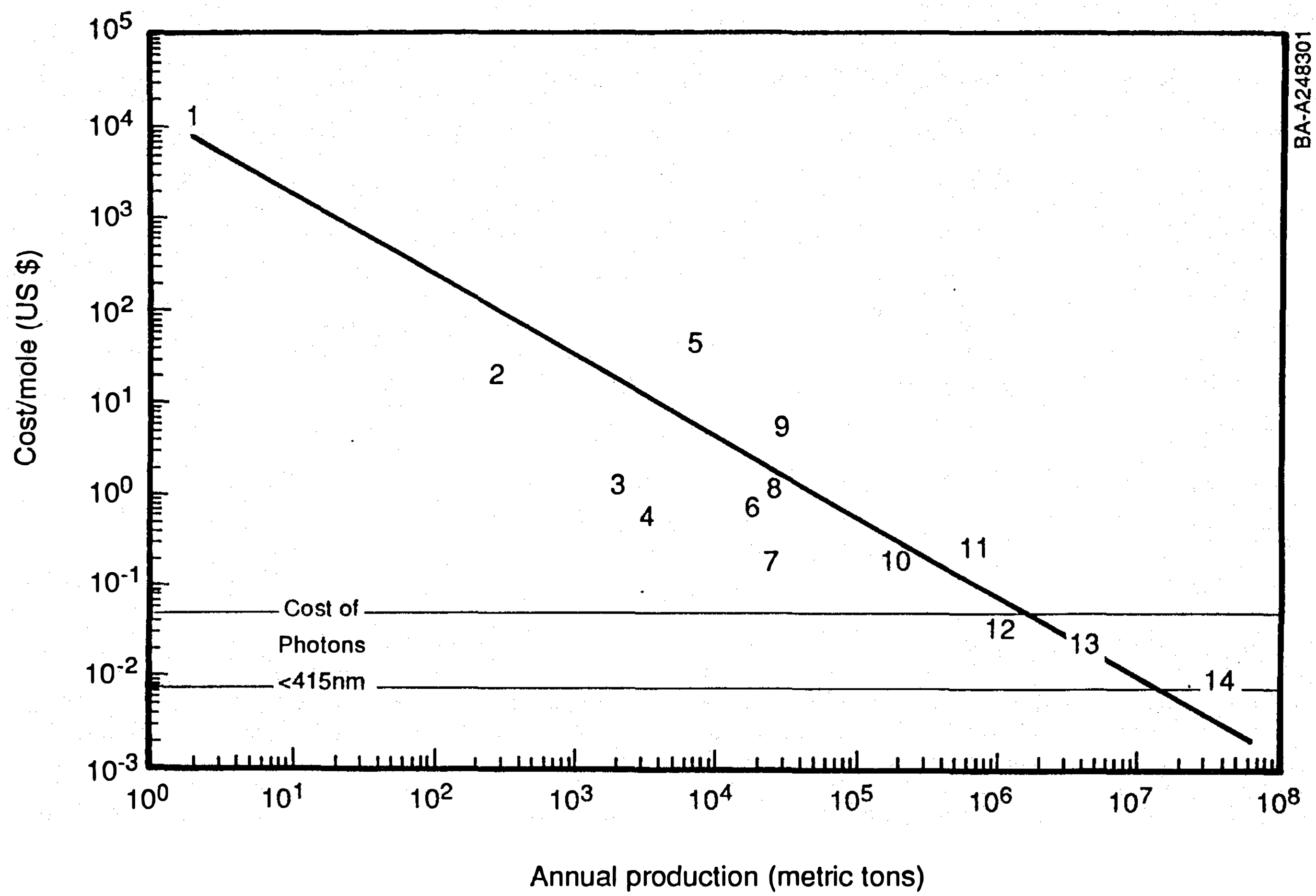
- The profit margins are low so R&D is on incremental improvements only
- Plant sizes are in the range of hundreds of thousands to millions of pounds of production per year so that a solar plant would be a very large investment in an industry that is very conservative.
- Production must proceed on a 24 hour/day basis with little down time.
- Most of the precursor compounds are colorless and do not absorb in the solar spectrum, hence photocatalytic or other processes must be developed.

For very different reasons it also may be unlikely, in the near term (<5 years) that fine or specialty chemicals at the very high value end of the price spectrum are candidates for an abiotic, commercial solar photochemical process. At first glance the opposite might seem to be the case because the production levels are small and the compounds are often produced by batch processes. However, the value of such chemicals is largely determined by factors such as structural complexity, synthetic difficulty, or quality requirements. As a consequence the cost component attributable to a photochemical step is likely to be small compared to the value of the product. The high value of the product and cost of the starting materials may dictate a degree of process control that could be more difficult to achieve in a solar reactor. Thus in a photochemical process step a producer is likely to elect tight control of conditions rather than the potential cost savings in a light source.

This leaves specialty and fine chemicals in the intermediate range of value as the most likely candidates to incorporate a solar photochemical production step. The initial identification of target compounds could focus on those procucts where there is a photochemical step in the synthesis or where a reasonable photosynthetic route can be inferred. This approach has been taken by the German solar program where dye sensitized oxidation was selected to produce compounds important in the flavorings and fragrance industry [21]. The search for dye sensitized oxidation and reduction reactions for organic synthesis is also being motivated by the desire to find synthetic methods that generate lower volumes of hazardous waste or use less energy than conventional methods. The hunt for "green" synthetic methods will provide opportunities for photochemical methods that can reduce the use hazardous reagents or solvents [20,32].

The use of solar energy for the production of commercially important chemicals might also be accomplished in the near term by targeting high- to moderate-value specialty chemicals or biochemicals that are uniquely found in high concentrations in photosynthetic microorganisms. This technology may provide a commercialization pathway for solar photochemistry that "leap frogs" conventional photochemical synthesis. Microorganisms have already developed the means to carry out complex photochemistry using light in the solar spectrum. This removes the problem of poor overlap of the solar spectrum with most compounds that are considered attractive chemical feedstocks. Photosynthetic organisms can convert

Figure 2. Cost of Chemicals Versus the Production Level



Note: 1 Cyanocobalamin, 2 Pheniramine Maleate, 3 HFC134a, 4 EDTA Acid, 5 Aspartame, 6 L-Lysine Hydrochloride, 7 Sodium Thiosulfate Pentahydrate, 8 Choline Chloride, 9 Aroma Chemicals (average), 10 Epichlorohydrin, 11 Caprolactam, 12 Cyclohexane, 13 MTBE, 14 Sulfuric Acid

simple feedstocks such as carbon dioxide, carbon monoxide/hydrogen (synthesis gas), and nitrogen into a wide array of chemical compounds, from simple to complex [8,26,33].

An underlying concept is that photosynthetic microorganisms, including both eukaryotic and prokaryotic strains, can produce a wide variety of chemical products. The best known eukaryotic strains are the microalgae that have been called the most productive biochemical "factories" in the world. There is already an industry in place that concentrates for the most part in specialty pigments (for food or animal feed), other specialty chemicals, and aquaculture feeds [33]. Examples of pigments are β-carotene, a food coloring (natural material has been reported to have human anti-cancer activity), and astaxanthin, a feed supplement for fish and shellfish. Also emerging are the ω-3 fatty acids which are important as supplements to aquaculture feeds and as potential human food supplements which may lead to reduced incidences of coronary heart disease [34].

The use of prokaryotic strains is less well developed. Systems or consortia of these organisms have been found which convert synthesis gas into biodegradable polymers. These same organisms can produce single cell protein and other high value chemicals [35].

Photobioreactor design has much in common with that for photocatalytic reactors used in the solar water treatment processes [36]. Large area, one-sun reactors, slurry separation, light penetration, oxygen and carbon dioxide transfer, and pH control are some of the common features. Solar hardware for the collection, concentration, transmission, and distribution of sunlight to bioreactors can provide new opportunities for the solar industry.

SUMMARY

A variety of engineering approaches (chemical, mechanical, biological, and genetic) will be 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 specialty and fine chemical products that can be made by photochemical processes. Some of them will provide a niche for the use of sunlight as the photon source. The continuing self-evaluation in the chemical industry will provide new opportunities. The push for waste minimization and "green" technology will provide further openings for solar chemical processes. The existing industry which produces fine and specialty chemicals from biomass and microalgae can provide an early entry for innovative solar technology.

CONCLUSIONS

The following conclusions can be made about the commercialization of solar photochemistry:

1) Solar photochemistry for production of fuels and commodity chemicals is in the realm of long-term research and development.
2) In the nearer term there will be opportunities in the synthesis of smaller production level compounds by abiotic solar photochemical methods, but solar will be at a disadvantage relative to artificial sources because of the intermittent nature of sunlight and the current availability of photoreactors designed for lamps.

3) The use of photosynthetic organisms to produce chemicals will provide the most likely avenue to expanding the use of solar technology in the near term.

RECOMMENDATIONS

The author recommends the following steps to advance the use of solar energy in the production of chemicals:

1) Identify and contact specialty and fine chemical producers that currently use photochemical methods.
2) Compile a list of important specialty and fine chemicals and the synthetic steps involved in their production.
3) For selected products, identify alternative photochemical methods that can replace one or more synthetic steps.
4) Develop designs for efficient solar photo-chemical reactors that incorporate low cost methods for using sunlight as the photon source.

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This paper reviews approaches that have been taken, progress that has been made, and gives some projections for the near and long-term prospects for commercialization of solar photochemistry.

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