REACTION ENGINEERING OF PHOTOREACTIONS – ASPECTS TO BE CONSIDERED AND POSSIBLE BENEFITS

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Abstract

Photochemical reaction engineering is currently of low priority in the scientific community. While this can be attributed to the high level of complexity and interactions, proper understanding of the reaction engineering aspects of photochemical reactions is required to correctly describe and compare photochemical processes. Furthermore, a sophisticated use of reaction engineering knowledge provides better reaction control as well as additional tools for investigations on reaction engineering issues. This contribution aims on shining some light on photochemical reaction engineering. For this general aspects will be discussed using examples from literature as well as from own work.

Keywords

Photochemical Reaction Engineering

Introduction

With the advent of a change in energy and raw materials, alternative ways for providing the activation energy to initiate reactions become increasingly more attractive. Beside electrochemical activation, photochemical activation is one alternative to initiate reactions. Photochemical routes are beneficial since they provide access to reaction pathways, which cannot be accessed via thermal approaches.(Hoffmann, 2004) Prominent examples are photooxygenations like the Schenck ene reaction, being a key step in the synthesis of the anti-malaria drug Artemisinin.(Joël Turconi et al., 2014) For this product it was found that photochemical generation of singlet oxygen is superior over the "dark" generation from H_2O_2 and Na_2MoO_4. With view on recent research activities visible light photocatalysis has to be named, allowing the use of visible light for chemical transformation with the benefit of higher selectivities.(Xuan and Xiao, 2012) In combination with the availability of micro- and millistructured photoreactors, photochemistry currently gains lots of attention in the scientific literature.(Oelgemöller, 2012) The current interest in photochemistry is additionally amplified by the long known photocatalytic water splitting, promising in principle cheap and unlimited access to hydrogen as energy storage.(Maeda, 2011)

Despite the promising advantages of photochemical reactions, industrial applications are seldom. This can be reasoned by increasing reaction engineering demands, arising from the utilization of irradiation. The exponential decay of the irradiation intensity, or in a chemical sense the photon flux, as well as secondary phenomena like scattering and reflection induce additional complexity to the description of photochemical processes. Accompanied with a limited availability of artificial light sources, the development and optimization of photochemical processes requires consideration of all aspects typical for thermal reactions moreover all relevant optical effects.(Aillet et al., 2015) Nonetheless, reaction engineering analysis of photochemical processes are rare.

With this in mind, the aim of this contribution is to shine some light on photochemical reaction engineering. Starting from fundamental considerations, possibilities and impossibilities for comparing photoreactors by use of single performance measures, such as conversion and selectivity, space-time-yield, productivity or energy efficiency, are discussed. This will be followed by a set of illustrative examples, demonstrating the potential benefits, which can be gained when the reaction engineering aspects are understood and considered.

Comparing (Microstructured) Photoreactors

The increasing availability of microstructured photoreactors, or as they are often called photochemical flow reactors, in combination with the availability of high-performance LEDs led to a still rising number of scientific publications using these tools to conduct photoreactions in in a fast and efficient manner.(Oelgemöller, 2012) The use of these kind of reactors is reasoned by a superior performance, quantitated with e.g. the space-time-yield or the energy efficiency.

In an attempt to objectify the comparison of different kinds of photoreactors the authors gathered data from published articles and evaluated them by the use of differ-

ent performance measures. The results are exemplarily shown for photooxygenation reactions in Figure 1. Data analysis revealed, that microstructured photoreactors show indeed a better performance when the space-time-conversion is considered, but lag performance when the productivity or the energy efficiency is taken into account. This can be explained by a significant loss of photons due to the small optical length in combination with inappropriate process conditions. Investigations on microstructured photoreactors for photooxygenations showed, that more than 80% of the photons are lost due to the lag of sufficient adaption of reactor geometry to the characteristics of the light source.(Ziegenbalg et al., 2014; Ziegenbalg et al., 2015)

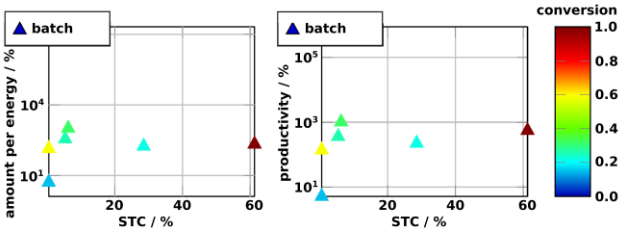

Figure 1. Relative comparison of different performance measures for microstructured and conventional batch photoreactors, taking photooxygenation as an example. 100% equals the performance of the microreactor.

Using Light to Provide Reaction Control

The use of light is often considered the use of a traceless reagent.(Hoffmann, 2012) This argument typically aims on the fact that photons vanish from the reaction solution immediately after the light source is switched off or the reaction solution leaves the irradiation zone. With this, an additional workup to remove the reagent is not necessary. This simplifies downstream processing. A closer look at these characteristic points out, that it also can be used to gain an improved reaction control. Furthermore, the ability to switch the reaction on or off enables the use of photochemical reactions as a tool for reaction engineering analysis, such as investigations on reactive gas/liquid mass transfer. Switching the light allows the separation of the mass transfer from the reaction and as a consequence an independent investigation of each process. Subsequently, the degree of coupling between mass transfer and reaction can be determined by simply carrying out the same experiments with permanent irradiation of the reaction solution.

The benefits of an improved reaction control will be discussed by taking the photosensitized generation of silver nanoparticles as an example (Figure 2). Results show, that it is indeed possible to control the amount of seeds and with this the size of the particles by influencing the rate of photon absorption. Hence, it is possible to tune the size of nanoparticles by adjusting the rate of photon absorption.

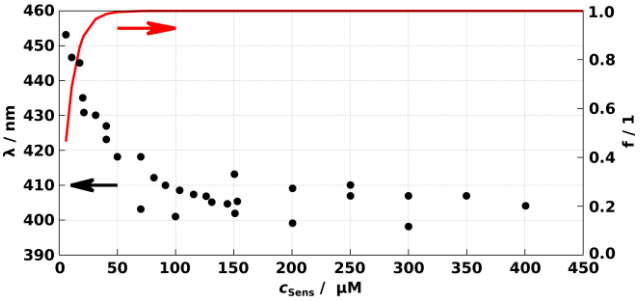

Figure 2. Ag nanoparticle absorption maximum as a function of the sensitizer concentration. (f: absorption factor).

Conclusions

A high level of complexity and interactions could be identified as reasons for a currently low priority of photochemical reaction engineering in the scientific community. On this account a proper understanding of the reaction engineering aspects of photochemical reactions is required to correctly describe and compare photochemical processes. Finally a sophisticated use of reaction engineering knowledge provides better reaction control as well as additional tools for investigations of reaction engineering issues.

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