# EUROPEAN ROADMAP OF PROCESS INTENSIFICATION

# - TECHNOLOGY REPORT -

TECHNOLOGY: PHOTOCHEMICAL REACTORS

TECHNOLOGY CODE: 3.3.4

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# 1. Technology

## 1.1 Description of technology / working principle

*(Feel free to modify/extend the short technology description below)*

Photochemical reactors use the energy of light to initiate or catalyze reactions. The basic principle is that light quanta are absorbed by chemical compounds (reagents, sensitizers or catalysts) which are electronically excited and become (more) reactive towards other compounds present. The wavelength of the light is in the range of 200 nm to 400 nm (UV) and 400 nm to 700 nm (visible light). IR induced photochemistry also exists, but is mainly used in analytical techniques and has not frequently been investigated for chemical process technology, except for some very specific applications in the USA. The light can originate either from the sun (4-5% UV) or from artificial sources (e.g., medium-pressure mercury or xenon lamp, excimer lamp). In the case of solar-driven photochemical reactors, the energy needs to be concentrated in order to reach sufficient efficiency.

In non-catalyzed photochemical reactions the light energy is absorbed by the reagent itself or by a sensitizer. A sensitizer transfers the electronic energy to the reagent or undergoes a reversible redox reaction with the reagent (which is then photocatalysis). The reagent becomes then electronically excited by the transfer of an electron to a higher energy band. Upon returning to its ground state, the molecule can either transfer its energy to another molecule (thus excitating this molecule) or produce reactive components such as radicals or ions.

Photocatalysis implies the acceleration of a photoinduced reaction by the presence of a catalyst. A catalyst can also be considered as a sensitizer. Photoinduced reactions are activated by absorption of a photon with sufficient energy, i.e. equal or higher than the band-gap energy ($E_{bg}$) of the catalyst. The absorption leads to a charge separation due to the promotion of an electron ($e^-$) from the valence band of the semiconductor catalyst to the conduction band thus generating a hole ($h^+$) in the valence band. In order to have a photocatalyzed reaction, the $e^-$-$h^+$ recombination, subsequent to the initial charge separation, must be inhibited by competition with other processes involving the produced $e^-$ and/or $h^+$. The most widely used semiconductor catalyst in photoinduced processes is titanium dioxide ($TiO_2$), because it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyse reactions, cheap and without risks to environment or humans. The only disadvantage of $TiO_2$ is that it is not activated by visible light, but only UV light. In order to overcome this disadvantage, the catalyst needs to be doped with impurities. Other photocatalysts include Pt, $RuO_2$ and $WO_3$.

In scientific literature there is a debate on the difference between photocatalysis and photosynthesis. The first is seen as merely catalyzing a reaction that would be possible even without the presence of the catalyst (although slower), whereas the latter implies a reaction that is thermodynamically impossible without the catalyst (positive sign of the change in Gibbs free energy of the reaction).

## 1.2 Types and "versions"

*(Describe the most important forms/versions of technology under consideration, including their characteristic features, differences and similarities)*

There is a wide variety of photochemical reactors being developed. However, the main components of these reactors include (see figure):

- a light source, including activator or concentrator if necessary;
- a cavitation for the chemical medium;

- reagents and reaction products;
- sensitizers or catalysts (on support) if necessary.

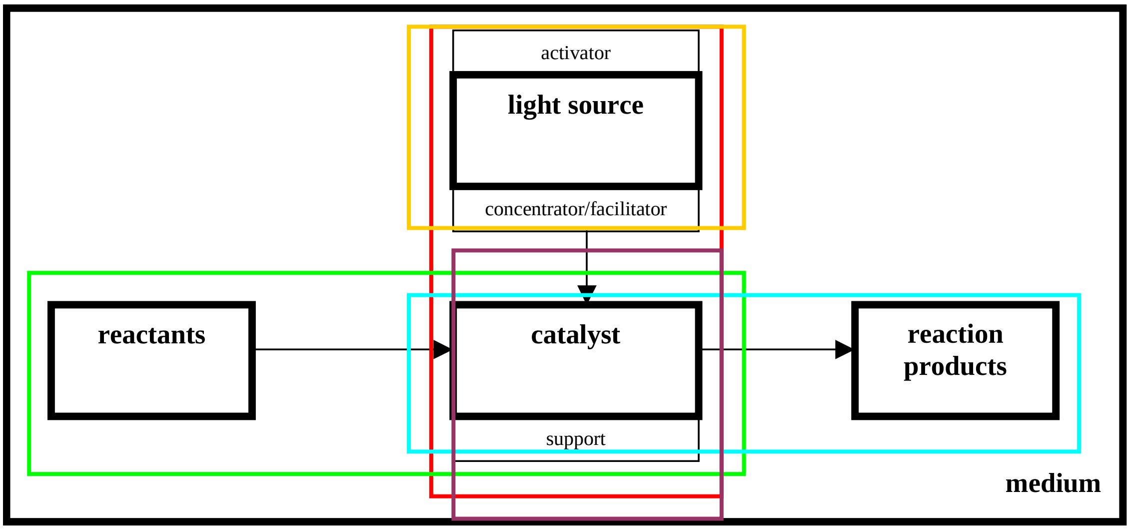

Figure: Scheme of a reactor set-up for photocatalysis.

Each of these components and the relation/contact between these components can be configured in several ways. The light source and its position are the major issues distinguishing photochemical reactors from other reactors.

The different positions of the light source relative to the cavity in which the reagents and/or catalysts are present can be summarized as follows:

- immersion of the lamp in the chemical medium (immersion reactors);
- external position of the lamp relative to the reactor (a transparent wall is required) (annular reactors);
- external light production with guided channelling through the reactor (optical fiber, hollow tube reactor);
- alternative set-ups, made possible by intensifying the reactor mass transfer (e.g. illumination of spinning discs);
- use of solar illumination generally requires concentration of the light energy by focusing with paraboles.

Until recently the light source was dimensioned towards the macro- (solar) or meso-scale (pressure lamps, excimer lamps). However, recent advances include microscale illumination (LED’s).

Photocatalytic reactors can use the catalyst in the form of a slurry (thus requiring a separation step after reaction) or immobilized on the wall or reactor internals (thus requiring excellent mass transfer).

## 1.3 Potency for Process Intensification: possible benefits

*(In Table 1 describe the most important documented and expected benefits offered by the technology under consideration, focusing primarily on energy; $CO_2$ emission and costs, providing quantitative data, wherever possible. Add other benefits, if needed).*

Photochemical reactions provide alternatives to a vast range of chemical reactions and technologies (see 2.4). The advantage of the photochemical alternative is often that it can be performed at low temperature, thus limiting side reactions. Selectivities and conversions of up to 100% can be achieved. However, it can be somewhat misleading to compare with traditional processes as often another chemical pathway is followed.

On the other hand, it must also be taken into account that the photochemical pathway is sometimes the only chemical pathway that is known. In this case no alternatives exist except the one of no-production. From this point of view, it can be expected that when the technology would be economically viable, new products will become commercially available.

Table 1: Documented and expected benefits resulting from technology application

| Benefit | Magnitude | Remarks |
|---|---|---|
| conversion/yield | can go up to 100% | Depends on the specific case, for example up to 100% in the case of toluene oxidation to benzaldehyde. |
| selectivity | can go up to 100% | Depends on the specific case, for example up to 100% in the case of cyclohexane oxidation to cyclohexanone (whereas in the conventional process this is about 75% cyclohexanone, 25% cyclohexanol). |
| low-temperature | can go down to room temperature | Depends on the specific case. Low temperature reactions also generate less by-products (increased selectivity). |
| solar (free) energy | running energy cost reduced to zero, large investment costs | At the earth's surface solar light contains about 4% of UV. This is a downside. However, sunlight can be concentrated (see table 3) and in the case of photocatalysis, the catalyst can be doped in order to be activated by visible light. |

### 1.4 Stage of development

The concept of photochemical reactors is already implemented in industry (see 2.2). However, applications remain limited due to issues such as costs (lamps, electrical energy) and energy efficiency (distance lamp – reactant, maximum illumination). Improvements on these issues are needed.

## 2. Applications

### 2.1 Existing technology (currently used)

*(Describe technology (-ies) that are conventionally used to perform the same or similar operations as the PI-technology under consideration)*

Some photoreactors have been implemented in industry. To date the main economical viable processes are chain reactions where thermal processes can be substituted by photochemical processes. Examples include chlorinations, sulfochlorinations, sulfoxidations, nitrosations (see 2.2.). In these cases the photoreactions appear to be performed with relatively low capital and electrical costs. However, the example of Toray (Table 2) shows that while this company uses the photochemical process, the majority of companies producing caprolactam prefer the conventional processes (95% of total production).
The only non-chain reactions that are photochemically produced in industry (vitamins, flavours) are compounds that can only be produced photochemically or with a high added value.

Commercial applications mainly use immersion or annular reactors

## 2.2 Known commercial applications

*(Is the technology broadly applied on commercial scale? In which process industry sectors is the technology most often applied: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? What is the estimated number of existing applications? In Table 2 provide the most prominent examples of realized applications and provide their short characteristics)*

The largest amount of photochemical applications in industry is found in the light induced polymerization for the production of protective and decorative coatings, inks, packaging and electronic materials. Commercial applications in bulk chemical, pharma and agro-sectors are more scarce. Some examples are given in table 2.

Table 2. Industrial-scale applications of the Technology (existing and under realization)

| **Sector** | **Company - Process/Product name/type** | **Short characteristic of application** | **Production capacity /Plant size** | **Year of application** | **Reported effects** |
|---|---|---|---|---|---|
| bulk | Toray Ltd. | cyclohexane to cyclohexanone oxime (for caprolactam production) | $1.7*10^5$ ton/y (2003) | 1963 | • conversion increase from 10% to 80% (cyclohexane to cyclohexanone oxime)<br>• elimination of intermediate process steps |
| bulk | Dow, Solvay, a.o. | 1,1,1-trichloroethane from 1,1-dichloroethane | ca. $3*10^5$ ton/y (1984) | 1950's to 1990's (banned by Montreal Protocol) | • higher product yield<br>• better selectivity<br>• lower specific energy consumption (decrease of process temperature from 350-450°C to 80-100°C) |
| bulk | Monsanto | benzylchloride production from toluene chlorination | 0.5-$1*10^5$ ton/y | n.a. | 90% yield |
| bulk | Hoechst (Sanofi-Aventis) | sulfonic acid production from parrafins and sulfur dioxide | $4.5*10^4$ ton/y | n.a. | 12% yield |
| specialty | BASF | production of *trans*-vitamin A acetate | 2500 ton/y | n.a. | no other process available |
| specialty | Dragoco (Germany) and Firmenich (Switzerland) | rose oxide (perfume) | 60-100 ton/y | n.a. | • yield = 60%<br>• no other process available |

## 2.3 Known demonstration projects

*(Are there any demonstration projects known related to the technology under consideration? In which process industry sectors are those projects carried out: large volume chemicals – specialty chemicals & pharma – consumer products – ingredients based on agro feedstocks? In Table 3 provide the short characteristics of those projects.)*

Table 3. Demonstration projects related to the technology (existing and under realization)

| **Sector** | **Who is carrying out the project** | **Short characteristic of application investigated, including product name/type** | **Aimed year of application** | **Reported effects** |
|---|---|---|---|---|
| wastewater treatment | Plataforma Solar de Almería, Spain | water decontamination, disinfection and desalination | not specified | • use of solar light |
| chemical synthesis | PROPHIS, Köln | pilot-installation (1 ton/y) for organic synthesis with solar energy: photo-oxygenation (rose oxide), heterocyclization, photo-Friedel-Crafts acylations, isomerizations | not specified | • lower temperature<br>• lower pressure<br>• increased yield<br>• lower energy requirements (solar light) |

## 2.4 Potential applications discussed in literature

*(Provide a short review, including, wherever possible, the types/examples of products that can be manufactured with this technology)*

Applications of photochemical reactors can be found in bulk chemical industry, fine chemical industry, pharmaceutical industry, the sectors of wastewater and air treatment, medicinal applications. The (catalyzed) reactions include:

- nitrosylations,
- chlorinations, brominations, fluorinations,
- sulfochlorinations, sulfoxidations, desulfonations, desulfonylations,
- decarboxylations,
- oxidations of alkanes to alkenes, oxidations of cyclo-alkanes to ketones, oxidations of alcohols to carbonyls, oxidations of aromatics to aromatics with alcohol, ketone or aldehyde groups,
- isomerizations,
- polymerizations.

# 3. What are the development and application issues?

## 3.1 Technology development issues

*(In Table 4 list and characterize the essential development issues, both technical and non-technical, of the technology under consideration. Pay also attention to "boundary" issues, such as instrumentation and control equipment, models, etc.) Also, provide your opinion on how and by whom these issues should be addressed)*

Table 4. Technology development issues

| Issue | Description | How and by whom should be addressed? |
|---|---|---|
| Improved/novel light sources and catalysts | Light sources remain too often the large, inefficient and short-lasting conventional lamps. Novel designs of light sources should aim at smaller, long-lasting light sources with a high energy conversion. Catalysts need to be developed that suit the features of the light source (wavelength, energy intensity). | Interdiciplinary R&D teams at universities (physics, chemistry, chemical engineering and electric/electronic engineering) in collaboration with light equipment manufacturers and catalyst producers. |
| Modelling | The physics of light need to be combined with chemistry and thermodynamics of chemical reactions in order to produce more complete models. These models should be used to devise optimal reactor configurations. | Interdiciplinary research teams at universities (physics, chemistry, chemical engineering and electronic engineering). |
| Scale up and optimal reactor configuration | Optimal configuration of light – (catalyst) – reactor cavity with minimum energy loss and maximum mass transfer. | R&D studies at universities (chemical engineering) in collaboration with reactor engineering companies. |

## 3.2 Challenges in developing processes based on the technology

*(In Table 5 list and characterize the essential challenges, both technical and non-technical, in developing commercial processes based on the technology under consideration. Also, provide your opinion on how and by whom these challenges should be addressed)*

Table 5. Challenges in developing processes based on the technology

| Challenge | Description | How and by whom should the challenge be addressed? |
|---|---|---|
| light efficiency | Reduce energy losses on the path from energy generation to molecule excitation | By improving existing designs (e.g. LED) or designing novel light sources. Within R&D projects including electric/electronic engineering and physics (both academia and industry). |
| penetration depth of light in view of scale up | Tackle scale up problems, e.g. by miniaturization of light and chemical tank (microreactors), by improved (micro)mixing, or by introduction of suspended, randomly distributed light sources in the bulk solution | Reactor design supported by improved models. Academia and industry within chemical engineering community. |
| optimal wavelength and intensity | Provide tailor-made light sources (and catalysts) for specific chemical processes. | Developing new luminescent molecules with the desired properties. R&D projects including electric/electronic engineering and physics (both academia and industry). |

| | | |
|---|---|---|
| exhaustive overview of potential applications | List the potential reactions/processes that could occur photochemically, together with the economy requirements to render them viable | feasibility studies by industry |

# 4. Where can information be found?

## 4.1 Key publications

*(Provide the list of key publications in Table 6)*

Table 6. Key publications on the technology

| Publication | Publication type (research paper/review/book/ report) | Remarks |
|---|---|---|
| A.M. Braun, M.T. Maurette, E. Oliveros, *Photochemical Technology,* Wiley & Sons Ltd., London, 1991. | book | photochemical technology |
| A. Mills, and S. Le Hunte, An overview of semiconductor photocatalysis, *J Photochem Photobiol A: Chem*, 108 (1997) 1-35. | review | photocatalysis / chemistry |
| O. Carp, C.L. Huisman and A. Reller, Photoinduced reactivity of titanium oxide, *Progr. Solid State Chem.*, 32 (2004) 33-177. | review | photocatalysis / chemistry |
| A. Mills and S.K. Lee, in S. Parsons (ed.), *Advanced oxidation processes for water and wastewater treatment*, IWA Publishing, London, 2004, pp. 137-166. | chapter in book | photocatalysis / chemistry |
| H. de Lasa, B. Serrano and M. Salaices, *Photocatalytic reaction engineering*, Springer, New York, 2005. | book | photocatalysis / engineering |

## 4.2 Relevant patents and patent holders

*(Provide the list of relevant patents in Table 7. Under "remarks" provide, where applicable, the names/types of products targeted by the given patent.)*

Numerous patents exist for the use of light in a photochemical process. A worldwide patent search on "photochemical", "photocatalysis" and "photochemistry" resulted in 1764, 186 and 23 patents, respectively. For "photochemical reactor" and "photocatalytic reactor" 89 and 40 patents were found, respectively.

The patents listed here consist of the first ones and the most recent ones, together with some specific break-throughs (micro-illumination and microreactors). Focus is on patents not exclusively directed towards air and water treatment.

Table 7. Relevant patents

| Patent | Patent holder | Remarks, including names/types of products targeted by the patent |
|---|---|---|
| WO2006087353 (2006), *Photoreactor* | C Sattler et al. | hollow tube reactor |
| US6827911 (2004), *Photoreactor with self-contained photocatalyst recapture* | KL Gering (Bechtel BWXT) | recovery of suspended catalyst |

| | | |
|---|---|---|
| EP1415707, EP1398077 (2004), *Method and microfluidic reactor for photocatalysis*,. | PJ Barthe et al. (Corning Inc.) | microreactor |
| DE10246626 (2004), *Selective halogenation of alkyl aromatic compounds, useful as intermediates for the production of plant protection agents, comprises insertion of halogenating agents in a micro-reactor under photochemical initiation* | K Morgenschweis et al. (BASF) | microreactor |
| US6633042 (2003), *Solar photoreactor* | KH Funken et al. | |
| WO02062465 (2002), *Photochemical reactor* | D Meissner | electromagnetic activation of light source |
| JP9299456 (1997), *Photocatalyst apparatus* | K Sakai et al. (Toyoda Gosei Co. Ltd.) | LED illumination |
| US4795617 (1989), *Electroluminescent chemical activation system* | L.R. O'Hare | electroluminescent illumination |
| US3458418 (1969), *Process for carrying out photochemical reactions and apparatus thereof* | W. Beckmann (BASF) | immersion photochemical reactor |
| US3431188 (1969), *Process and apparatus for photochemical reaction* | I Stoichi et al (Toray) | |
| US266186 (1953), *Two-stage photochemical reactor* | LJ Governale et al. (Ethyl Corp.) | |

## 4.3 Institutes/companies working on the technology

*(Provide the list of most important research centers and companies in Table 8)*

Table 8. Institutes and companies working on the technology

| **Institute/Company** | **Country** | **Remarks** |
|---|---|---|
| Plataforma Solar de Almería | Spain | solar-driven wastewater treatment, thermochemical synthesis reactions driven by photovoltaic cells |
| Prof. Frei, Laboratory of Chemical Biodynamics, Lawrence Berkeley Laboratory, University of California, Berkeley. | USA | photochemical synthesis |
| Prof. Funken, Deutsche Forschungsanstalt für Luft- und Raumfahrt, Köln | Germany | solar photochemistry |
| Prof. A.K. Ray, Dept. of Chemical Engineering, National University of Singapore | Singapore | photocatalytic reactors |
| Prof. A.M. Braun, Lehrstuhl fur Umweltmesstechnik, Universität Karlsruhe | Germany | photochemical synthesis and destruction |
| Dr. M.T. Maurette, CNRS Toulouse | France | photoreactions (synthesis and destruction) and photoreactors |

In addition several companies are working on photochemical technology. More details are found in paragraphs 5.1 (suppliers) and 5.2 (end users).

# 5. Stakeholders

## 5.1 Suppliers and developers

*(Provide the list of key suppliers/developers in Table 9)*

Table 9. Supplier and developers

| **Institute/Company** | **Country** | **Remarks** |
|---|---|---|
| *Photochemical reactors for chemical industry* | | |
| The Southern New England Ultraviolet Company (Rayonet) | USA | • ultraviolet reactors |
| Grantzel | Germany | • photochemical reactors<br>• patent for photochemical reactor, FR2397874 (1979), GB1461506 (1977), FR2306734 (1976) |
| Hans Mangels GmbH | Germany | DEMA photochemical reactor |
| *Light sources* | | |
| Heraeus Instruments GmbH | Germany | • UV lamps for photochemistry<br>• patent for immersion lamp, US5334905 (1994) |
| Philips Electronics | Nederland | several types of lamps, not specifically for photochemistry |
| Osram | Germany | several types of lamps, not specifically for photochemistry |
| Canrad-Hanovia | USA | several types of lamps, not specifically for photochemistry |
| *Photochemical reactors for air and water treatment* | | |
| Babcock Hitachi KK | Japan | • polluted air treatment<br>• patents for photochemical reactors, JP2159377 (1990), JP1312077, JP1312076, JP1312075, JP1242142, JP1139770 |
| Zentox/Photox Corporation | USA | • wastewater cleaning<br>• patent for immobilized photocatalyst, WO9740936 (1997) |
| Wedeco | UK | • wastewater cleaning<br>• UV photochemical reactors<br>• several patents |
| Matrix Photocatalytic Inc. | Canada | • wastewater cleaning<br>• no patents |
| Clearwater Industries | USA | • wastewater cleaning<br>• no relevant patents |
| Photox Bradford Ltd. | UK | • wastewater cleaning<br>• no patents |
| Lynntech Inc. | USA | • wastewater cleaning,<br>• patent for a fixed-bed photocatalyst reactor, US6409928 (2002), US6136186, US6117337, US5779912 |

| | | |
|---|---|---|
| Purifics Environmental Technologies Inc. | Canada | • air and wastewater cleaning<br>• patent for Photo-Cat water and air automated treatment system, US2005211641 (2005), US6136203, US5589078, US5462674 |

## 5.2 End users

*(Describe the existing and potential end-users, other than those already listed in Table 2)*

Various companies could/can be end-users of an economically viable photochemical process. Several photochemical processes are known and have obvious advantages over the conventional processes. The main barriers these processes currently face are the technological problems regarding scale up and illumination efficiency, thus keeping the process economically uninteresting. However, if these barriers can be overcome, not only the currently known photochemical reactions can be implemented, but also new products and new end users are envisaged to become available.

Industrial patent holders related to photochemical reactors include BASF, Ciba, DowChemical, DuPont, Ethyl Corp., Philips Petroleum Co., Toray. Corning and Degussa hold patents related to photocatalysis (see also Table 7).

# 6. Expert’s brief final judgment on the technology

*(maximum 5 sentences)*

Photochemical technology has a certain future as a niche application in chemical industry. Although new industrial applications of this technology have been scarce in the last 20 years, recent advances in scientific literature do show that major improvements in illumination efficiency (LED or even nanoscale illumination) and scale up (or actually scale down to microreactors) are feasible within the next 10 years. With these improvements the technology should become a competing technology. If, in a next stage, solar illumination could be incorporated (either as a substitute for the artificial illumination, or as energy source for photovoltaic cells generating electricity for the artificial illumination), this technology will have a comparative advantage over the conventional technology.