SOLAR PHOTOCHEMISTRY TECHNOLOGY

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Contents

Summary

Solar photochemical detoxification technologies can provide the environmental waste management industry with a powerful new tool to destroy waste with clean energy from the sun. Solar collectors are traditionally divided into three categories: non-concentrating (or low temperature, up to 150ºC), medium concentrating (or medium temperature, from 150ºC to 400ºC) and high concentrating (or high temperature, over 400ºC). Concentrating solar systems make use of direct radiation and need solar tracking mechanisms. Non-concentrating systems are much simpler as they do not need solar tracking and can collect direct and diffuse solar radiation with slightly lower yearly efficiencies. The specific hardware needed for solar photocatalytic applications is very similar to that used for conventional thermal applications with the following main differences: the fluid must be exposed to the ultraviolet solar radiation, so the absorber must be transparent to this radiation and no thermal insulation is required as the temperature does not play a significant role in the photocatalytic process.

Non-concentrating solar collectors are the choice for solar photocatalytic applications. They are more efficient than concentrator-based systems due to the use of both direct and diffuse UV light and their intrinsic simplicity. The CPC (static collectors with a reflection surface following an involute around a cylindrical reactor tube) are a very

interesting cross between trough concentrators and one-sun systems and have been found to provide the best optics for low concentration systems. CPC's designed with a CR=1, or near one, are one of the best options for solar photocatalytic applications.

Aluminum is the only metal surface that offers high reflectivity values in the UV spectrum. Electropolished anodized aluminum and organic plastic films with an aluminum coating film are the most appropriate reflective surfaces to be used for solar detoxification applications. Photocatalytic reactors must be both transmissive and resistant to UV light. Common materials that meet these requirements are fluoropolymers, acrylic polymers and borosilicate glass and tubular photoreactors designs are the best option. In TiO_2 heterogeneous photocatalysis, suspended catalyst systems give efficiencies higher than supported catalysts. After their use, titania powders can be agglomerated and sedimented.

1. Introduction

Solar photochemistry technology can be defined as the technology that efficiently collects solar photons and introduces them in an adequate reactor volume to promote specific chemical reactions. The equipment that performs this function is denominated solar collector. Traditionally, solar collector systems have been classified into three types depending on the level of concentration attained by them, which is directly related with the achievable system temperature:

- Non concentrating or low-temperature, up to 150ºC
- Medium concentrating or medium temperature, from 150ºC to 400ºC
- High concentrating or high temperature, over 400ºC.

Non-concentrating solar collectors are static and non-solar-tracking. Usually, they are flat plates, often aimed at the sun at a specific tilt, depending on the geographic location. Their main advantage is their simplicity and low cost. An example is traditional domestic hot-water technology.

Figure 1. Medium concentration solar collector. One-axis parabolic trough collector (PSA, Spain)

Medium concentrating solar collectors concentrate sunlight between 5 and 50 times, so continuous tracking of the sun is required. Parabolic trough collectors (PTC) and holographic collectors (Fresnel lenses) are in this group. The first have a parabolic reflecting surface that concentrates the radiation on a tubular receiver located in the focus of the parabola. They may be one-axis tracking, either azimuth (east-west movement around a north-south-oriented axis) or elevation (north-south movement around an east-west-oriented axis), or two-axis tracking (azimuth + elevation). Figure 1 shows a one-axis PTC collector with its linear focus in operation. Fresnel lens collectors consist of refracting surfaces (similar to convex lenses) which divert the radiation at the same time they concentrate it onto a focus.

High concentrating collectors have a focal point instead of a linear focus and are based on a paraboloid with solar tracking. Typical concentration ratios are in the range of 100 to 10000 and precision optical elements are required. They include parabolic dishes and solar furnaces. Figure 2 shows a group of parabolic dishes with a Stirling engine coupled to a generator mounted on its focus to directly transform thermal energy into electricity.

Figure 2. High concentration solar collector. Parabolic dish solar reactor (PSA, Spain)

As temperature usually does not play a relevant role in solar photochemical processes, the associated technology is based on non-concentrating and medium concentrating solar collectors. An important difference between the two categories is that non-concentrating solar technology can profit both direct and diffuse radiation while concentrating solar technology can profit only the direct radiation. *Direct radiation* is the radiation that has no interference with the atmosphere and, consequently, with a known direction, and can therefore be concentrated. *Diffuse radiation* is the radiation that has interference with the atmospheric particles and reaches the earth surface with a random direction. *Global radiation* is composed of direct and diffuse radiation.

The *concentration ratio* (CR) can be defined as the ratio of the collector aperture area to the absorber or reactor area. The *aperture area* is the area intercepting radiation and the absorber area is the area of the component (either fully illuminated or not) receiving the solar radiation. This traditional classification considers only the thermal efficiency of the solar collectors. Solar thermal and thermochemical processes are based on the collection and concentration of large number of photons from all wavelengths to achieve a specific range of temperature, in opposition to solar photochemical processes, which are based on the collection of only high energy photons from short wavelengths to promote photochemical reactions. The majority of solar photochemical process uses the UV or near-UV solar light (300 to 400 nm), but some photochemical synthesis process can absorb useful solar light up to 500 nm and the Photo-Fenton heterogeneous photocatalysis use sunlight up to 580 nm. Solar light of wavelength higher than 600 nm is normally not valid for any photochemical process.

Nevertheless, the specific hardware needed for solar photochemical applications have much in common with those used for thermal applications. As a result, both photochemical systems and reactors have followed conventional solar thermal collector designs, such as parabolic troughs and non-concentrating collectors. At this point, their designs begin to diverge, since:

- the fluid must be directly exposed to solar radiation and, therefore, the absorber must be transparent to the photons, and
- the temperature usually does not play a significant role in photochemical processes, so no insulation is required.

The majority of photochemical processes take place in liquid phase, so the technology is mainly addressed to handle photochemical reactions that occur in water or solvent medium. There are also gas phase photochemical processes and their associated technology is discussed at the end of this article.

2. Solar Collectors for Photochemical Processes

2.1. Parabolic Trough Collectors (PTCs)

Solar photoreactors for photochemical applications were originally designed for use in line-focus parabolic-trough concentrators. This was in part because of the historical emphasis on trough units for solar thermal applications. Furthermore, PTC technology was relatively mature and existing hardware could be easily modified for photochemical processes. There are two types of PTCs:

- One-axis parabolic trough

- Two-axis parabolic trough

The first engineering-scale solar photochemical facility to water detoxification was developed by Sandia National Labs (USA, 1989) using one-axis PTCs and the second by CIEMAT (Spain, 1990) using two-axis PTCs. Both facilities are considerably large pilot plants (hundreds of square meters of collecting surface) and can be considered the first steps in industrialization of the photochemical processes.

Two-axis PTCs consist of a turret on which there is a platform supporting several parallel parabolic trough collectors with the absorber in the focus. The platform has two motors controlled by a two-axis (azimuth and elevation) tracking system. Thus the collector aperture plane is always perpendicular to the solar rays, which are reflected by the parabola onto the reactor tube at the focus through which the contaminated water to be detoxified circulates. One-axis PTCs have only one motor and a one-axis solar-tracking system; the reactor tube (linear focus of the parabola) is then positioned in the same plane containing the normal vector of the collector aperture plane and the solar vector. The angle formed by these two vectors is called the incident angle of solar radiation. Figure 3 shows how the light is reflected by the collector parabola while a one-axis PTC is following the sun.

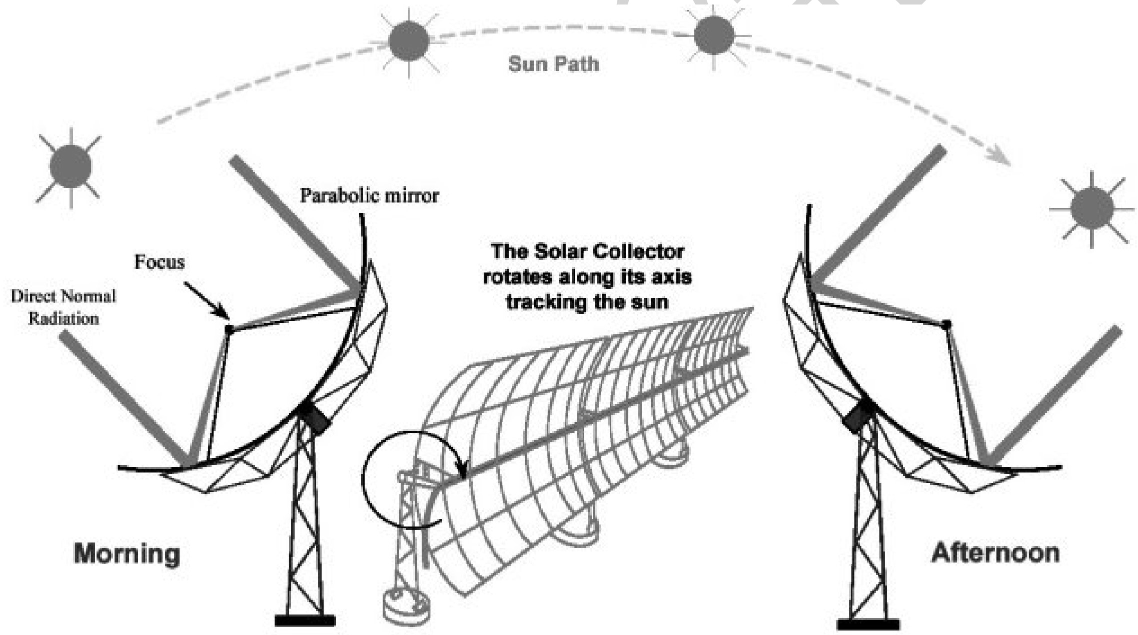

Figure 3. Solar ray reflection on a one-axis parabolic trough collector

The equation of the PTC parabola is:

$$y = \frac{x^2}{4f} \qquad (1)$$

where *f* is the focal length. If *D* is the aperture width and *d*, the reactor tube diameter, the geometric concentration of the collector *C* is:

$$C = \frac{D}{\pi d} \qquad (2)$$

The basic components of a parabolic-trough collector for photochemical applications are the reflecting concentrator, the absorber tube (photoreactor), the drive-tracking system and the overall structure. After optical losses have been considered, the effective concentrating ratio of PTCs is usually between 5 and 20. Typical overall optical efficiencies in a PTC are in the range of 50 to 75%, with the following breakdown:

- Tracking system: 90 to 95%
- Reflector/Concentrator (reflectivity): 80 to 90%
- Absorber/Reactor (transmittance): 80 to 90%
- Mechanical collector errors: 90 to 95%

Parabolic-trough collectors make efficient use of direct solar radiation and, as an additional advantage, the thermal energy collected from the concentrated radiation could be used in parallel for other applications. The size and length of the reactor is smaller, receiving a large amount of energy per unit of volume, so handling and control of the liquid to be treated is simpler and cheaper. This can also be translated into a reactor able to withstand higher pressures.

2.2. One-Sun Collectors

One-sun (non-concentrating) collectors (CR = 1) are, in principle, cheaper than PTCs as they have no moving parts or solar tracking devices. They do not concentrate radiation, so the efficiency is not reduced by factors associated with concentration and solar tracking. Manufacturing costs are cheaper because their components are simpler, which also means easy and low-cost maintenance. Also, the non-concentrating collector support structures are easier and cheaper to install and the surface required for their installation is smaller, because since they are static they do not project shadows on the others.

Based on extensive effort in the designing of small non-tracking collectors, a wide number of non-concentrating solar reactors have been developed for solar photochemical applications in general and specially for solar photocatalytic processes. These can be classified as follows:

- Trickle-down flat plate, based on a tilted plate facing the sun over which the process fluid falls slowly; a catalyst is normally fixed on plate surface.
- Free-falling film, similar to the trickle-down flat plate, but with a higher flow rate and normally with a catalyst attached to the surface on which the process fluid circulates. It is usually open to the atmosphere.
- Pressurized flat plate, consisting of two plates between which fluid circulates using a separating wall.
- Tubular, consisting of many small tubes connected in parallel to make the flow circulate faster than a flat plate.
- Shallow solar ponds. Small on-site built pond reactors having little depth.

Although one-sun collector designs possess important advantages, the design of a robust one-sun photoreactor is not trivial, due to the need for weather-resistant and chemically inert ultraviolet-transmitting reactors. In addition, non-concentrating systems require significantly more photoreactor area than concentrating photoreactors and, as a consequence, full-scale systems (normally formed by hundred of square meters of collectors) must be designed to withstand the operating pressures anticipated for fluid circulation through a large field. As a consequence, the use of tubular photoreactors has a decided advantage because of the inherent structural efficiency of tubing; tubing is also available in a large variety of materials and sizes and is a natural choice for a pressurized fluid system. Finally, its construction must be economical and should be efficient with low-pressure drop.

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Biographical Sketches

Julian Blanco Gálvez Dipl. Industrial Engineer by the *Escuela Superior de Ingenieros* (Seville, 1984), and Master in Environmental Sciences by the *Instituto de Investigaciones Ecológicas* (Málaga, 1994) has 16 years of experience having worked at different industrial sectors. His professional activities started in 1985 as Production Manager in a machinery assembly factory in Gerona (Spain); in 1988 he joined the engineering department of the American multinational electrical company AMP Inc. in Barcelona (Spanish branch). During 1989 he was also consultant of Spanish Normalization Institution AENOR.

Since 1990 he has been working at the Plataforma Solar de Almería (PSA-CIEMAT) in R&D projects linked to the solar and environmental areas. He was the project leader for the design and construction of the first pilot plant for experimentation in solar detoxification of industrial wastewaters existing in Europe (E.U. DGXII Direction C Project nº BRPR-CT97-0424.). Besides, he has been involved in 7 EU, 9 National R&D Projects and 5 R&D Contracts (with Private Companies) related with wastewater treatment.

In 1993 he became the leader of PSA Solar Chemistry department. Since 1994 he is the head of the Solar Chemistry Area of CIEMAT, being several scientific installations in Almería and in Madrid under his responsibility. In 1995 he became the Spanish National Representative in the Task II group of IEA-SolarPACES.

He is co-author of 2 books, 13 specific technical reports, 28 international publications and 64 contributions to National and International Congress and Symposiums (19 of them personally presented), up to date. Also, he has participated as teacher in 12 courses and has given multiple lectures in conferences and seminars.

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). 14 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 has been working 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 6 EU, 7 National R&D Projects and 5 R&D Contracts (with Private Companies) related with wastewater treatment. He was involved in the design and construction of the three pilot plants for experimentation in solar detoxification of industrial waste waters existing in Europe.

He is author of 1 book, co-author of other 2 books, 40 international publications in refereed journals, 80 contributions to 49 different International Congress and Symposiums (15 of them personally presented), 17 contributions to 13 different National Symposiums, 11 technical journals. Also, he has directed 1 PhD Thesis and participated as teacher in 7 courses related with Advanced Wastewater Treatment.