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Continuous-flow photochemistry: A need for chemical engineering

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ABSTRACT

The present paper aims to illustrate that chemical engineering enables to address some of the current challenges and issues in continuous-flow photochemistry. For that, some common limitations encountered in industrial photochemistry are firstly highlighted and a general overview on flow photochemistry equipment is presented. The main challenges linked to photochemical (micro)reactor engineering are subsequently stated. By considering only the case of a purely direct photochemical reactions $A \xrightarrow{h\upsilon} B$ in homogenous medium, the key factors to consider when implementing such photochemical reactions in microstructured technologies are outlined. Their influence on the outputs (conversion, productivity, photonic efficiency) of this simple type of photochemical reaction is then discussed. The significance of chemical engineering frameworks is finally demonstrated using several examples concerning the understanding of the coupling between the different phenomena involved, the predictions of the performances obtained, the acquisition of kinetics data and the elaboration of strategies for photochemical process intensification and smart scale-up. In the future, the challenge will be to integrate the complexity of photochemistry (e.g. heterogeneous phase reactions) into the present modelling tools so as to enlarge the spectrum of strategies devoted to photochemical process intensification.

1. Introduction

Organic photochemistry has the potential to emerge as a key synthesis pathway in sustainable chemistry. In recent years, photochemical reactions have significantly enriched the methodology of organic synthesis [1–4]. In contrast to thermal reactions, photochemical reactions are induced via the electronically excited state possessing a different electron configuration than their corresponding thermal ground states [5–8]. Consequently, the chemical reactivity of excited molecules is considerably different from that of ground state molecules. The following points are particularly interesting in the context of sustainability: (i) multi-step syntheses of complex molecules are shortened and simplified; often, a high molecular complexity is generated in one step from simple precursors, (ii) a portfolio of novel compound families (e.g. strained rings) is becoming accessible or more easily accessible, and (iii) in many reactions, the photon acts as a "traceless reagent", and no chemical catalysts (acid, base, metal, etc.) or activating groups are needed [9–11]. The 12 guiding principles of Green Chemistry [12,13] are thus addressed by photochemistry. In addition, photochemical reactions are currently becoming an indispensable tool in the search of new biologically active compounds for applications in medicine, fine chemical and pharmaceutical industries, as well as in many other fields (e.g. material and environmental sciences) [14–23].

At the same time, continuous-flow technologies, in particular microstructured reactors, have emerged as alternatives to batch processing and their implementation in process intensification strategies is likewise crucial for sustainable chemistry [24]. Recently, various works have shown that these technologies are also suitable and beneficial for preparative photochemistry [25–31], boosting the interest in continuous-flow photochemistry.

The present paper aims to illustrate that some of the current challenges and issues in continuous-flow photochemistry can be addressed using a chemical engineering framework. Such a framework is indeed essential to elaborate a process intensification strategy which enables adaptation of the microstructured

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Nomenclature

A_e^0	Reference absorbance (−)
a_{irrad}	Specific irradiated area (m^{-1})
C	Concentration ($mol\,m^{-3}$)
C_0	Initial concentration ($mol\,m^{-3}$)
Da_I	Damköhler one number defined in Eq. (13) (−)
Da_{II}	Damköhler two number defined in Eq. (14) (−)
d_{pen}	Light penetration distance (m)
D_m	Diffusion coefficient ($m^2\,s^{-1}$)
e	Characteristic dimension of the microphotoreactor with respect to the light penetration direction (m)
e^a	Local volumetric rate of photon absorption (mol photon $m^{-3}\,s^{-1}$)
E	Spherical irradiance (mol photon $m^{-2}\,s^{-1}$)
F_0	Photon flux density received at the microphotoreactor's walls (mol photon $s^{-1}\,m^{-2}$)
Fo	Fourier number (−)
L	Length of the microphotoreactor (m)
r_A	Rate of consumption of the species A ($mol\,m^{-3}\,s^{-1}$)
R^X	Productivity to reach a conversion X ($mol\,s^{-1}$)
q_p	Incident photon flux (mol photon s^{-1})
$\overline{U}$	Mean velocity in the microreactor ($m\,s^{-1}$)
V_r	Volume of the microphotoreactor (m^3)
X	Conversion (−)

Greek symbols

α	Napierian linear absorption coefficient (m^{-1})
β_A	Competitive absorbance factor with respect to the species A (−)
κ	Napierian molar absorption coefficient ($m^2\,mol^{-1}$)
λ	Wavelength (m)
η^X	Photonic efficiency (−)
ϕ	Quantum yield of the reaction ($mol\,mol\,photon^{-1}$)
τ	Residence time (s)
χ	Function defined in Eq. (10)

photoreactor design (channel design, dimensions, light source, etc.) to photochemical reaction specificities, and more generally a transfer from batch to continuous mode operations.

Firstly, the common limitations encountered in industrial photochemistry will be identified and a general overview on flow photochemistry equipment presented (Section 2). The main challenges linked to photochemical (micro)reactor engineering will then be exposed (Section 3). By considering only the case of purely direct photochemical reactions $A \xrightarrow{h\upsilon} B$ occurring in homogenous medium, the key factors to consider when implementing such a photochemical reaction in microstructured technologies will be outlined basing on modeling considerations (Section 4). In the last section (Section 5), some examples will be presented to illustrate, for this particular case of a photochemical reaction, how a chemical engineering framework enables to understand and formalize the positive effect of microstructured technologies for photochemistry.

2. Industrial photochemistry: a «renaissance»?

Since 1975, 8000 photochemical reactions for organic synthesis have been referenced [32]. Despite this huge portfolio, organic photochemistry has not found widespread implementations in chemical industry [33,34]. It is difficult to obtain a global overview on currently existing photochemical activities as industrial processes are often kept confidential. Nevertheless, it is known that many industrial photoreactions have been established decades ago and have since been operational largely unchanged [35]. Based on the information available by Braun et al. [34], the worldwide electrical power installed for the radiation sources used in preparative photochemical equipment represents almost 30 MW, thus demonstrating its significant importance. Photochemical synthesis is mostly applied by chemical companies that produce intermediate and/or fine chemicals (e.g. pharmaceutical, agrochemical, food processing and fragrance industries) and by companies producing basic or final products (e.g., food, electronic, automotive, furniture, building and packaging industries). It should be noted that the production of highly priced fine chemicals (e.g. fragrance, pharmaceutically active compounds) represents the minor fraction of the installed electrical power previously mentioned [34]. Among the well-known examples of industrial photochemistry, one can mention the synthesis of vitamin D_3 and vitamin A (BASF, Hoffmann-LaRoche), the photooximation of cyclohexane (Toray), the photochlorination of toluene, the synthesis of rose oxide (Symrise) [36] and more recently the synthesis of artemisinin [37].

The reluctance to transfer preparative photochemistry to large-scale is mainly due to the limitations of the currently available technology, which requires outdated immersion-type reactors, often operating in semi-batch mode (circulation of the reaction medium between a large central reservoir and the reactor), equipped with expensive and energy-demanding mercury lamps. In these installations, process limitations are numerous due to the uncontrolled coupling between hydrodynamics, light, mass transfer and photochemical kinetics. As a result, lower selectivity and yields than on lab-scale are commonly obtained. Many of these systems furthermore need optical filters to cut off undesired radiation, large dilutions to overcome unfavorable light absorption and intensive cooling to counter the heat generation by the lamps.

By combining the benefits of micro-scale with continuous-flow mode, microstructured reactors enable, when compared to conventional photochemical equipment, higher conversions and selectivities while reducing irradiation time [25–31]. Some of their specific advantages are: (i) extensive penetration of light, even for concentrated chromophore solutions, (ii) minimization of side reactions or decompositions by flow-operation, (iii) easy control of the irradiation time and (iv) safer conditions (for example when involving heat-sensitive oxygenated intermediates). The combination of microstructured technology with new light sources (e.g. Light-Emitting Diodes (LED) or excimer lamps) additionally offers promising perspectives in terms of energy-savings [38]. Consequently, there is at present an increasing interest in continuous-flow photochemistry, leading to a "renaissance" of preparative photochemistry. Most studies are dedicated to the production of small quantities in often improvised 'in house'-made reactors (Fig. 1a). The results obtained have nevertheless strengthened this technology and have sparked the development of dedicated and more advanced equipment. Currently, commercial technologies (e.g. from the companies YMC [39], Mikroglas [40], Ehrfeld [41], Future Chemistry [42]) (Fig. 1b) and internally developed reactors [43–45] mainly enable continuous-flow photochemistry on lab-scales, although isolated examples of meso-scale photoreactions in flow have been reported as well. However, a scale-up to industrially relevant amounts, i.e. above a few hundred kilograms per year, has not been realized yet. Thus far, very few flow photoreactors are available for several grams per day (Vapourtec UV-150 [46]) or kilogram per day operations (Corning® G1 Photo Reactor [47], Heraeus Noblelight [48]) (Fig. 1b). A flow-photochemical production facility for the synthesis of low-volume anticancer compounds has recently been erected by Heraeus Noblelight [48], thus demonstrating the potential of this emerging new technology.