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Efficiency vs. productivity in photoreactors, a case study on photochemical separation of Eu

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HIGHLIGHTS

- The impact of photoreactor geometry to its productivity and efficiency was investigated.
- The case demonstrated was the photochemical separation of europium.
- A model was developed to calculate local rate of radiative energy absorption.
- The optimization problem between productivity and energy efficiency was demonstrated.
- Compromising 40% of the space-time yield doubled throughput and tripled energy efficiency.

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ABSTRACT

Photo-flow chemistry has become an important research area due to the ability of this technology to boost reaction rates and productivity. This field unites the mass transfer enhancement of flow chemistry with the high energy field density of microstructured geometries. However, even though the space-time yield increases dramatically with microphotoreactors, the overall productivity of a single microreactor module remains low for many applications. This study shows that for a photochemical rare earth element separation reactor, choosing a five-times thicker characteristic length compromises 40% of the space-time yield due to lower energy density. However, this can triple the product throughput and improve energy efficiency, which is important when numbering-up photoreactors. This work addresses the question of "How micro?" and aims to introduce a new methodology to seek an optimum point of energy efficiency without compromising the high productivity achieved by photo-flow chemistry.

1. Introduction

Flow chemistry has been going hand in hand with photochemistry for some time already [1]. The first and main reason for this collaboration is the fact that the photochemical reactor productivity increases exponentially with increasing rate of absorbed radiative energy, which drives the reaction forward.

In most photochemical and photocatalytic degradation reactions, the stoichiometry of photons to products is one [2,3]. In other words, one photon is theoretically necessary to excite one photosensitive molecule, which will then undergo either oxidative or reductive quenching towards a new synthesis or a degradation route.

However, the photosensitive molecule has a very short lifetime at its excited state and it recombines to the ground state in less than nanosecond timescales [4]. This high reactivity of photocatalysts has the potential of depleting the substrate reagents in reactor zones where the photon flux is high, forcing the reaction mechanism towards undesired recombination as previously shown by Leblebici et al. [2]. In their phenol degradation reactor modelling paper, CFD tools were used to couple irradiance intensity to $^{\cdot}$OH radical generation rate to prove the existence of depleted zones in the titania coating of a parallel-plate photocatalytic reactor. This finding shows that the light can penetrate throughout a catalyst coating, but due to the diffusion limitations, only a third of the catalyst can be utilized in this particular phenol degradation reactor. The existence of these depleted zones decreases the reaction rate and intensifies the loss of photonic efficiency due to the mass transfer limitations. In a standard catalytic reactor, mass transfer limitations at the porous catalyst surface are common. This phenomenon is always evidenced by a steep substrate concentration gradient within the porous medium. This is unwanted since it means that where there is valuable catalyst, there is less

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reagent while the exact opposite is desired. In an immobilized photocatalyst coating, in addition to the valuable catalyst surface being suboptimally utilized, the photons are wasted too due to the favoured recombination reaction in depleted zones.

Reactor designers have been trying to overcome these limitations via different process intensification approaches [5,6]. A survey on different intensification efforts on the photoreactors have been recently published by Leblebici et al. [7] which focuses on 12 photoreactor designs comparing their advantages as well as disadvantages. A more extended book chapter on this matter has also been published recently [8].

One of the approaches to overcome the mass transfer limitations is the use of micro-flow chemistry [7,9,10]. Microreactor technology (characteristic dimension in the sub-mm range) enables rapid mass and heat transfer by both shortening the diffusion length while introducing new mixing mechanisms by means of chaotic advection e.g. the Taylor flow. Owing to the reduced characteristic length, it was shown that photon transfer limitations were also addressed together with the mass transfer issues previously stated. Significant developments on the scale-up of microreactor cascades are also being made [1,11]. However, the scalability of the microreactors are still their weak point.

For photocatalytic degradation reactions, Visan et al. have shown a productivity enhancement of more than two orders of magnitude (apparent rate constant $\sim 15\ \mathrm{s^{-1}}$) in their microreactor in comparison to the parallel-plate reactors with 3 mm flow thickness (apparent rate constant $\sim 0.1\ \mathrm{s^{-1}}$) [2,9]. However, high productivity is not always associated with high energy efficiency. Microreactors are shown to have high space-time yields (STY), which refers to the productivity per unit volume. However, due to their small volumes, the overall volumetric flow rate of microreactors is low ($\mathrm{ml\ min^{-1}}$). This low throughput, when coupled with the light source technologies, which are usually designed to illuminate much larger volumes, results in waste of lighting power, thus decreasing the overall energy efficiency of the considered reactor.

This energy efficiency issue was recently addressed by Leblebici et al. by the introduction of the term photocatalytic space-time yield (PSTY) [7]. In their work on benchmarking photoreactors, Leblebici et al. emphasize the requirement of a solid method to assess the productivity and energy efficiency of different photoreactor designs.

Prior to the introduction of PSTY, two benchmarks have been widely used in the relevant literature. The first one is the apparent first-order reaction rate constant, k. It is usually expressed in terms of $\mathrm{min^{-1}}$ and gives a direct view on the conversion rate, which is quite useful when comparing different reactors with similar volumes. However, it gives no information on the throughput since it is volume-dependent. For example, a parallel-plate reactor working as a loop will give a much lower k when connected to a 10 L vessel than a 50 ml vessel although it will perform just the same since the active area does not vary. Furthermore, in some photochemical systems, the photon field is the limiting “reagent”, which results in a zero-order kinetics as evidenced by Van den Bogaert et al. [12]. This study will be elaborated in later sections. This benchmark is also light intensity- and catalyst load-dependent.

The second popular benchmark is the photonic efficiency, also known as the quantum yield, which is expressed as [2];

$$\varepsilon = z\frac{R}{\Phi} * 100 \tag{1}$$

where ε is the dimensionless photonic efficiency, R is the reaction rate ($\mathrm{mol\ L^{-1}\ s^{-1}}$), z is the amount of electrons transferred per molecule to be degraded or converted and Φ is the photon flux ($\mathrm{mol\ L^{-1}\ s^{-1}}$).

ε expresses the light utilization efficiency of the reactor. However, neither ε nor k provide information on the electrical consumption or productivity of the reactor. As an example, an annular reactor and a parallel-plate reactor may have the same photonic efficiencies [2] and/or the same k. However, the two reactors may need lamps of very different powers and may work at different throughput levels.

The simple benchmark introduced by Leblebici et al. [7] for the wastewater treatment example, is the ratio of space-time yield to the standardized electricity expenditure of lamp. STY is the measure of productivity in reactor design. It can be defined as the mass (g) of product per volume of reactor (L) per unit time (day). For the case of this work, benchmarking a batch reactor will be necessary. For this case, STY is equal to the reaction rate as shown below;

$$STY_{batch} = M_w(dc/dt) \tag{2}$$

where M_w is the molecular weight ($\mathrm{g\ mol^{-1}}$). It can be seen that the STY ($\mathrm{g\ L^{-1}\ day^{-1}}$) is a different form of benchmark than ε and k. It can, however, be derived from k by the aid of V_R. STY only gives a measure of productivity. Therefore, in order to include the lighting energy efficiency to the benchmark, it needs to be adapted. To do this, the calculated STY was divided by the lamp power. The lamp power (LP) was scaled to the value for which one unit-volume (L in this case) of the reactor would be illuminated by the following relation [7].

$$LP = P \times \frac{1\mathrm{L}}{V_R} \tag{3}$$

where LP is the standardized lamp power (kW or W), P is the lamp power of the experimental setup (kW or W) and V is the volume of the reaction medium in the experimental setup (L).

Hence, the overall photocatalytic space-time yield (PSTY) is defined as [7];

$$PSTY = \frac{STY}{LP} \tag{4}$$

The productivity of a photoreactor therefore can be assessed via the STY (mass or volume of product per time per volume of reactor) and the energy efficiency can be evaluated via the PSTY (mass or volume of product per time per unit energy input per volume of reactor).

There are four main aspects to consider, which may affect STY and PSTY in different reactor geometries and reaction schemes. These aspects are:

1. the local volumetric rate of radiative energy absorption (LVREA);
2. the outward photon flux;
3. the mechanism of the photochemical reaction;
4. the presence and physics of solids.

The STY and the PSTY are dependent on these aspects.

The LVREA is the total amount of energy absorbed via radiation at any given point in a reactor per unit time ($\mathrm{W\ m^{-3}}$). It can be given as [1];

$$LVREA_\lambda(s,t) = G_\lambda(s,t)k_{a,\lambda} \tag{5}$$

where G ($\mathrm{W\ m^{-2}}$) is the scalar incident irradiation for wavelength (λ) at any position (s) at any time (t) and k_a is the absorption coefficient in $\mathrm{m^{-1}}$ for wavelength (λ). Calculation of the $G_\lambda(s,t)$ requires the solution of the radiative transfer equation (RTE), which is further elaborated on in the modelling section of this work. The *LVREA* has a direct effect on productivity. This term can also be converted to the volumetric rate of radiative energy absorption *VREA*, which is the integrated form of *LVREA* throughout the reactor volume and it bears the term W. The *VREA* can also be converted to the rate of photon absorption via;