

# SOLAR CHEMISTRY USING CONCENTRATING SOLAR FACILITIES

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## 1. Introduction

In the long term serious changes may occur for both the availability and the proper distribution of fossil energy and material resources. During the next decades a drastic increase of the primary energy demand can be expected worldwide which will result in increasing CO<sub>2</sub>-emissions as well [1]. In the today's hydrocarbon-based economy carbonaceous fuels play a dual role as the most important primary energy carrier and as the feedstock for the production of numerous user goods. The use of solar energy in industrial processes may help to extend the availability of fossil hydrocarbons and to mitigate CO<sub>2</sub>-emissions.

Research and development in SOLAR CHEMISTRY intends to establish useful applications of concentrated solar radiation for the processes of the chemical, oil and gas processing, smelting and ceramic industries. The ultimate goal is the chemical storage of solar energy to make that energy source available regardless of time and location. In the long term future also fossil fuels as required for the conversion of crude feedstocks or the production of basic chemicals could be substituted by solar energy if the costs are acceptable [2,3]. The technical feasibility of solar reforming of methane has already been demonstrated at an engineering scale applying different reactor concepts [4,5]. For the short to mid term future some market niches can already be identified today [6]. These include the solar photochemical production of specialty chemicals and the solar detoxification of polluted water and hazardous wastes. Concentrating solar technologies can also be used beneficially for the manufacture, testing and heat treatment of materials.

The sun is an excellent radiation source in quality [7]; its surface temperature is  $T_S = 5,777$  K and its radiosity is  $M_S = 63.2$  MW m<sup>-2</sup>. However due to the distance sun - earth solar radiation is "diluted"; the extraterrestrial solar constant is  $E_{SC} = 1.367$  kW m<sup>-2</sup>. Its intensity is reduced further by absorption and scattering in the atmosphere. At clear sky conditions the maximum irradiance to be expected at the surface of the earth is about 1 kW m<sup>-2</sup>. Day - night rhythm, seasonal and meteorological constraints determine the operability of a solar plant as well. The challenge for solar engineering is to make the best use of the high quality solar radiation at a minimum expense for collection and for control of the non-steady-state energy delivery to the respective process [9].

Several research laboratories are attempting to establish reactions and technologies which are adapted to the boundary conditions of solar energy delivery. Because the direct transfer of laboratory results to pilot facilities is a risky enterprise, a high flux solar furnace (up to 22 kW scale) started its operation at the DLR research center in Köln-Porz, Germany. The furnace is supposed to bridge the gap between laboratory experiments and large scale demonstration experiments. For both industrial clients and academic researchers the furnace serves as the tool to develop solar chemical processes at relatively low expenses [8]. Subsequent pilot tests

would be carried out at solar test centers such as the Plataforma Solar de Almería in Southern Spain where larger solar concentrating systems ( $> 5$  MW thermal) are available.

To show the potential of solar chemistry development of eventual processes is outlined in more detail. The highlighted processes were taken out of recent r+d activities of the author. It is the purpose of the paper to discuss general criteria for solar chemical process development and to explain them by the examples. This paper highlights also test facilities which are needed for the development of solar chemical processes.

## 2. The DLR High Flux Solar Furnace [8]

To develop eventual solar chemical processes and applications of solar radiation in materials research an easily accessible experimentation device was needed. Due to this reason at the DLR research center Köln-Porz a high flux solar furnace was built in 1993/4 and it started its operation in summer 1994. The function of a solar furnace is to provide concentrated solar radiation. Development, construction, and operation of the facility are part of a project of the "solar working party of the Federal State Northrhine-Westphalia" (AG Solar NRW), Germany. Researchers and practitioners of science and industry have access to the solar furnace to explore new techniques and applications of solar chemistry and materials research. Per year up to 500 hours at direct irradiances above  $300 \text{ W/m}^2$  out of an sunshine offer of appr. 1500 hours above a threshold value  $120 \text{ W/m}^2$  could be used for experiments.  $300 \text{ W/m}^2$  is considered a lower limit for successful operation of the solar furnace. Fig. 1 shows the eventual number of experiments which could theoretically be carried out [10]. As compared to some other existing furnaces at better solar conditions the specific advantage of the furnace is its location in Köln having an excellent research infrastructure and short distances to partners of universities, research institutions, and industry.

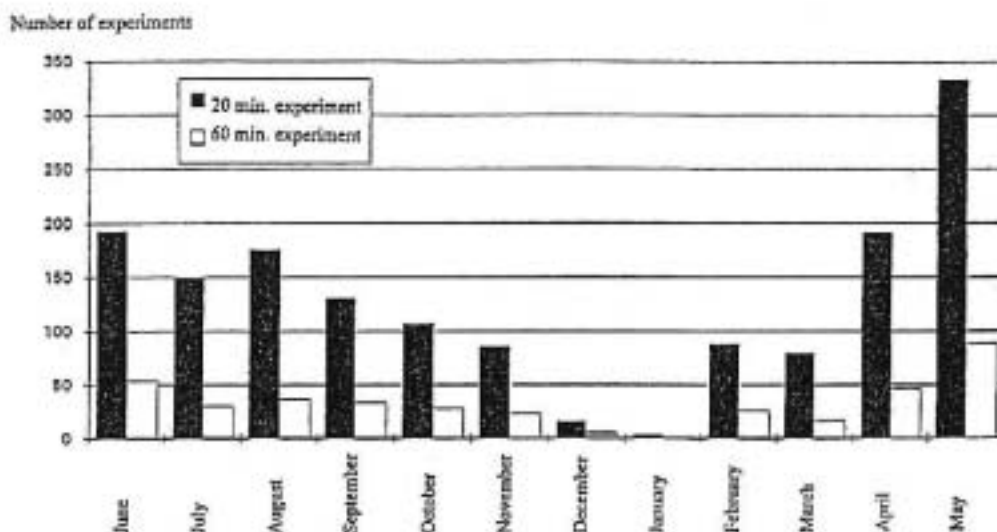


Fig. 1: Eventual number of experiments per year requiring solar direct radiation above  $500 \text{ W/m}^2$  (based on direct insolation data recorded at the location of the furnace over the period of one year May 17, 1993 until May 16, 1994)

The performance objectives set for the furnace resulted in a specific design which is characterized as a two-stage "off-axis" configuration [11]. As opposed to most other solar furnaces in the world the design is similar to the solar furnace at the National Renewable Energy Laboratory (NREL) in Boulder, Colorado, USA [12]. Researchers of NREL and of the University of Munich supported design work for the furnace in Köln. Fig. 2 shows the geometric dimensions and the essential arrangement and fig. 3 is an areal view of the solar furnace test facility. The light is concentrated with the aid of mirrors to form an image of the sun onto a focal plane. According to the position of the sun at the sky the parallel mirrors of the biaxially tracking heliostat redirect the practically parallel direct solar radiation on the concentrator. The concentrator focuses the rays into a building where the experimentation is carried out. The more brilliant the sun shines the higher a concentration ratio can be achieved. The availability of direct solar radiation is a condition for the operation of a solar furnace. Concentration aims at an increase of the flux density as required by the considered process. The geometric concentration ratio is defined as the quotient of the concentrating mirror area and the area of the focal spot. Recently peak irradiance  $I = 5 \text{ MW/m}^2$  was measured in the focal spot of the furnace at direct solar radiation  $920 \text{ W/m}^2$  [13]. Table 1 outlines the main specifications of the solar furnace and also contains performance data [14].

A stationary focal area was mandatory because of the nature of many anticipated experiments to create process conditions capable of generating very high flux concentrations. It was also desirable to move the focal area "off-axis" which means the focal area to be completely removed from the beam between the heliostat and the concentrator. An off-axis system would allow for considerable flexibility in size and bulk of experiments as well as eliminate partial shadowing of the concentrator and consequent reduction in power if test specimen and experimental set-up would be between the heliostat and the concentrator ("on-axis"). The combined shutter / attenuator which is located between the concentrator and the focal area allows a fast shut-off of the radiation and control of the level of power reaching the target with little modification of the shape of the flux profile.

The heliostat is one of the 30 test series heliostats constructed by MBB for the GAST technology program (GAST: GAs cooled Solar Tower) [15] which was originally installed and tested at the Plataforma Solar de Almería. For the use at the solar furnace a higher tracking accuracy and reduced optical errors were required as compared to the originally intended application in a solar tower power plant. Thus, the drive and control systems, mirrors and frame structure were modified. Originally, the control system provided a 'stop and go' operation of asynchronous motors, now there is a speed-control for DC servomotors. The actual angular velocity of the sun is calculated and the azimuth and elevation axes of the heliostat are speed-controlled, continuously, and synchronously tracked according to the sun half angles. By this strategy vibrations due to the stop and go operation are avoided. The surface of plane float glass is sufficient for the required beam accuracy without further polishing of the surfaces. The heliostat comprises 32 mirror facets two at a time mounted on a module frame which is fixed in a three-point bearing on the support structure to give an overall flat heliostat mirror surface. The new flat mirrors are a combination of a back-surface silver reflector and a very thin titanium dioxide front-surface coating which allows also to reflect the UV-part of the solar spectrum. That part of the spectrum is required for several photochemical experiments.

The concentrator is a multi-faceted, front-surface, aluminium reflector (reflectance averaged over the solar spectrum: 89 % at AM 2) on a 2 cm thick glass substrate. An aluminium reflector was chosen because of its high reflectance in the UV portion of the solar spectrum. A

thin film coating ( $\text{SiO}_x$ ) protects the surface from environmental effects. The concentrator consists of 147 hexagonal mirror facets (length of edge: 32 cm) mounted on a flat supporting structure. They are distributed in three groups with different focal lengths: (1) 6.95 m, (2) 7.30 m, and (3) 8.20 m. Ideally, each facet should have its own spherical curvature but the selected size of the facets and their division into three groups resulted as the best compromise of performance and costs.

A water-cooled turning mirror can be placed just in front of the focal point in order to direct the concentrated beam downward. This feature allows experiments in which samples must be oriented horizontally and receive the concentrated beam from a vertical direction.

The solar furnace is equipped with a combined flux and temperature measurement system (called FATMES). An infrared camera measures the temperature profiles in a range of -50 up to 3000 °C. To determine the flux profiles a white and diffuse reflecting screen coated with alumina is moved through the beam. The image of the beam diffusely reflected is recorded by a video camera being calibrated in absolute units (e.g.  $\text{kW/m}^2$ ). Two-dimensional flux profiles are the results after image processing. The furnace operates an own meteorological station to measure continuously direct, global, and diffuse irradiance as well as ambient temperature, humidity, and wind velocity and direction.

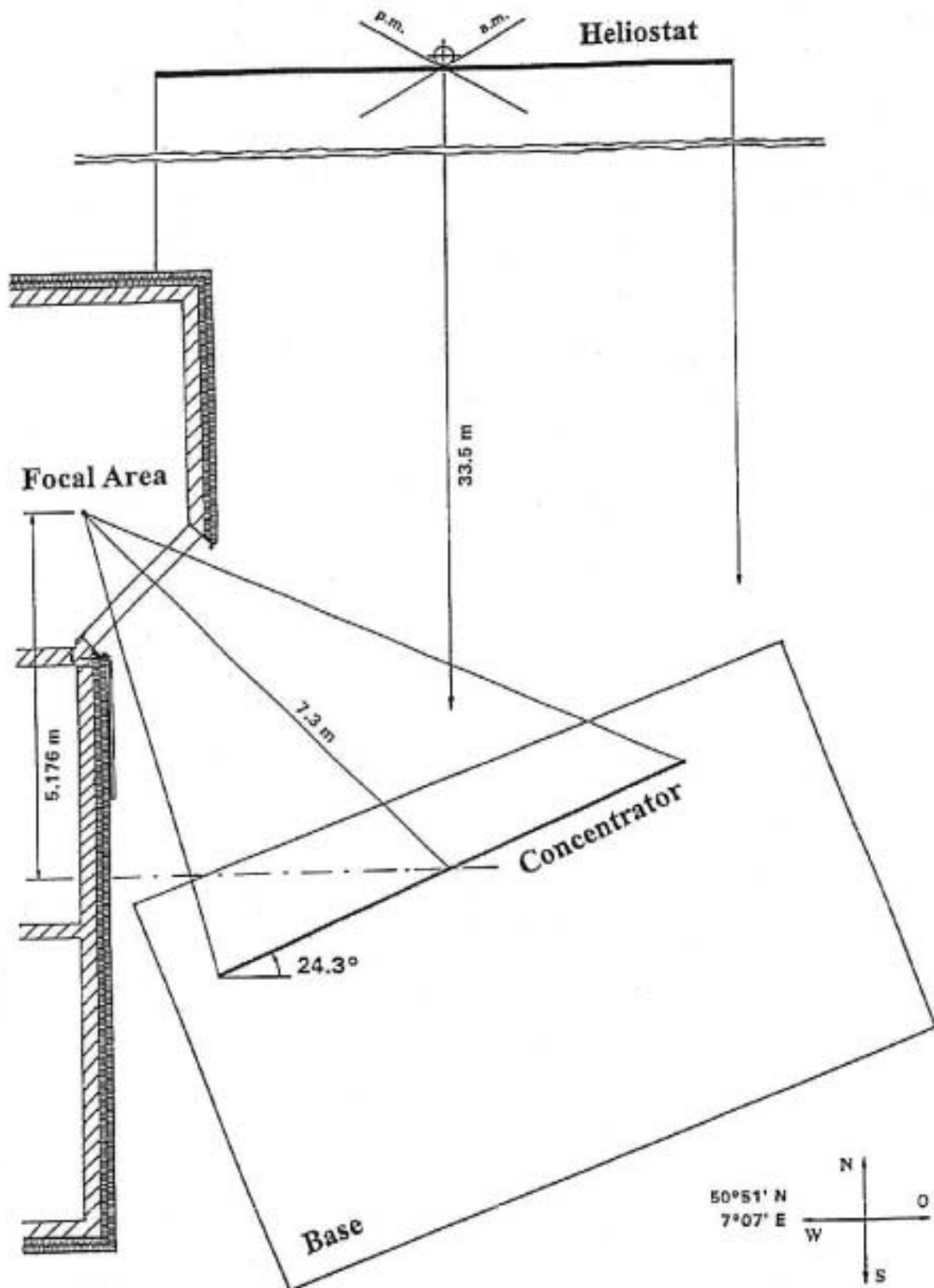


Fig. 2: Most essential geometric dimensions of the high flux solar furnace



Fig. 3: Up: Areal view of the outdoor solar test facilities at the DLR in Köln-Porz, Germany. Foreground from left: laboratory building, concentrator building of the solar furnace, IST trough for solar process heat applications. Background from left: heliostat of the solar furnace, PROPHIS-plant for photochemistry, PAREX-plant for thermal components' tests, fix focus trough for thermal tests. Below: View of the concentrator, 147 spherical facets. One can see the opening to direct the light beam into the experimental room and the combined shutter / attenuator in a closed position on the right hand side.

### 3. Development of Processes for the Application of Concentrated Solar Radiation in the Chemical Industry

In solar thermal concentrating plants process heat can be provided at high temperature levels [7]: in receivers which have already been developed in a multi MW scale for high temperature heat generation in central receiver systems at 500-1000 °C and in an experimental scale up to 2000 °C, in parabolic dish concentrators and in solar furnaces even at more than 2000 °C. Thus it is useful to investigate whether such plants - besides of solar thermal power production - could meet the energy demand for the established high temperature processes in the primary industry.

As opposed to a "separated" or "indirectly heated" reactor the so-called "integrated" receiver-reactor concept is unique and most attractive for solar chemical engineering. In the separated process concept a receiver absorbs the radiant energy and is heated to high temperatures. A heat transfer fluid transports the heat from the receiver to the reactor where it is transferred to the reactants by convection. In an integrated receiver-reactor either a stationary receiver structure ("volumetric" receiver-reactor) is directly irradiated with concentrated solar radiation and the fluid reactants passing over this structure are heated and converted. The volumetric receiver structure may be catalytically active. On the other hand an integrated receiver-reactor may also be a "direct absorption" receiver. The difference is that in a direct absorption receiver-reactor the fluidized reactants or catalysts absorb the concentrated solar radiation [16].

As compared to separated receiver-reactor concepts volumetric and direct absorption receiver-reactors show several features which - in consequence - allow to expect improved efficiencies:

- (1) The absorption of the concentrated solar radiation and the reaction proceed into the depth of the absorber. In a separated receiver-reactor concept radiation is absorbed at the receiver surface and a heat transfer fluid is heated.
- (2) The highest temperatures are at the reactive sites because the concentrated solar radiation will be absorbed by the reactants directly or by the catalytic surface of a volumetric receiver structure. Thus it is expected that endothermic reactions are kinetically limited and not heat transfer limited as opposed to allothermally heated reactors.
- (3) The capability to cope with very high heat flux densities ( $> 1 \text{ MW/m}^2$ ) allows to construct very compact receiver-reactors having relatively small apertures and small losses due to thermal emission. Heat flux densities allowable to direct absorption receiver-reactors are more than one order of magnitude higher than to tubular receivers.
- (4) Compact and low mass receiver-reactors allow fast responses on thermal transients which have to be considered for solar applications.
- (5) The unidirectional fluxes of the incoming concentrated solar radiation and of the reactants reduce the surface temperature of the volumetric structure or of the absorbing reactants as compared to an equivalent tubular receiver of a separated process concept. Thus the losses due to thermal emission of the absorber are lower.
- (6) There are indications that rates of chemical reactions are increased as the irradiance rises. Accordingly photolytic effects may also play an important role at the high temperatures in integrated receiver-reactors as opposed to separated reactors working at the same temperature.

However there is also one limitation of volumetric or direct absorption receiver-reactors if air sensitive compounds have to be converted or if the desired reaction shall be carried out at elevated pressures. The reactor volume has to be separated by a transparent window from the environment. Windows resistant to high pressures are actually developed for use in an industrially relevant scale.

### **3.1. Solar Purification and Recovery of Waste Sulfuric Acid: An Example for Solar Detoxification of Hazardous Wastes**

Numerous industrial processes yield hazardous wastes as by-products which are removed conventionally by high temperature incineration, special techniques which are also distinguished by a very high specific energy demand, or disposal in landfills. The energy demand of the conventional techniques is met by the combustion of fossil fuels, either directly for high temperature incineration or indirectly for electrically driven detoxification processes and for chemical neutralization and detoxification. In principle, the application of solar radiation may be an alternative. In a solar detoxification plant hazardous wastes are irradiated directly with highly concentrated solar radiation in a direct absorption receiver-reactor.

Sulfuric acid is a most important basic chemical; the production rate is approx. 160 million tons per year world wide. In many cases after use the acid ends up as a waste by-product highly loaded with organic impurities. Neutralization and drain-off has been more and more restricted. To protect the North Sea a step-wise decrease of sea dumping was concluded by European industry in 1988. Today for ecological and legal reasons dumping into the North Sea is prohibited. To recycle the sulfuric acid the impurities have to be removed and diluted acid must be reconcentrated. The recovery techniques require a high specific energy input which is conventionally supplied by the combustion of fossil fuels. The use of concentrated solar radiation has been chosen to reconcentrate and to purify diluted waste sulfuric acid loaded with organic impurities as an example for low calorific liquid wastes [17].

Commercially available high temperature splitting processes to recycle waste sulfuric acids run at  $T > 1,300$  K. The organic pollutants are mineralized and splitting of sulfuric acid yields sulfur dioxide which is converted to fresh sulfuric acid subsequently.

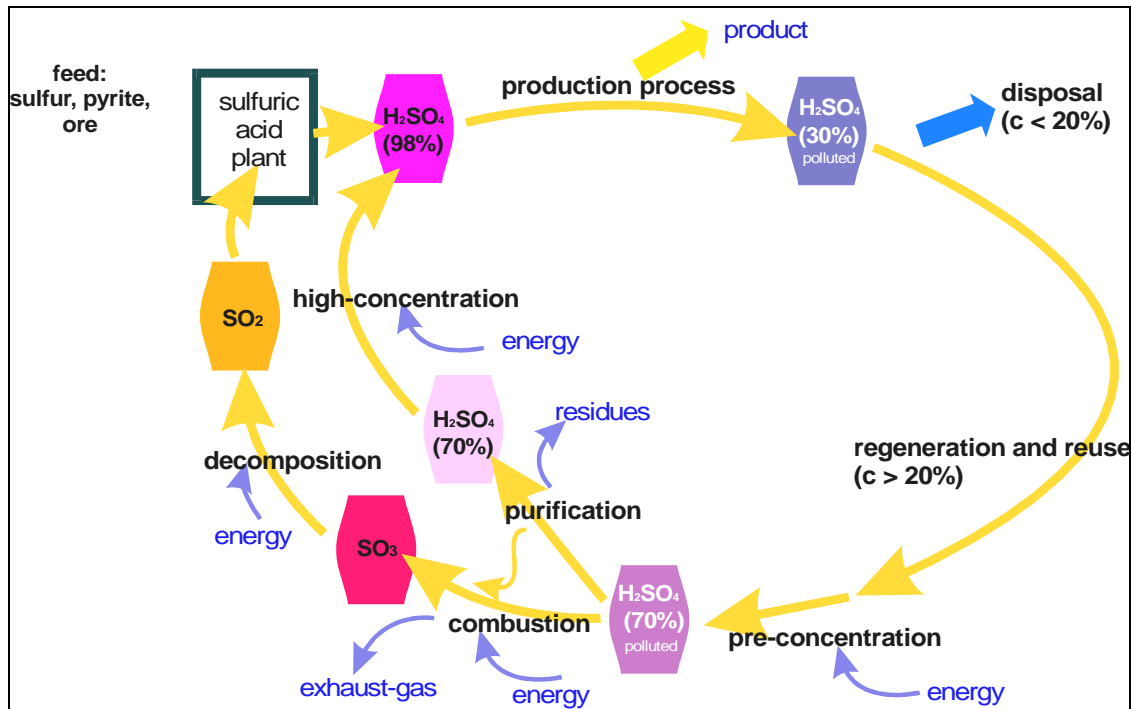


Fig. 4: Simplified scheme of the sulfuric acid cycle [18].

Depending on concentration and on contamination different ways of reuse are applied (fig. 4). In numerous processes a direct reprocessing via intermediate purification is integrated. Weakly concentrated acid ( $c < 20$  % wt.) mostly is neutralized and drained off. Concentration and purification by precipitation of inorganic salts or oxidation of organic matter are common for waste acid of medium concentration [19]. If the waste acid contains resistant or toxic organic compounds it is often required to decompose the material at high temperatures (Table 2).

$\text{H}_2\text{SO}_4 \cdot x\text{H}_2\text{O}_{(\text{liq})} \Rightarrow \text{H}_2\text{SO}_{4(\text{liq})} + x \text{H}_2\text{O}_{(\text{g})}$	$(\Delta H^\circ_{\text{R}} = f(x))$	(1)
$\text{H}_2\text{SO}_{4(\text{liq})} \Rightarrow \text{SO}_{3(\text{g})} + \text{H}_2\text{O}_{(\text{g})}$	$(\Delta H^\circ_{\text{R}} = +176.5 \text{ kJ/mol})$	(2)
$\text{SO}_{3(\text{g})} \Rightarrow \text{SO}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})}$	$(\Delta H^\circ_{\text{R}} = +98.5 \text{ kJ/mol})$	(3)
$\text{C}_x\text{H}_y\text{O}_z + \text{O}_2 \Rightarrow x \text{CO}_2 + \frac{1}{2}y \text{H}_2\text{O} + \dots$	$(\Delta H^\circ_{\text{R}} < 0)$	(4)

Table 2: Energy demand of the decomposition of sulfuric acid.

The total energy demand of the decomposition of sulfuric acid (70%) amounts to 6.4 MJ per kg of  $\text{H}_2\text{SO}_4$  [20], this equals 2,500 kilowatt-hours per metric ton of waste acid. By process integration with the production of fresh sulfuric acid part of this energy can be recovered.

The complete decomposition of waste sulfuric acid at 1,300 – 1,400 K gives  $\text{SO}_2$ -containing (5-6%) off-gas. The organic substances are mainly oxidized into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Splitting processes have been performed industrially for decades. The conventional energy feed is oil, coke, or sulfur. The off-gas is washed, cooled, and subsequently oxidized into  $\text{SO}_3$  in the

double contact process to give fresh concentrated sulfuric acid or oleum (fig. 4). The recycled portion of the German sulfuric acid production amounts to 30% (1991).

The experimental set-up enables comparative measurement of thermal and of solar irradiated gas phase oxidation of organic impurities of a model waste sulfuric acid, respectively. A cavity serves as thermostated chamber for the quartz glass reactor. At the front of the cavity an opening lets the concentrated solar radiation enter into the cavity. Diluted waste sulfuric acid (30 wt.%  $H_2SO_4$ , 22,500 ppm TOC-content - Total Organic Carbon -, origin: production of p-nitrotoluenesulfonic acid) is dispersed and mixed with air. That mixture is fed into the transparent direct absorption receiver-reactor where it is irradiated with highly concentrated radiation at elevated temperatures. The absorption of sunlight takes place in the sulfuric acid aerosol droplets. At elevated temperatures either due to thermal heating or due to solar radiation sulfuric acid dehydrates at 100 – 340 °C (1) and then dissociates to water and sulfur trioxide at appr. 300 – 450 °C (2). Sulfur trioxide splits partially into sulfur dioxide plus oxygen at appr. 700 – 1000 °C (3) and the organic pollution is mineralized at the same time within a temperature range 450 – 1100 °C (4). Behind the reactor undissociated sulfuric acid and residual organic pollution are condensed. Subsequently, the exhaust gas stream is split and one part passes to the analytic detectors. Fig. 5 explains the experimental set-up schematically. TOC-reduction was used as a cumulative parameter to evaluate the effect of the radiation on the oxidation of the organic impurities. The experiments proved accelerated TOC-reduction in waste sulfuric acid under high flux irradiation within a temperature range of 800 – 1,100 K as compared to purely thermal destruction within the same temperature range and an increasing oxidation rate with increasing irradiance (fig. 6) [17].

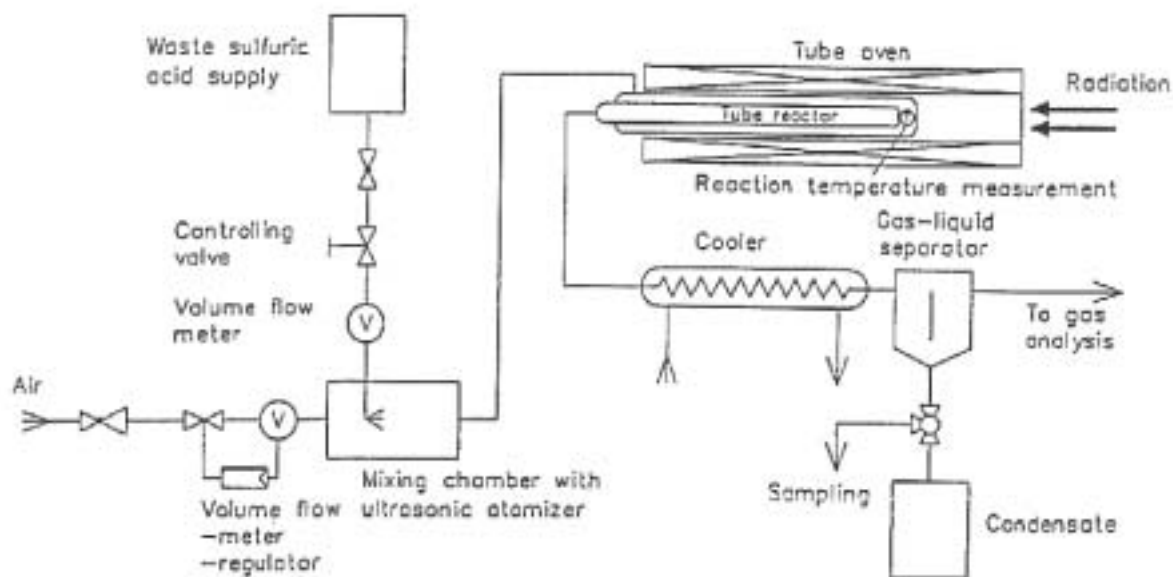


Fig. 5: Schematic testing device for the investigation of high flux purification of waste sulfuric acid

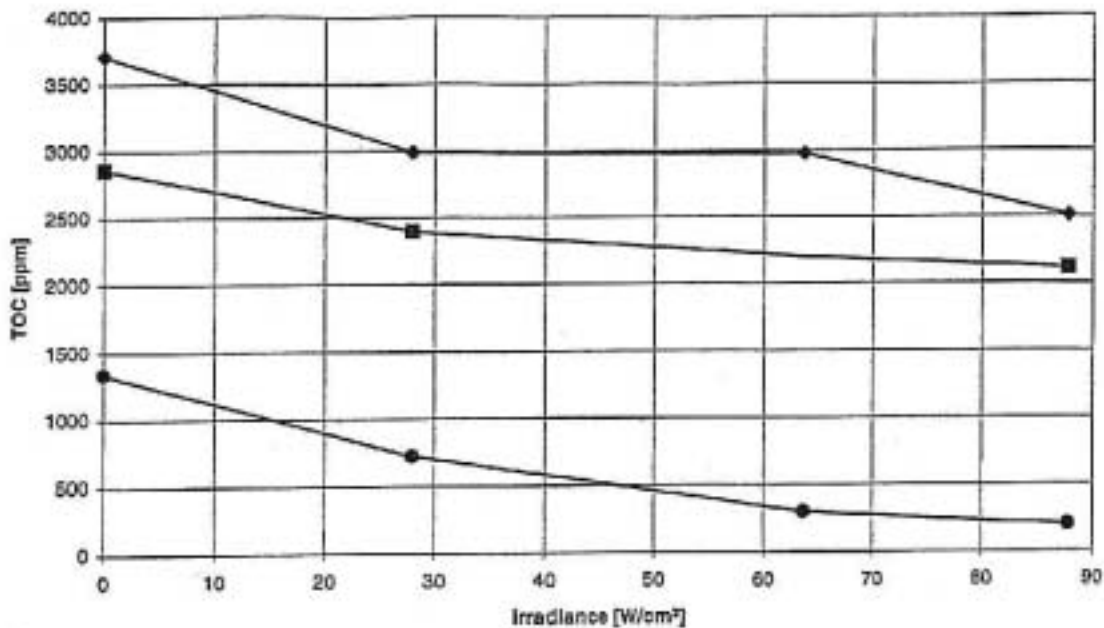


Fig. 6: Residual TOC of the condensate vs. mean irradiance for different reaction temperatures (mass flow rate liquid waste sulfuric acid: 0.2 l/h, volume flow rate air: 1 l/min., initial TOC: 22,500 ppm, ◆ : 500 °C, ■ : 600 °C, ● : 800 °C)

Kinetic studies showed that the decomposition of sulfur trioxide to sulfur dioxide is accelerated by concentrated sunlight [18].

In a solar plant employed for the recovery of waste sulfuric acid contaminated with organic impurities the use of a direct absorption receiver-reactor has significant advantages beyond saving of fossil fuels. As compared to a purely thermally heated recovery reactor either the temperature level to be applied could be lowered or the space-time could be increased at the same temperature level to achieve the same purification degree. A process using highly concentrated solar radiation for the recovery of waste sulfuric acid exhibits several other benefits: (1) Because solar energy is applied carbon dioxide emissions due to the combustion of a fuel do not occur; (2) a lower air stream must be fed to the reactor as specifically required for the oxidation of the organic pollutants of the waste acid as compared to a thermal reactor where also the fuel needs oxygen; thus the gas volume to be purified after the dissociation reactor is lower; (3) due to the reduced temperatures less nitrogen oxides are formed.

### 3.2. Solar Recycling of Aluminium Scrap in a Rotary Kiln Receiver-Reactor

Industrial residues, e.g. filter dusts, sulfuric acid, aluminium dross, foundry sand, or waste water, often do not have a sufficient calorific value to cover the heat demand if they are subjected to thermal treatment at elevated temperatures. High temperature treatment powered by combustion of fossil fuels has the disadvantage to generate large off-gas streams.

A potential alternative to these combustion processes is the use of highly concentrated sunlight. Besides saving of fossil fuels or electricity expected advantages of solar thermal waste treatment are:

- reduction of the exhaust gas stream,
- photolytic destruction of organic wastes,
- reduction of CO<sub>2</sub> production.

Central receiver systems have been proven to achieve high temperatures, power and heat flux densities. The maximum power of today's demonstration plants is up to 50 MW<sub>th</sub> [7] and for future solar thermal power plants it may be one order of magnitude larger. In figure 7 a sketch of a central receiver system is shown. A field of heliostats, three-dimensional tracking mirrors, concentrates the direct-beam solar light on a receiver system. The high temperature process takes place in the central receiver [7]. As opposed to receivers that are only used to generate high temperature process heat there are receiver-reactors for an integrated conversion of high flux radiation and physico-chemical conversion of material.

In dependence on the desired process different receiver systems are being developed:

- directly heated rotary kiln receiver-reactor for the treatment of solid, pasty or liquid wastes,
- particle cloud receiver-reactor for the treatment of powdered materials [21,22,23],
- aerosol cloud receiver-reactor for the treatment of liquid wastes like sulfuric acid or waste water [17,18,24],
- volumetric receiver to achieve high temperatures in the gas phase (30 MW<sub>e,l</sub>), developed for electricity production [25,26] and reforming of light hydrocarbons respectively [27,28].

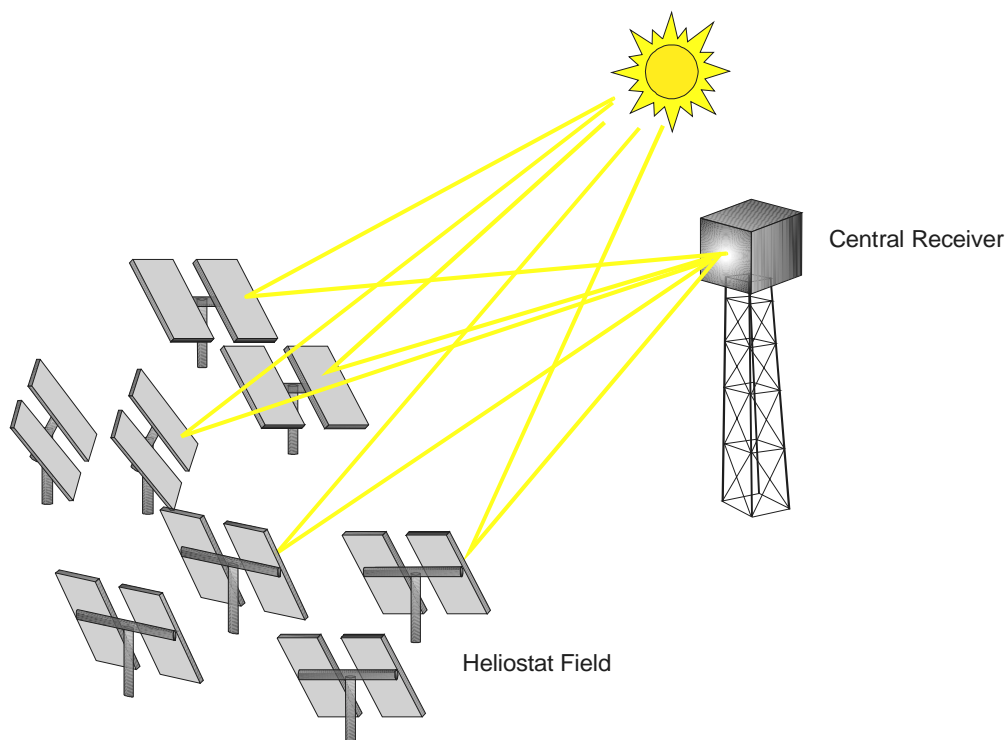


Figure 7: Sketch of central receiver system. The direct solar beam is concentrated on a receiver which is placed on the top of a tower.

A rotary kiln is as well established apparatus for the incineration of toxic wastes or the recycling of aluminium. Therefore a directly solar heated rotary kiln as central receiver was suggested for the solar high temperature treatment of wastes [29]. To realize high temperatures and to minimize heat losses by thermal radiation the directly heated rotary kiln makes use of the cavity effect. This means that the sunlight is absorbed inside the rotating tube which diameter reduces to the diameter of the focused beam in the focal plane (Fig. 8).

For the provision of process heat the feasibility of a solar heated rotary kiln was tested in a 500 kW scale [30]. In this rotary kiln sand was heated as heat transfer medium. Temperatures up to 940 °C were achieved.

The application of a solar heated rotary kiln for the treatment of wastes at elevated temperatures was investigated in a theoretical study [31]. The calculations were undertaken with a simple model of a rotary kiln considering previous design studies [29,32]. The considered waste was a filter dust of a waste incineration plant with a melting temperature of 1200 °C. With the assumption of 1800 h/a direct insolation and a reflector surface of 550 m<sup>2</sup> (14 heliostats of the SSPS field at PSA, Spain) [31] 550 t/a filter dusts could be melted in a fictive pilot application.

To examine the feasibility of solar waste treatment a rotary kiln was constructed in a mini-plant scale. It which is designed to meet the technical data of the solar furnace of the DLR in Cologne and it consists of a crucible which is isolated in alumina insulant and fixed in a housing, a framework with four roller bearings to mount the rotary kiln on the triaxial table a motor with converter, a temperature measurement system, an electrical heating, a clearing unit, and a data acquisition system. The technical data of the mini-plant are summarised in table 3.

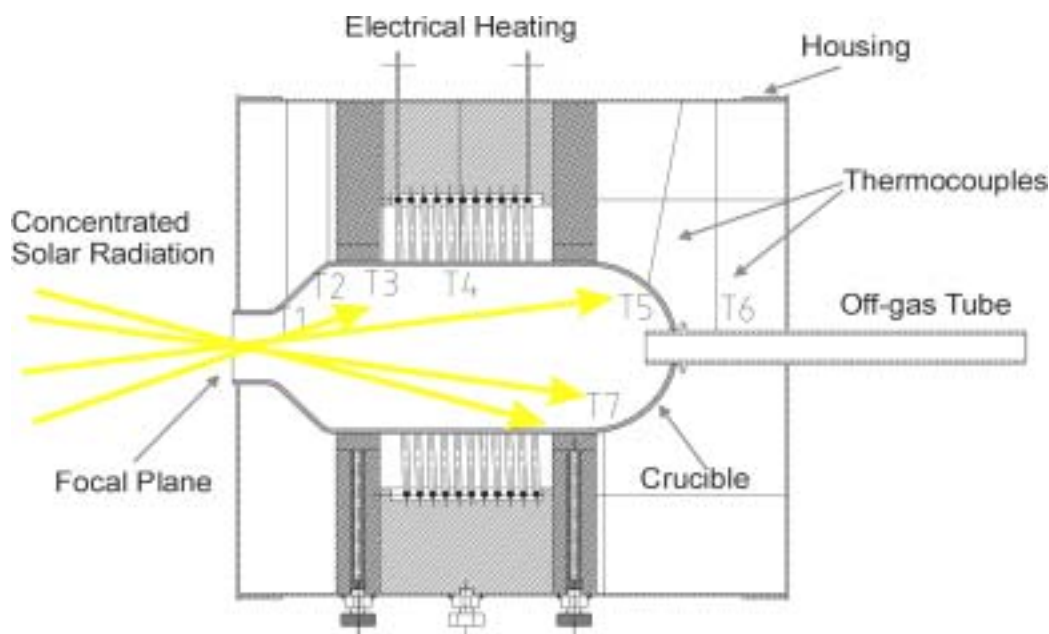


Figure 8: Scheme of the rotary kiln designed for the solar furnace in Cologne. The concentrated solar radiation is absorbed inside the crucible.

As shown in figure 8 the crucible expands behind the entrance for the concentrated radiation to a diameter of 0.2 m over a length of 0.4 m. In the back of the crucible an off-gas tube

allows to suck a gas stream through the crucible. Seven thermocouples are installed on the outer surface of the crucible and the off-gas tube to measure the temperature on-line during the experiments. The signals of the thermocouples are transformed in an analog/digital-converter which is installed on the housing and are transmitted radio-controlled to a personal computer.

Table 3: Components and Dimensions of the Rotary Kiln Mini-Plant.

Component	Device	Data
rotary kiln	crucible	SiSiC length: 0.4 m diameter: 0.2 m
	housing	aluminium length: 0.66 m diameter: 0.63 m
	insulation	alumina ceramic plates:
drive	electric motor with inverter	engine torque: 120 Nm rotation speed: 0 to 20 r. p. m.
complementary heating	electric heater with transformer	max. electric power: 4.7 kW maximum temperature: 1350°C
data acquisition	thermocouples	7 PtRh-Pt thermocouples
	analog-digital converter telemetric data transfer	
	data registration	

This temperature measurement system was designed to give fundamental information of the temperature distribution for a heat balance and for modeling of the rotary kiln. The operational test of the rotary kiln was carried out with annealing the empty crucible and melting different salts with melting points at 380°C and 780°C. As shown in figure 9 with 3.4 kW concentrated sunlight into the crucible a temperature level of more than 1000°C can be achieved. The temperatures measured by the thermocouples correspond to the position of the thermocouples on the outer surface of the crucible.

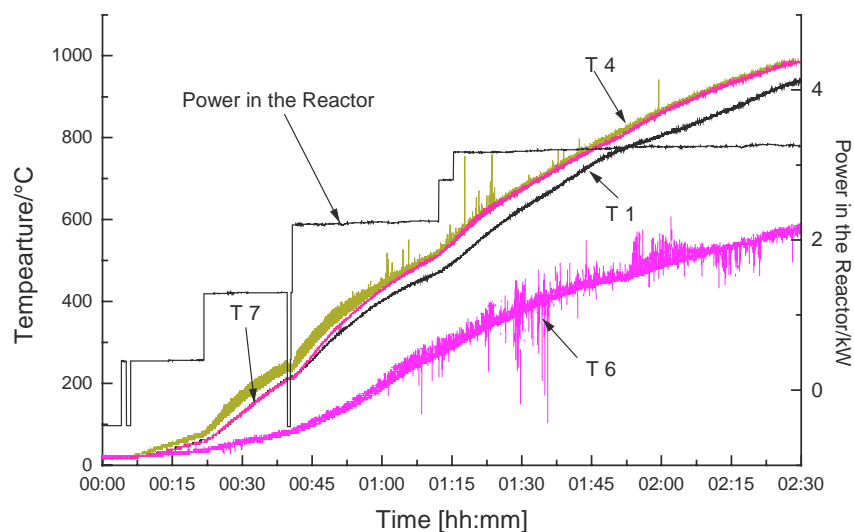


Figure 9 Temperature development on the crucible and power into the crucible during the annealing.

### 3.3. Solar-Photochemical Syntheses of Chemicals

The beginning of photochemistry was in the 18th and 19th century, and the systematic basis of the scientific discipline "photochemistry" was created in the first decades of the 20th century [33]. At that time the sun was the only suitable light source which could be used for photochemical experiments. Thus, photochemistry is an intrinsic solar discipline. In the year 1912 G. Ciamician [34] already noticed the technical potential of solar photochemistry and shortly after the second world war G.O. Schenck [35] carried out solar photochemical syntheses of important fine chemicals in a larger plant. Recently, solar photochemistry attracted attention again for the manufacture of fine chemicals.

Often photochemical syntheses can be carried out to yield high value products in excellent selectivities applying mild reaction conditions. Some compounds of interest can merely be prepared in a reasonable way photochemically. Despite of these advantages photochemical syntheses play only a limited role in the industrial chemistry because the costs for electricity, light sources, and photochemical installations are prohibitive. Disadvantages of electrically operated photochemical processes are also the operation hours of the lamps which are limited to 1,000 to 8,000 hours and the production of useless low temperature heat due to the cooling demands of the lamps. Basically primary energy - such as coal, oil, gas, uranium, - can only be converted to artificial radiation at low efficiencies due to the conversion losses on the path primary energy - electricity - artificial radiation. Aside from that in many cases only part of the radiation is required to carry out the respective photochemical reaction. The shortwave radiation must be filtered out to avoid undesired side reactions and the longwave radiation is not energetic enough for the excitations.

Solar photochemistry does not exhibit the disadvantages of the technology operated with artificial light, provided that the photochemical system can absorb radiation of the solar spectrum. Moreover a solar photochemical technology has an inherent safety benefit in that the light source is in a large distance to the reaction mixture as opposed to typical mercury high press-

ure immersion lamps which always cause a risk of fire and explosion due to their hot surfaces (more than 600 °C) being in a close distance to inflammable organics.

Photochemically initiated radical chain reactions, among them photohalogenations, photosulf-oxidations, and photosulfochlorinations, will probably not play a role in solar photochemistry because the energy costs are insignificant at quantum yields  $\Phi \gg 1$ . On the other hand for one quantum processes the profitability is determined by the light costs more significantly. Apart from the photonitrosylation of cyclic alkanes this condition only applies to the photochemical synthesis of specialities at present. In the latter field of applications there is the best chance that solar radiation may enter into competition with artificial radiation [36].

For the solar photochemical syntheses the most suitable photoreactors have to be selected. Laboratory prototypes of flat plate collector-reactors as well as voluminous vessels - such as Schenck's plant - exposed to the solar radiation have already been tested in several cases. They show the advantage in their capability also to use diffuse solar radiation. In technical plants, however, high space-time-yields are desirable and reactors should be constructed as compact as possible. For this reason receiver-reactor designs actually being developed use concentrated solar radiation. Principally the same devices are used for the concentration of solar radiation as in the solar thermal power plant technology: line-focusing parabolic trough collectors and point-focusing solar furnaces. Line-focusing parabolic trough collector-reactors have been applied by Demuth et al. in a laboratory scale [37,38]. Subsequently DLR and RWTH Aachen jointly performed the SOLARIS-experiment in a kilogram-scale at the Plataforma Solar de Almería [39,40].

The PROPHIS test facility (Parabolic tRough collector for Organic PHotochemical syntheses In Solar light) is located besides of the high flux solar furnace at the DLR research center Köln-Porz [41]. It is designated to qualify solar photonic reactions and syntheses beyond the laboratory scale and is the most powerful facility of its kind at present. In that plant reaction classes such as sensitized singlet oxygen reactions, sensitized photoisomerizations, photocycloadditions, and photoassisted homogeneous catalytic cyclizations have already been carried out successfully to yield high value specialities.



Fig. 10: PROPHIS test facility at the DLR research center in Köln-Porz, Germany

The center part of the PROPHIS facility is a line-focusing "Helioman"-collector (fig. 10) which originally was built for solar thermal power generation in the distributed collector system power plant at the Plataforma Solar de Almería [42]. The collector consists of a turret, a traverse beam, four collector troughs, piping and electrical equipment, and disposes of a biaxially tracking system to align the collector with any position of the sun. Direct solar radiation hits the collector aperture rectangular and the parabolically shaped mirrors reflect the radiation into the transparent receiver-reactor tubes which are positioned in the four focal lines. The reaction mixture (up to appr. 100 l) is pumped through the receiver-reactor tubes connected in series until the desired conversion has been achieved. In an external heat exchanger excess heat is removed and rejected to the ambient by an air cooled process cooler.

#### 4. Conclusions

Today nobody knows whether a chemical industry based on solar energy will be realized in a larger scale. Nevertheless, there is a chance that solar energy may contribute to an environmentally benign and sustainable development in the process industries of the next century. To evaluate an eventual transfer of solar chemical processes to a broad industrial practice at economically acceptable conditions in parallel to basic research also the instrumental prerequisites must be developed and qualified. At present it is necessary above all to collect further experiences to operate solar chemical processes and to test such innovative techniques in a small engineering scale which are already running in the laboratory. The DLR high flux solar furnace has been placed at disposal for appropriate development of technologies. Technology

development includes integrated receiver-reactors, windows for volumetric and direct absorption receiver-reactors, secondary concentrators, and specific high temperature high flux measurement techniques.

Volumetric and direct absorption receiver-reactors show a promising potential which by far is not yet exhausted. Aside from possible effects on the reaction rates due to the highly concentrated radiation the main technological features are that energy transfer is by massless high flux radiation and that allowable heat flux densities are more than one order of magnitude higher than in conventional reactors.

Due to the experiences collected so far the direct use of solar radiation instead of artificial lamps is highly attractive for the photochemical or photocatalytic production of industrially important fine chemicals. Photochemical syntheses could be easily developed to early applications of solar radiation in the chemical technology.

For the near term future only niche industrial applications can be expected such as the photochemical production of specialities, detoxification of specific hazardous wastes, or testing and treatment of materials. Whilst developing the first niche applications an intended effect is to establish specific know how in solar chemical engineering and to collect those experiences which are required to carry out solar chemical bulk processes. At the same time also further specific applications of solar radiation should be inspired.

The feasibility of a solar chemical technology has been demonstrated in an engineering scale. The chances for the industries of the industrialized world are twofold: solar chemical techniques could be employed directly at locations in the industrialized countries if there is enough sun (e.g. in Southern Europe, in the Southern States of the U.S.A., in Israel, in Australia) or could be exported to non-industrialized or industrializing countries which have good solar conditions (e.g. North African countries, South Africa, Namibia, Arab countries, Mexico). In a future world economy these countries could export chemically stored solar energy instead of oil and natural gas or they could export solar processed basic chemicals instead of the mineral raw material.

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