Exploiting two- and three phase flow for photochemical transformations: An experimental and modeling study

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Highlights

- Photon flux per liquid volume is significantly dependent on the phase distribution.
- Coupling the light transport with hydrodynamics is crucial to understand the reactor behavior.
- Three-phase flow increases sustainability by enabling photocatalyst recycling.

1. Introduction

In order to achieve climate neutrality by 2050, the European Union is expanding the renewable energy production. The surge of sustainable energy sources such as wind and solar energy opens up opportunities to electrify the chemical industry and reduce greenhouse gas emissions. These sustainable energy sources can be directly used to activate chemical transformations, e.g. for light mediated processes (photochemistry). Flow photo microreactors are a promising tool for gas-liquid photoreactions such as photooxidations and fluorinations due to their small penetration depth and the promotion of segmented flow which leads to good mass transfer of the gas in the liquid [1-3]. However, reaction condition optimization in microreactors and scale-up to milli-reactors requires an extensive parameter study [4,5]. Nevertheless, the optimal light source intensity, reagent concentration and total flow rate are determined by photon transport and hydrodynamics in the employed gas-liquid photoreactors. When these phenomena are understood at a fundamental level, the optimization and the scale-up procedure become faster and cost efficient. Three-phase flow photooxidations are a less explored area and holds great potential for different applications of process intensification. Recycling of the phases reduces energy input and cost and increases sustainability. In a multiphase reaction system, recirculating the catalyst phase keeps the catalytic activity less affected by the reaction environment. Additionally, recycling the product phase enables efficient product recovery. In this contribution two-phase gas-liquid (G/L) and three-phase gas/liquid/liquid (G/L/L) Taylor flow in a photo microreactor is characterized and critical operational parameters' effect on hydrodynamics and conversion are extracted. The experimental work is supported by ray-tracing simulations.

2. Methods

The microreactor used in this work consists of a glass plate with a serpentine channel characterized by a volume of 0.6 mL and a diameter of 1 mm (Fig. 1a)). The milli-scale reactor is a Corning Advanced-Flow G1 Photo Reactor which is composed of heart-shaped elements and is characterized by a volume of 8 mL and a channel height of 1.1 mm. Both reactors are irradiated by green Light-Emitting Diodes (LEDs). The actinometric measurements are performed in single liquid phase and in gas-liquid two-phase flows. The total flow rate is 1.3 mL/min in the microreactor and between 35 and 42 mL/min in the milli-scale reactor. Nitrogen is used as inert gas with volumetric gas transport fractions (β_G) comprised between 0.2 and 0.9 in the microreactor and between 0.2 and 0.5 in the milli-scale reactor. In addition, the obtained flow patterns were analyzed by imaging and residence time distribution (RTD) measurements. The photosensitized production of singlet oxygen ($^1O_2$), which is a model reaction for characterizing flow photo microreactors, is conducted. 1,3-diphenylisobenzofuran (DPBF) is used as a substrate, which is a trapping agent for the $^1O_2$. Rose Bengal (RB) is chosen as a photosensitizer, and O_2 is used as the gas phase. An in-house three-dimensional ray tracing model is developed and validated. This ray tracing model is used to compare the light absorption in Taylor, annular, and two bubbly flow configurations.

3. Results and discussion

It is observed that the photon flux in two-phase flow experiences an exponential increase with the gas transport fraction, resulting in 2 two-fold increase compared to single phase flow at β_G=0.9 in the microreactor, but only a minor increase at β_G=0.5 in the milli-scale reactor. These observations are explained by correlating the results of chemical actinometry to the flow pattern characteristics such as bubble, slug and film volumes. The developed model shows that the liquid volume located close to the channel wall is the determining factor, and not the light scattering or liquid mixing. These results are also corroborated by the ray tracing models, where mass transfer limitations are only observed for either low flow rates or high substrate concentrations. Advancing to three-phase flow, image analysis reveals that by changing the flow rate ratio of each phase, different patterns and unit cell configurations (Fig. 1b) in the flow could be obtained, which can be used for tuning the mass transfer between the phases. Among various flow rate ratios investigated, the highest DPBF conversion is obtained for two flow conditions that display significantly lower diffusion distance between the RB slug and the O_2 bubble. These two specific flow conditions are investigated further in detail. The influence of various operating conditions, such as total flow rate, initial concentration of DPBF and RB, and photon flux on conversion, is explored. Recycling of the two liquid phases in the G/L/L flow is simultaneously realized, and results are displayed in Fig. 1c, showing that a full DPBF conversion is reached within three hours.

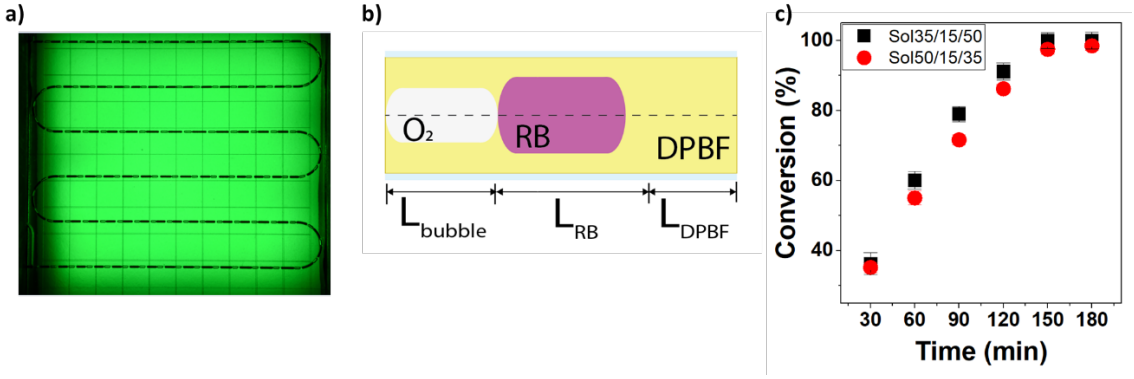

Figure 1. a) Channel configuration of the photo microreactor, **b)** Unit cell configuration of flow conditions with high conversion, and **c)** Recycling results (Sol35/15/50 shows the flow with O_2/DPBF/RB flow rate of 0.35/0.15/0.50 mL min^{-1}. Error bars represent the standard deviations of the six measurements.).

4. Conclusions

Our study shows that the influence of the phase distribution on the photoreactor performance is connected to the liquid distribution in the reactor channel. The light scattering affected solely the distance traveled by the light in the liquid phase. The simultaneous analysis of the light transport and hydrodynamics enables a rational optimization of the photoreaction conditions at different scales and the design of improved multiphase photoreactors. G/L/L flow enables a successful recycling strategy for both substrate and photosensitizer, achieving full DPBF conversion within three hours. This study highlights the potential of multiphase flow in microreactors by demonstrating their improved mass and photon transfer characteristics.

References

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Keywords

photochemistry, transport phenomena, Taylor flow, three-phase flow