Principles of co-axial illumination for photochemical reactors: Part 2. Model Validation

Glen Meir¹, M. Enis Leblebici², Simon Kuhn¹, Tom Van Gerven^{1*}

¹ KU Leuven, Department of Chemical Engineering, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

² KU Leuven Lab4U, Faculty of Industrial Engineering, Agoralaan Building B, B-3590 Diepenbeek, Belgium

*Corresponding author. Email address: tom.vangerven@kuleuven.be

Compliance with ethics guidelines

Glen Meir, Mumin Enis Leblebici, Simon Kuhn, and Tom Van Gerven declare that they have no conflict of interest or financial conflicts to disclose.

ABSTRACT

This study reports the principles and model equations for co- and counter-current illumination, validated by experimental data. Current photochemical reactors which are homogeneously illuminated suffer from a light efficiency problem resulting in low light absorption and subsequent low productivity. Hence the use of co- and counter-current illuminated reactors, implementing larger path lengths, without altering the reactor's geometry, is of interest. In this paper, we report a simple model to determine the conversion obtained by co- and counter-current illumination techniques and compare against the current state-of-the-art. Via experimental validation, we report the use of co- and counter-current illumination to significantly boost the PSTY, a measure for photochemical reactor productivity, by a factor of 5 - 6 for same input concentration of reagent, solely by illuminating the reactor via co- and counter-current axially instead of cross-current. Furthermore, we report that simply increasing the reagent concentration, thus absorbance, has a large influence on productivity, thus PSTY, of the reactor. By assessing the

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record. Please cite this article as doi: 10.1002/amp2.10045

reactor's performance parameters, derived by modelling, which are the initial absorbance value (A) and the quantum photon balance ($\rho\phi$), the reactor's operating point can be determined and adapted to operate in a more productive and efficient regime.

Key words: photochemistry, photoreactors, cross-current, co-current, counter-current, co-axial illumination, model validation, photochemical reactor design

1 Introduction

Photochemistry is one of the more promising routes^{1,2} for a sustainable chemical production, however, energy efficiency is still lacking with respect to industrial competitiveness³ of this process. The state-of-the-art photochemical reactors are operated using homogeneous illumination⁴, resulting in two problems. The first is an energy efficiency problem, and the second is the creation of dark zones⁵ at higher absorbance values as has been described by Meir et al.⁶

Meir et al. described the use of co- and counter-current illumination (co-axial illumination) as a solution to these two problems in which the light source is placed in line with the flow of the reagent. By design of this novel illumination technique, unwanted dark zones are eliminated combined with an increase in light absorbance. Using co-axial illumination, significant improvements in PSTY (photochemical space time yield) were proven by the use of theoretical models for both the plug flow and laminar flow regime.⁶

In this work, the validation of these novel illumination models is performed as well as the experimental comparison of the state-of-the-art photoreactor design and the novel illumination techniques. In the first step, the received light flux of the reactor's LEDs is measured via spectrometry and validated via actinometry using the isomerization of azobenzene⁷⁻⁹. In the second step, the conversion of 2-chloroacetophenone is used as a model reaction for a non-competitive, non-reversible photochemical reaction.¹⁰

Photochemical reactor model

The equations modelling the energy efficiency and the performance of cross-, co- and counter-current illuminated reactors were derived earlier by Meir et al.⁶ These equations use simplification assumptions. In terms of the cross-, co- and counter-current light source, the models assume it to be collimated and have a homogeneous intensity along its irradiated surface. The LEDs or non-ideal light sources can be modelled by the implemented spectral distribution.

The use of an average quantum yield (ϕ_{avg}) and average specific absorbance (ε_{avg}), as shown in Part 1 of this study⁶, significantly simplifies these models without losing accuracy. In Part 2 of the paper and in the parameter study of Part 1, competitive absorption of light is not considered as the reagent is the only light-absorbing component in this reaction set-up. In terms of flow regime, the residence time distribution (RTD) is implemented for each of the illumination techniques. In total three situations will be considered in the comparison of experimental data to the model: plug flow, laminar flow and a measured RTD curve which represents the flow in the reactor using experimental tracer data. This leads to the following simplified equations, as shown in Table 1, that will be validated in this work, these equations are the ones for which a parameter study was done by Meir et al.⁶

Table 1: Simplified equations to model cross-, co- and counter-current illumination which will be used in this work. The equations include complex flow regimes via residence time distribution (in red), with initial conditions (I.C.).⁶

X [–] the conversion, ι [–] the dimensionless light fraction with respect to incident light flux, ϕ [mol einstein⁻¹] the quantum yield, ρ [einstein mol⁻¹] the photon balance, θ [–] the normalized residence time, A [–] the absorbance, ζ [–] the normalized axial reactor coordinate, and $E(\theta)$ [–] residence time distribution. Note that (ζ) signifies a dependency regarding the axial coordinate of the reactor and is placed between brackets after the respective parameter. The index A refers to the reagent species.

2 Material and Methods

In order to validate the model, a reactor and different light sources were designed and a chemical model reaction was selected. A series of parameters have to be determined beforehand to accurately make a model prediction. The first parameter is the average quantum yield (ϕ_{avg}), which is determined via

degradation of the reagent (2-chloroacetophenone) in batch by using a calibrated light source and a known reagent absorbance. The second parameter is the photon balance ($\rho = \frac{q_0}{Qc_0}$) from which the received light flux (q_0) is determined via a ray tracing model which is calibrated using spectrometric measurements and validated by actinometry. The third parameter is the absorbance of the reagent ($A = \epsilon c_0 \ell$). Herein the specific absorbance (ϵ) is determined via UV-Vis spectrometry. The average path length (ℓ) is determined via ray tracing for cross-current illumination and the length of the reactor is used for co- and counter-current illumination. The last parameter is the RTD of the reactor, this is determined via pulse injection of acetone in aqueous medium and calculated via the procedure shown in Supplementary information S7.

2.1 Reactor design

The reactor for this validation of the model aims to provide radial mixing as much as possible at the typical low Re-numbers in photochemical reactors. A chaotic mixing regime is selected by the configuration of the reactor. The reactor configuration and behaviour of chaotic mixing is well described by Fonte et al and includes a tubular design with injectors.^{11–18} The dimensions and geometry are described below and presented in Figure 1. The diameter of the main tube (11.3 mm) in relation to the diameter of the injectors (1.59 mm) is selected based on sources for optimal mixing^{12,13,15,16}. The reactor length is 165 mm long to accommodate the cross-current light source, longer than described in the cited literature. As it is longer, it is expected that chaotic mixing only occurs at the inlet and it gradually transitions to laminar flow towards the outlet^{11,15,16}. The reactor has an internal volume of 16.34 mL and is made out of aluminium blocks and a borosilicate tube to facilitate reproducible alignment of the injectors and the light sources. In Figure 1, a graphical presentation is shown of the reactor and light sources.

Figure 1: Graphical presentation of the experimental setup, with the reactor tube (1) in borosilicate glass held between two aluminum support pieces (2). The reactor is illuminated radially by a series of 10 LEDs for cross-current illumination, mounted to a heat sink (3), and illuminated axially by an LED mounted to a bigger heat sink (4).

2.2 Light sources

Two light sources will be used; one for cross-current (state of art) and one for co-axial illumination. For cross-current, a series of 10 high power LEDs (type CUN66B1B, 365 nm, 1000 mW, Roithner Lasertechnik, Vienna, Austria) are selected. The typical spatial and wavelength distribution is found in S1. These LEDs are mounted to a PCB and heat sink at 1 cm intervals for even illumination of the reactor tube. The LEDs can be controlled individually via a controller board to set the current per LED between 0 – 500 mA. A schematics of the connections is found in Supplementary information S2.

For co-axial illumination, a collimated LED, provided by Mightex (type LCS-0365-48-11, 365 nm, 50 W, Mightex, Pleasanton, USA) was used. The LED has an operating range of 0 – 12 A and provides up to 4 W of collimated optical output at a diameter of 11 mm. The LED is driven by a current and voltage controlled power supply (RND 320-KA3005P, Reichelt) and monitored via a multimeter (UT71C, uni-T). A typical wavelength distribution of the LEDs is found in S1. This normalized distribution is later used to determine the average specific absorbance (ϵ_{avg}) of the reagent using the strategy as explained by Roibu et al.¹⁹ and Meir et al.⁶ for λ [330 400] nm. The normalized version of the spectral irradiance of the light sources is shown in S1 and is used to determine $g(\lambda)$. The specific absorbance ($\epsilon(\lambda)$) of the components is shown in S4, which is used to determine ϵ_{avg} .

2.3 Determination of received light flux in reactor

2.3.1 Spectrometric method

A portable spectrometer of type QE65 Pro by Ocean Optics (Duiven, The Netherlands) is used to determine the emitted light flux of the utilized LEDs. The co-axial LEDs light flux is determined by averaging 300 measurements at a set distance from the light source.

The cross-current LEDs are characterized by their intensity vs. viewing angle and intensity vs. current profiles. Both were measured with the same spectrometer as specified above. The intensity vs. current profile serves as the reference of the LEDs response of current and is used to scale the total light flux. The

total light flux is determined via a numerical model in COMSOL 5.4 which utilizes the measured intensity vs. viewing angle profile. The model utilizes a ray tracing algorithm to determine the received light flux in the reactor channel. The details of this model are found in Supplementary information S1.1.

2.3.2 Actinometric validation

Actinometry is utilized to validate the spectrometric method of calibrating the LED output. Azobenzene in methanol is used as actinometer, the photo-isomerization reaction is the following:

Herein, azobenzene photo-isomerizes from its trans- (E) to cis- (Z) state via absorption of UV-radiation and undergoes a reverse reaction from its cis- to trans-state via absorption of UV-radiation as well as thermal energy. However, the latter is significantly slower compared to the isomerization via absorption of UV-light and can be omitted as the samples are measured immediately after production.⁷

The actinometric method used in this work is based on the model of Achi et al.⁷ and the measuring technique is based on the technique employed by Gauglitz and Hubig⁸, quantum yield values are reported by Gauglitz and Hubig⁸ and absorbance values for cis-azobenzene are reported by Vetrakova et al.²⁰. This actinometer is used for cross- and co-current illumination validation. The method utilizes azobenzene (98%, VWR, Geel, Belgium) dissolved in methanol (Chromasolv 99.9%, Sigma Aldrich, Diegem, Belgium) at various concentrations that are pumped through the reactor and illuminated via either cross- or co-current illumination. Samples are taken at the reactor outlet at a stable flow regime and diluted by weight as necessary.

The concentration of trans-azobenzene is determined by UV-VIS at 358 nm. This wavelength is chosen as it was reported as optimal by Gauglitz and Hubig⁸ and later shown by Vetráková et al.²⁰ that the $\frac{\epsilon_{trans}}{\epsilon_{cis}} \gg 22$ at 358nm, hereby the absorbance of cis-azobenzene is minimal, although it will not be neglected in this work. The concentration is determined by the following formula:

$$A_{meas} = A_{trans} + A_{cis} \quad (2)$$

$$A_{meas} = \varepsilon_{trans} c_{trans} \ell + \varepsilon_{cis} (c_0 - c_{trans}) \ell$$

$$c_{trans} = \frac{A_{meas} - \varepsilon_{cis} c_0 \ell}{\varepsilon_{trans} \ell - \varepsilon_{cis} \ell}$$

In practice, a calibration line is used to convert A_{trans} to its concentration, with b the intercept of the calibration line.

$$A_{meas} = \varepsilon_{trans} c_{trans} \ell + b + \varepsilon_{cis} (c_0 - c_{trans}) \ell \quad (3)$$

$$c_{trans} = \frac{A_{meas} - \varepsilon_{cis} c_0 \ell - b}{\varepsilon_{trans} \ell - \varepsilon_{cis} \ell}$$

The calibration line is shown in S3.4, the specific absorbance value of $\varepsilon_{cis} = 73 \pm 13 [\text{M}^{-1} \cdot \text{cm}^{-1}]$ is used.²⁰ Once the concentration of trans-azobenzene is known, the received light flux is calculated based upon the obtained conversion. Two different models will be utilized, for cross- and co-current respectively. For cross-current, the model starts from a photochemical reaction that is reversible, with the starting equation being the following, based on^{7,21,22} and building further on the work of Meir et al.⁶:

$$\begin{aligned} \frac{dc_E}{d\tau} = & -\phi_E(\lambda) \frac{q_0(\lambda)}{V} \frac{\varepsilon_E(\lambda) c_E}{\varepsilon_E(\lambda) c_E + \varepsilon_Z(\lambda) c_Z} (1 - 10^{-(\varepsilon_E(\lambda) c_E + \varepsilon_Z(\lambda) c_Z) dx}) \\ & + \phi_Z(\lambda) \frac{q_0(\lambda)}{V} \frac{\varepsilon_Z(\lambda) c_Z}{\varepsilon_E(\lambda) c_E + \varepsilon_Z(\lambda) c_Z} (1 - 10^{-(\varepsilon_E(\lambda) c_E + \varepsilon_Z(\lambda) c_Z) dx}) \end{aligned} \quad (4)$$

With τ the average residence time, $\phi_E(\lambda)$ the quantum yield of the forward reaction ($E \xrightarrow{h\nu} Z$), $q_0(\lambda)$ the light flux received by the reactor, V the reactor volume, $\varepsilon_E(\lambda)$ the specific absorbance of component E – azobenzene, c_E the concentration of E – azobenzene as function of time. Parameters with index Z are linked to Z – azobezene (cis-azobenzene).

After grouping dimensionless terms and rearrangement of terms, the following equation is derived for cross-current with homogeneous illumination and $\iota(0, \lambda) = 1$. Intermediate steps are found in S3. This

equation is solved with initial reagent fraction $X'(0) = 1$ and initial light flux $\iota(0, \lambda) = 1$. Note that for homogeneous illumination the incident light flux equals 1 at all times, $\iota(\zeta, \lambda) = 1$.

$$\frac{dX'(\zeta)}{d\zeta} = \iota(\zeta, \lambda) \rho(\lambda) \frac{\phi_E(\lambda)}{X'(\zeta) + \beta(\lambda)(1 - X'(\zeta))} \left(1 - 10^{-A_E(\lambda)(X'(\zeta) + \beta(\lambda)(1 - X'(\zeta)))} \right) (-X'(\zeta) + \alpha(\lambda)\beta(\lambda)(1 - X'(\zeta))) \quad (5)$$

Hence, the use of $X'(\zeta)$ indicating the fraction of reagent (E-azobenzene). Note the similarity compared to the equations in Table 1 and Part 1 of this study⁶. The only newly introduced terms are $\alpha(\lambda)$ and $\beta(\lambda)$. $\alpha(\lambda)$ ($= \frac{\phi_Z(\lambda)}{\phi_E(\lambda)}$) is the relative reverse quantum yield and $\beta(\lambda)$ ($= \frac{A_Z(\lambda)}{A_E(\lambda)}$) is the relative reverse absorbance. The other non-dimensional parameters, $\rho(\lambda)$, $\phi(\lambda)$ and $A(\lambda)$, have the same meaning as the equations which were previously introduced.

For co-axial illumination, a similar set of equations is obtained yielding the same parameters, hereby the same steps are performed as used in the article by Meir et al.⁶:

$$\frac{dX'(\zeta)}{d\zeta} = \iota(\zeta, \lambda) \rho(\lambda) \phi_E(\lambda) \ln(10) A_E(\lambda) (-X'(\zeta) + \alpha(\lambda)\beta(\lambda)(1 - X'(\zeta))) \quad (6)$$

$$\frac{d\iota(\zeta, \lambda)}{d\zeta} = \pm \iota(\zeta, \lambda) \ln(10) A_E(\lambda) (X'(\zeta) + \beta(\lambda)(1 - X'(\zeta))) \quad (7)$$

With a plus-sign in Equation (7) for counter-current and a minus-sign for co-current. These equations are solved with $X'(0) = 1$ and $\iota(0, \lambda) = 1$ for co-current and $X'(0) = 1$ and $\iota(1, \lambda) = 1$ for counter-current. Note that $\alpha(\lambda)$ and $\beta(\lambda)$ are in effect wavelength dependent. Since the quantum yield (part of $\alpha(\lambda)$) and the dependency on the wavelength is well determined in literature, this α_{avg} value is easily calculated for the average wavelength spectrum as shown in Part 1 of this study⁶ via the same procedure as ε_{avg} . The average specific absorbance of trans-azobenzene is determined via UV-Vis spectrometry. However, this is not possible for the average specific absorbance of cis-azobenzene, even literature spectra are absent to perform this calculation well. Therefore, this value is determined via illumination until an equilibrium is reached in a batch reactor, similar to the method established by Achi et al.⁷. The derivation and obtained

β_{avg} value are found in Supporting information S3.5. These two simplifications make it possible to use a single ρ_{avg} value, independent of wavelength, taking into account the total incident light flux expressed in [einstein s^{-1}].

These equations are solved for ζ [0 – 1] and a ρ value is determined via the ‘fsolve’ algorithm for each individually measured data point and model output via MATLAB 2019 until convergence is achieved. Via this algorithm, the difference between $(X'_{e,model} - X'_{e,measurement})$ is minimised using ρ as a fitting factor. Note that $X'_{e,model}$ is determined via a simple ode45 solver as used by Meir et al in part 1 of this paper.⁶ The average of all calculated ρ values is used to calculate the received light flux in the reactor, which makes it possible to report a standard deviation. Alternatively ‘lsqnonlin’ could be used to fit the best fitting ρ value on the set of measurements. The fit between model and experimental results is shown in S3.5.

2.4 Photochemical reaction and analytical methods

The model reaction that is used in this report is the synthesis of phenylacetic acid from 2-chloroacetophenone via a photo-favorskii rearrangement, based on the work of Baumann and Baxendale¹⁰. The reaction is shown below. The solvent that is used is 90 vol% acetone (Chromasolv 99.9%, Sigma Aldrich, Diegem, Belgium) / 10 vol% ultrapure water (18.2 M Ω , Sartorius Arium pro, Göttingen, Germany) to which 2 vol% propylene oxide (99%, Sigma Aldrich, Diegem, Belgium) is added as scavenger for the released HCl to avoid consecutive reaction leading to side products.

Figure 2: Synthesis of phenylacetic acid from 2-chloroacetophenone via a photo-favorskii rearrangement, after¹⁰
The yield of phenylacetic acid was reported by Baumann and Baxendale¹⁰, however conversion was lacking but expected to be >95% based on other experiments in the paper. Their optimized conditions consisted of a concentration of 0.100 M 2-chloroacetophenone and 2 vol% propylene oxide at 65°C to achieve 84% yield for a similar reaction. The reaction was carried out in a 10 mL reactor, with a lamp

source set at 120 W and a residence time of 20 minutes to yield a PSTY of 0.025 [$\text{mol h}^{-1} \text{kW}^{-1}$] or 0.00227 [–]. Dhavale et al.²³ report a yield of only 24% phenylacetic acid, 37% acetophenone and 29% 1,4-diphenylbutane-1,4-dione by photolysis of 2% 2-chloroacetophenone and a conversion of 90% using a residence time of 4 h irradiated by 300 nm lamps in a Rayonet RPR 208 photoreactor at room temperature with insufficient data to determine the PSTY.

2-Chloroacetophenone (98%, Sigma Aldrich, Diegem, Belgium), phenylacetic acid (99%, Sigma Aldrich, Diegem, Belgium) and acetophenone (99%, Across Organics, Geel, Belgium) are used for calibration, dissolved in 90% acetone (Chromasolv 99.9%, Sigma Aldrich, Diegem, Belgium) / 10% ultrapure water (18.2 M Ω , Sartorius Arium pro, Göttingen, Germany). Furthermore, the absorbance of all components is measured by UV-VIS (Lambda 365, Perkin Elmer) and shown in S4 using acetonitrile (Chromasolv 99.9%, Fisher Scientific, Merelbeke, Belgium) as solvent with in Table 2 the average specific absorbance values for the different chemicals as used in the model equations and determined as shown in Part 1 of this study⁶. The UV-spectrum of 2-chloroacetophenone with the superimposed LED spectrums is shown in Figure 3.

Figure 3: UV absorbance spectrum of 2-chloroacetophenone measured in acetonitrile (orange) via Lambda 365 (Perkin Elmer). Normalized intensity distribution of cross-current LEDs (by Roithner, green) and the co-axial LED (by Mightex, blue).

Table 2: Specific absorbance values of reagent, product and one of the expected side-products in the wavelength range emitted by the co-and cross-current LEDs. These values are different for each LED, due to the slightly different spectral distribution.

In this paper, room temperature will be employed, contrary to the conditions (65°C) as applied by Baumann and Baxendale¹⁰ due to physical limitations of the reactor. This change in temperature results in a reduction in selectivity. However, our goal is to use the reaction to validate the model in terms of conversion of the reagent. For this model validation, it is important that the reaction can be performed reproducibly for accurate measurements which is easier at room temperature. In this paper, we are

demonstrating the applicability and reproducibility of the novel illumination technique rather than achieving high selectivity and yield. Achieving higher selectivity can be done later via optimisation of the chemistry. The latter can be achieved by setting an optimum temperature and e.g. manipulation of the solvent as described in literature.^{10,23}

2.5 Determination of quantum yield

To determine the quantum yield of the reaction, a cube-size batch reactor (borosilicate, $4 \times 4 \times 4$ cm) is used. To this reactor, 60 mL of 10 mM 2-chloroacetophenone with 2 v% propylene oxide in 90/10 v% acetone/water is added. The reactor is stirred at the highest possible speed without creation of a vortex using a magnetic stirrer and illuminated using the collimated co-axial LED from which the light flux is determined via a spectrometer and verified by actinometry for which the method is described in Section 2.3.2. Samples are taken after a known illumination time and analysed via HPLC analysis. It is important to note that the path length is constant at 4 cm and all incident light passes through the reactor's solution.

2.6 Continuous experiments

Continuous experiments regarding validation of the models as mentioned in Section 0 are performed using the setup that contains the reactor described in Section 2.1, using cross-current LEDs and the co-axial LED as described in Section 2.2 in conjunction with a membrane pump (SIMDOS 02, KNF). Two kinds of experiments are performed; cross-current illumination and co-axial illumination (co- and counter-current). A schematic of the set-up regarding both illumination schemes is shown in Figure 1. Note that the distance between the lens of the LED and the outer diameter of the tube is set to 2 mm to avoid accidental deformation of the silicone LED lens. Furthermore, the co-axial LED is centred with respect to inlet window for reproducibility.

The general procedure for the continuous experiments is to pump the reagent feed through the reactor with the light source set to the correct intensity and have it run for at least three residence times to obtain a stable regime. After three residence times, a sample is taken in a vial and immediately capped to avoid

evaporation of the solvent, a second sample is taken one residence time later. The samples are stored in a fridge at 4°C prior to analysis via HPLC. Afterwards the flow rate of the pump is checked.

The flow rate used in these experiments for 10 mM 2-chloroacetophenone is set to 10 mL.min⁻¹, for experiments using 25 mM 2-chloroacetophenone this value is set to 4 mL.min⁻¹. The light flux is adapted to yield corresponding $\rho\phi$ -values as required for the experiment. For cross-current operation, experiments at higher $\rho\phi$ values are performed using constant (maximum light flux) and reduced flow rate; [7 – 1.4 mL.min⁻¹] for 10 mM experiments and [2.8 – 0.58 mL.min⁻¹] for 25 mM experiments.

2.7 HPLC analysis

Samples obtained via batch or continuous experiments are analysed by HPLC (1200 series, Agilent) using a Luna C18(2) column (5 µm particles, 100 Å pores, 4.6 mm diameter, 250 mm length) from Phenomenex (Utrecht, Netherlands). 0.1 vol% H₃PO₄ (85%, Janssen Pharmaceutica, Geel, Belgium) in ultrapure water and acetonitrile (Fisher Scientific, Merelbeke, Belgium) is used for gradient elution. The applied gradient is shown in Supplementary information S5. The detector is a diode array (1200 series, Agilent) set to measure the absorbance signal at 210, 240, 245 and 280 nm for the quantification of the reagent, product and side-product. The calibration lines are found in S5.

3 Results and Discussion

The main goal is to validate the derived models as shown by Meir et al.⁶ using the conversion of 2-chloroacetophenone. In these models, the light flux reaching the reactor, flow rate, absorbance and input concentration of feed are important variables which have to be known in advance. The method of determining these parameters is given in the previous section.

3.1 Calibration of the light sources

3.1.1 Cross-current

In order to accurately determine the received photon flux in the reactor channel, a combination of spectrometric analysis and ray tracing is utilized. Firstly, from a representative LED of the series of 10 LEDs, the total integrated emitted intensity [W m^{-2}] of the LED is measured at a known distance with respect to the current [A] driving the LED. This graph is shown in Supplementary information S1 and forms the backbone of the calibration curve as it describes the response of the LED with respect to input current. Secondly, the intensity of the LED was measured using the spectrometer at a viewing angle of -45° to $+45^\circ$ relative to the centre of the LED at a fixed normal distance, this is displayed in Supplementary information S1 along with the validation of COMSOL results and a sketch of the experimental procedure and geometry. This measurement is used to calibrate the results acquired via COMSOL v5.4. Thirdly, a ray tracing simulation using a model in COMSOL v5.4 is utilized in order to determine the received photon flux at the reactor's surface for a specific input current of the LED. This measurement is used to scale the intensity vs. input current (in S1) to received photon flux vs. input current of the LED (as shown in Figure 4). A scheme of the setup constructed in COMSOL v5.4 is displayed in S1.

The obtained result is verified using azobenzene (2.5 mM) in methanol as actinometer at three input currents. The method is described in Section 2.3.2. The results are shown in Figure 4.

Figure 4: Cross-current LEDs calibration per LED. The diamonds indicate the total light flux emitted by the LED, the circles indicate the received light flux in the reactor (OD 15 mm, ID 11 mm, borosilicate) with a distance of 2 mm between LEDs and reactor. The triangles indicate the validation of the simulation data by actinometry, two replicates are performed.

This method of calibration is not only easier, but also more accurate than the regular method, which only employs the use of an actinometer and has typical error margins of around 10%.^{7,24,25} In this case, due to the use of spectrometric methods to determine the received photon flux, the margin of error is reduced significantly.

3.1.2 Co- and Counter-current

The output of the co-axial LED is calibrated using spectrometry as described before in Section 2.3. However, not all light emitted by the light source passes the inlet window of the reactor as some light is stopped by the reduced aperture (due to construction of the reactor) and some is reflected due to Fresnel reflection. This results in a fraction of the calibrated light flux (total emitted light flux) that can enter the reactor. Using co-current actinometry, this fraction is determined and the curve is rescaled to the light flux that is received in the reactor. The results of this actinometry calibration are shown in Figure 5.

Figure 5: Coaxial LED calibration. The circles indicate the total light flux emitted by the LED, the triangles indicate the received light flux in the reactor with an aperture of 11 mm. The triangles indicate the received light flux, determined by a scaling factor via actinometry. The diamonds are the actinometry results used to scale down the total emitted light flux to the absorbed light flux due to reflection and reduction in aperture.

3.2 Determination of quantum yield

To the best of our knowledge, the quantum yield of this reaction has not been determined before. In order to do so, a batch reactor with a known optical path length of 4 cm is utilized. This enables the calculation of the quantum yield for each separate measurement point, using the well-established photochemical reaction rate equation, reported^{19,26} as:

$$\phi_A = \frac{\ln[(10^{A_A(0)} - 1)/(10^{A_A(t)} - 1)]}{\ln(10) \frac{A_A(0)}{c_{A,0}V} q_0 t} \quad (8)$$

With ϕ_A [mol einstein⁻¹] the quantum yield of the reaction, A_A [–] the average absorbance of the reagent at time 0 and time t , $c_{A,0}$ [mol m⁻³] the initial concentration, V [m³] the reactor volume, q_0 [mol s⁻¹] the incident light flux, t [s] the reaction time. Note that average absorbance and quantum yield is used, thereby removing the dependency on the wavelength. The degradation of 60 mL 10 mM 2-chloroacetophenone is shown in Figure 6 (left). On the same figure (right), the selectivity for phenylacetic acid (product) as well as the quantum yield determined by Equation (8), are shown. It must be noted that the quantum yield of the reaction is relatively stable as function of time, thus conversion, as is the

selectivity of the product for the conversion of 10 mM of 2-chloroacetophenone. This makes it an ideal candidate for the validation of the different models, each with a different illumination technique. The average quantum yield, determined by the data from 2 min and onwards is equal to:

$$\phi = 0.364 \pm 0.022 \quad (9)$$

This value is used to determine the fit between experimental data for batch degradation as represented in Figure 6 (left). Furthermore, the selectivity for the product (phenylacetic acid, PA) is also determined based on the degradation in batch starting from 2 min.

$$S_{PA} = 0.190 \pm 0.008 \quad (10)$$

This value is within the same range of the work by Dhavale et al.²³, as they obtained a selectivity value of 0.24 for this specific reaction in aqueous acetone using propylene oxide as HCl scavenger.

Figure 6: Conversion of 10 mM 2-chloroacetophenone in a 60 mL batch reactor with a path length of 4 cm (a), the model fit is based on the average quantum yield ($\phi = 0.364 \pm 0.022$) as determined by the experiments. Selectivity towards product (phenylacetic acid) and quantum yield of the reaction for the batch degradation of 2-chloroacetophenone is calculated based on conversion (b).

The quantum yield is also determined for a starting concentration of 25 mM as the quantum yield cannot be assumed to be constant as the relative concentration of scavenger varies. This HCl scavenger (propylene oxide) is kept constant at 2 vol% since it is considered sufficient by literature¹⁰. The results are presented in Figure 7.

Figure 7: Conversion of 25 mM 2-chloroacetophenone in a 60 mL batch reactor with a path length of 4 cm (a), the model fit is based on the average quantum yield ($\phi = 0.275 \pm 0.021$) as determined by the experiments. Selectivity towards product (phenylacetic acid) and quantum yield of the reaction for the batch degradation of 2-chloroacetophenone are based on the measured conversion (b).

From Figure 7, it can be observed that the quantum yield is not stable in time and thus with conversion. At high conversion (> 0.7), deviations from the model start to occur, combined with decreasing quantum yield. This deviation can be related to an absorptive peak at 365 nm (irradiation wavelength) that was observed at higher conversions via HPLC analysis. The nature of this compound is unknown, but its influence on the model fit and conversion is present in Figure 7. One must note the difference in model fit between 10 mM and 25 mM. At 10 mM and 25 mM, the absorbance in the reactor is equal to 0.22 and

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0.56 respectively. These values indicate that the competitiveness for light is slightly more pronounced at higher absorbance, thus higher concentration. Furthermore, the more of this unwanted product is formed, the higher its absorbance and competition for light in the reactor. This also has an influence on the continuous experiments. However, continuous experiments also show that this cannot only be related to competitive absorbance. It is known that selectivity at higher concentrations starts to decrease as its concentration effects are not negligible, especially for the case of cross-current operation since absorbance is a factor 4 lower compared to batch. Baumann and Baxendale also reported the reduced selectivity towards the product when increasing the reagent concentration.¹⁰

For 25 mM starting concentration, the quantum yield and selectivity for the product based on the data between 3 and 20 min and 3 and 30 min, respectively, can therefore be given as;

$$\phi = 0.275 \pm 0.021 \quad (11)$$

$$S_{PA} = 0.217 \pm 0.023$$

3.3 Validation of the models

Using the aforementioned quantum yields ϕ , all required data to calculate the models is now collected in order to evaluate them and compare to experiments. These models only require the quantum yield of the reaction as ‘fitting parameter’, which is determined in section 3.2. The remainder of the parameters include the absorbance of the solution (determined by UV-Vis), flow rate, light intensity and initial concentration which are measured, and thus not fitted to any data.

Model validation was performed using two initial concentrations of reagent. A lower concentration (10 mM) solution of 2-chloroacetophenone is used to start with, as this chemistry yields a constant quantum yield which is assumed in this photochemical reaction model, and by extension most models. Afterwards, the performance of the model is assessed using the higher concentration (25 mM) solution to check if the predictions are accurate in higher concentration (thus absorbance) regions.

3.3.1 Low concentration (10 mM) experiments

For the low concentration (10 mM) experiments, the initial absorbance values of the reagent in the reactor are equal to 0.0742 and 0.906 for cross-current and co-axial illumination, respectively. In terms of model data, the best fitting is shown in this section, the remainder of the model data and experimental comparison is shown in Supporting information S6. The RTD data of the reactor is used for a Re-number of 100 calculated for the injectors of the reactor by using acetone as pulse tracer and measured by inline UV-VIS. This data is presented in Supporting information S7. Even at lower Re-numbers the curve does not change significantly.

Cross-current

For cross-current, which is the current state-of-the-art, experiments are performed using the reactor setup and a series of 10 LEDs (with respective calibration curve) mounted to a heatsink as described in Section 2.1 & 2.2 respectively.

Two series of experiments are performed. The first (indicated in blue in Figure 8) uses constant flow rate to keep mixing constant, therefore the flow rate is set to 10 mL min^{-1} and light intensity is varied to acquire $\rho\phi$ – values between 0 – 3.5. The second series aimed to obtain higher $\rho\phi$ – values and thus conversion X . For that, the flow rate is decreased to 1.4 mL min^{-1} while fixing q_0 to acquire ~95% conversion. This dataset is indicated in Figure 8 using blue diamonds. Modelling data (using the RTD) is plotted with red crosses.

Figure 8: Validation of cross-current model (using RTD data, red) to predict conversion by photochemical reactor using a series of cross-current LEDs and experimental data (blue) for variation of flow rate (Q , $10 - 1.4 \text{ mL min}^{-1}$, in blue diamonds) and light flux (q_0 , $1.9 - 16 \times 10^{-6} \text{ einstein s}^{-1}$, in blue circles) for a concentration of 10 mM 2-chloroacetophenone.

Figure 8 shows a good agreement between the cross-current model and experimental data based on conversion. The average deviation between experiments and model is $0 \pm 2\%$, indicating good agreement.. The best fit was obtained by incorporating the RTD curve in the model. When using laminar

flow the conversion was underestimated and when assuming plug flow it was overestimated, as shown in Supplementary information S6. It is important to note that the data obtained by variation of flow rate or by variation of incident light flux match the model results accurately in this range containing flow rates of $10 - 1.4 \text{ mL min}^{-1}$ and incident light fluxes between $1.9 - 16 \times 10^{-6} \text{ einstein s}^{-1}$ ($0.59 - 5.36 \text{ W incident (optical)}$), which is already towards the high optical regime and is thus more interesting regarding upscaling of the reactor. Note that for the large light fluxes, also lower flow rates are used to yield high conversion.

It must also be noted that in order to obtain 95% conversion, a $\rho\phi$ value of 25 is required as predicted by the model and validated by experimental data. This value implies that 25 times more light has to reach the reactor than reagent, this is true due to the low absorbance of the reagent which is only 0.0734. In this work, a large (11 mm) path length was used which increased the absorbance, however in the experiments of Baumann and Baxendale¹⁰ smaller tubular commercial photochemical reactors are used. A quick estimation based on the applied concentration (100 mM) and tube size (Vapourtec reactor, FEP <1 mm ID) in their case indicates an absorbance that is even lower than used in our experiment and subsequently lower energy efficiency. For this specific reaction, using such small reactors sizes is unfavourable in terms of energy efficiency.

Coaxial-illumination

For co-current, which is one of the novel illumination techniques discussed in this work, the light is introduced axially, which in the same direction as the flow of reagent. Herein, the flow rate is kept at 10 mL min^{-1} , the same as for cross-current. The incident light flux is between $2 - 12.6 \times 10^{-6} \text{ einstein s}^{-1}$ ($0.65 - 4.12 \text{ W optical}$), comparable to the cross-current experiments. Note that the outside of the reactor tube is covered in aluminium foil to reflect all light rays inwards, except for the outlet window. This is assumed in the model and should in theory occur via total internal reflection at the glass-air interface, but some light losses were observed without the coating. The results of this experiment using the coating are shown in Figure 9a and b.

Figure 9: Validation of co-current model (using laminar flow, crosses, (a)) and counter-current (using laminar flow, crosses, (b)) to predict conversion by photochemical reactor using a collimated co-axial LED at a constant flow rate (10 mL min^{-1}) and variable light flux ($1.3 - 8.3 \times 10^{-6} \text{ einstein s}^{-1}$) for a concentration of 10 mM 2-chloroacetophenone.

The average deviation between experiments and model is $1 \pm 2\%$ -point for co-current, indicating good agreement as shown in Figure 9a. It must be noted that since the light flux and axis of flow is the same, a residence time distribution physically does not make sense any more to implement since the degree of radial homogeneity is not uniform throughout the axial direction of the reactor.

Comparing Figure 9 to Figure 8 shows that for a conversion of $\sim 82\%$, only a $\rho\phi$ -value of 1.77 is required for co-current versus 10.2 for cross-current. This novel technique of axial illumination thus appears to be significantly more efficient and productive ($6 \times$) as compared to the state-of-the-art.

For counter-current, similar results are obtained as compared to co-current. Herein, the same flow rate of 10 mL min^{-1} is applied and an incident light flux between $2 - 12.6 \times 10^{-6} \text{ einstein s}^{-1}$ is used for the experimental data as found in Figure 9b.

The data in Figure 9b shows good agreement between experimental data and the counter-current model calculated using a laminar flow distribution, which is the same model as used in co-current. The average deviation between model and experimental results is $-2 \pm 2\%$ -point. The same conclusions as for co-current also apply here. For counter-current slightly higher conversions are achieved as the light goes from outlet of the reactor to inlet with the highest concentration of reagent at the inlet, acting as a ‘light sweeper’. This ‘light sweeper’ is capable to absorb slightly more light as compared with co-current. Furthermore, a significant increase in efficiency is observed when comparing counter-current to the state-of-the-art, i.e. cross-current. Via the novel technique, a ca. $6 \times$ increase in conversion is observed for the same light input, i.e. $\rho\phi$ value.

At this absorbance (and concentration range) a good fit is obtained between all models and experimental data, showing that the novel illumination technique obtains significantly increased conversion for the same incident light flux.

3.3.2 High concentration (25mM) experiments

Validation of the model is also assessed at higher concentration, i.e. 25 mM of 2-chloroacetophenone. This input concentration results in the following initial absorbance values in the reactor: 0.185 and 2.26 for cross-current and coaxial illumination, respectively.

Furthermore, any competitive absorbance of side-products as shown in the batch results will significantly influence obtained conversion as competition for light is more pronounced for higher absorbance values. The observed effects are in fact also linked to concentration effects as explained before.

Cross-current

For 25 mM 2-chloroacetophenone as reagent, the same procedure as for lower concentration is followed with the results shown in Figure 10.

Figure 10: Validation of cross-current model (using RTD data, red crosses) to predict conversion by photochemical reactor using a series of cross-current LEDs and experimental data for variation of flow rate (Q , $4 - 0.5 \text{ mL min}^{-1}$, blue diamonds) and light flux (q_0 , $1.9 - 16 \times 10^{-6} \text{ einstein s}^{-1}$, blue circles) for a concentration of 25 mM 2-chloroacetophenone.

For higher concentrations, the fit between model (including the residence time distribution) and experiments deteriorates compared to the lower concentration experiments. The average deviation between experiments and model is $5 \pm 2\%$ -point, indicating still an adequate agreement. Furthermore, it must be noted that by increasing the concentration, the reactor operates in a much more efficient fashion, this is observed by comparing Figure 8 and Figure 10: in the region of $\rho\phi$ value between 0 and 3, conversion is nearly doubled. This can simply be explained by the increase in absorbance from 0.07 to 0.18, leading to an almost linear increase of light absorbance which drives the chemical reaction. So, by choosing the initial absorbance in a more suitable region, higher efficiencies can be achieved easily.

Overall, also in this region, the model is capable of predicting the conversion. These results indicate that competitive absorption by a side-product is not the full explanation, it can be seen that the fit is only good at the low and the high end of the $\rho\phi$ range. This misfit indicates that the effects seen in batch are linked to the increase in input concentration of the reagent, and not only the increased absorbance of the competitive side-product. The absorbance in the reactor is lower as compared to the absorbance in both batch reactors, making competitive absorption of light negligible.

Coaxial-illumination

The evaluation of co-current and counter-current for higher concentrations is shown in Figure 11.

Figure 11: Validation of co-current model (using laminar flow, crosses, a) and counter-current model (using laminar flow, crosses, b) to predict conversion by photochemical reactor using a collimated co-axial LED at a constant flow rate (10 mL min^{-1}) and variable light flux ($1.3 - 8.3 \times 10^{-6} \text{ einstein s}^{-1}$) for a concentration of 25 mM 2-chloroacetophenone.

For co-current, it is observed that the fit between the laminar flow model and experimental data is good to the same degree as for cross-current. The average deviation between experiments and model is $7 \pm 3\%$ -point, indicating reasonable agreement. The same trend of partial underestimation by the model is observed at low conversion. In general, this co-current model is valid for higher concentrations as well, yielding a reasonably good approximation of the potentially obtained conversion values.

The results for counter-current at higher concentrations are shown in Figure 11b. The average deviation between experiments and model is $-4 \pm 9\%$ -point, indicating poor agreement towards higher conversions. For 25 mM reagent concentration, experiments using counter-current do not show improved conversion to co-current. However, at 10 mM initial concentration, counter-current still proved to be more efficient and productive than the cross-current operation. By comparing Figure 9b and Figure 11b, it can be observed that the zone of model underprediction at lower conversion values is not present in this situation, indicating that competitive absorption of light is gradually increasing with increasing $\rho\phi$ values. Counter-current illumination significantly suffers when competitive absorption of light is present, which is

significant at 25 mM of initial reagent concentration. For the higher conversions, the absorbance in the reactor can be assumed to be around $1.5 \left(A_{initial} \times \frac{1+(1-X)}{2} \right)$ which assumes a linear concentration gradient. This value results in the transmission of light of only 3%, indicating that the reagent is capable of absorbing nearly all light. In this configuration, the competing product is pushed to the light inlet via convection and hinders the propagation of light towards the light outlet, suppressing the reaction drastically.

As discussed before, the nature of this competing compound is unknown but its presence is verified using HPLC-UV (S8). By comparing Figure 9a and Figure 9b, it can be observed that there is competition for light in counter-current mode as the experimental results drop below the model results, which is not observed in the co-current mode. Furthermore, the absorbance of the reagent at 10 mM over the whole reactor is only 0.90 at low conversion and even only 0.5 at high conversion (assuming 85% conversion and linear concentration gradient). This in turn results in transmission of 31% of the light. At these values, competition for light is less pronounced, but observable, compared to the higher absorbance values, as shown in Figure 11b. Lastly, it is generally observed that at higher concentration, deviations in quantum yield and selectivity occur, which is also observed in Figure 10 for cross-current at low absorbance.

In order to adapt the model to acquire a better fit between model and experimental data, the absorbance of this competing product (species B) can be incorporated. Since the concentration of this component increases with conversion, this can be easily done if the specific absorbance (ϵ_B) and selectivity (S_B) is known. Using these parameters, the absorbance of the component can be written as function of conversion in the following way using a path length ℓ dependent on the illumination technique:

$$A_B(\zeta) = \epsilon_{B,avg} c_B \ell = S_B X(\zeta) \epsilon_{B,avg} c_{0,B} \ell = S_B X(\zeta) A_{B,avg} \quad (12)$$

The equations for coaxial illumination become the following with the implementation of this competitive absorbance and are adapted from the equations shown in Table 1.

Table 3: Simplified equations to model cross-, co- and counter-current illumination with the addition of competitive absorbance by formed products (in green). The equations include complex flow regimes via residence time distribution (in red), with initial conditions (I.C.).⁶

Since nature of the competitive product is not known, and neither is it possible to obtain the specific absorbance data via HPLC-UV detection. As in this case, neither S_B nor $A_{B,avg}$ is known, both parameters would need to be fitted based on the experimental data of cross-, co- and counter-current illumination, which goes beyond the scope of this paper.

3.3.3 Comparison of illumination techniques

To accurately compare the experimental data on cross-, co- and counter-current illumination, the PSTY benchmark is utilized to indicate the productivity of the reactor using the three illumination techniques. PSTY was introduced by Leblebici et al.²⁷ and provides a benchmark for the reactor performance by dividing the space time yield [$\text{mol s}^{-1} \text{m}^{-3}$] of the reactor by the normalized lamp power [W]. A slight modification to this benchmark is performed to improve comparison of the illumination techniques, rather than the full setup, as this is still a proof-of-concept. The lamp power will be expressed in [einstein s^{-1}] of incident light in the reactor and will not consider the power drawn by the entire setup. The benchmark is already introduced by Meir et al.⁶ and shown below, yielding a unitless parameter since an einstein equals a mol of photons.

$$PSTY = \frac{STY}{LP} = \frac{\frac{Xc_0V}{\tau V}}{\frac{q_0}{V}} = \frac{Xc_0V}{\tau q_0} = \frac{Xc_0VQ}{Vq_0} = \frac{X}{\rho} [-] \quad (13)$$

First, a comparison is made between all illumination techniques using the same parameters on the x-axis as before, i.e. $\rho\phi$ ($= \frac{q_0\phi}{c_0Q}$). This value is proportional with the incident light flux (q_0) and the inverse of the flow rate (Q). Thus, the higher the PSTY at a certain $\rho\phi$ – value, the more efficient the light is used and the more productive the reactor is. The results of this comparison are shown in Figure 12a. A different point of view, based on the achieved conversion by the reactor, is shown in Figure 12b.

Figure 12: Comparison of experimental data for cross-, co- and counter-current based on energy scale ($\rho\phi$) (a) and conversion (X) (b) versus PSTY for an initial concentration of 10 mM 2-chloroacetophenone.

The higher the $\rho\phi$ - value, the more energy (light) is introduced in the reactor to achieve the measured PSTY. The higher the conversion in either technique, the lower PSTY as absorbance of the medium decreases. Figure 12a indicates that for every $\rho\phi$ – value, a higher PSTY is observed for co-axial illumination. This implies that the reactor is not only more efficient for co- and counter-current, hence yielding higher conversion for the same introduced light flux, compared to cross-current, but also more productive. Thus, solely by altering the way of illuminating the reactor, more light is absorbed, more product is formed and the productivity of the reactor increases. Note that for microreactors using this reaction, the PSTY for co- and counter-current modes would be lower than for the cross-current mode, as indicated in Figure 12a, due to the thinner light-path.

By comparing the PSTY versus the acquired conversion (Figure 12b) that is achieved by the reactor, it is shown that for the novel co- and counter-current illumination, a 5-6 times higher PSTY is obtained for any given conversion. This clearly indicates that this novel design performs significantly better compared to the current state-of-the-art. Future improvements to the design, including a non-collimated, more efficient LED for coaxial illumination could increase the overall PSTY even further.

At higher concentration (Figure 13a and b), a different result is obtained; counter-current no longer yields higher productivity than co-current. Furthermore, cross-current yields higher productivity by increased absorbance compared to the lower (10 mM) input concentration of the reagent. Counter-current compares less efficient than the co-current as before, due to the mentioned competitive absorption of light and concentration effects, which is more pronounced by this illumination technique. Co-current illumination does not suffer from this competitive absorption that much, as the products are evacuated from the light source by design. This is shown in the results as well, since its PSTY value does not decrease as much. Furthermore, it must be noted that for co-current operation, the productivity increases only slightly. Cross-

current mode shows an increased PSTY solely by the increased absorbance along the reactor, the difference in PSTY is around a factor of 2 as compared to cross-current (Figure 12b). Overall, for co- and counter-current, increasing the absorbance from 0.9 to 2.2 by increasing the concentration does not lead to a significant increase in conversion since concentration effects decrease the quantum yield and the slight increase in light absorbance does not allow a significant increase in light absorption.

Figure 13: Comparison of cross-, co- and counter-current based on energy scale ($\rho\Phi$) (a) conversion (X) (b) and PSTY for a concentration of 25 mM 2-chloroacetophenone.

Our results can be compared to the optimized results of Baumann and Baxendale¹⁰ regarding conversion while taking into account the efficiency of our LEDs (30%), the illumination efficiency of the reactor (70%, Figure 4) and the efficiency of the control board (90%). The PSTY at 95% conversion using cross-current equals 0.014 for 10 mM and 25 mM. Taking into account the efficiency of the aforementioned components (0.7×0.9), the following value is obtained for the whole system (starting at the power source): 0.00265 [–], which is an improvement of 16% compared to Baumann and Baxendale for cross-current illumination.

4 Conclusions

The new concept of co-axial (co- and counter-current) illumination for photochemical reactors was established in the previous part of this study and was shown by modelling to be promising in terms of efficient reactor design. Experimental results in this paper were able to validate the models derived for each illumination technique. A good match was observed for cross-current operation between the experimental results and the model for which the residence time distribution was incorporated. For co-axial illumination, a good match was obtained by using the laminar flow model and using reflective material to keep the incident light in the reactor as assumed in the model. The level of fit is surprising considering the degree of simplicity for which the model is derived, i.e. homogeneous and perfectly collimated light, both of which are difficult to accomplish in reality.

By comparing the reactors performance using the PSTY benchmark, it was observed that for low concentration (10 mM) reagent solution, in all cases, the use of coaxial illumination (either co- or counter-current) yields significantly better reactor performance as compared to the state-of-the-art. The increase in efficiency between co-axial illumination and cross-current illumination is a factor of 5-6 for the same obtained conversion. At higher concentration (25 mM) the limitations of counter-current illumination start to show. It was observed that competitive light absorption was present in the reactor which had a significant influence on the performance of the reactor. In this case, it was observed that co-current did not suffer from any performance limitation due to competitive absorption. This is so because the products, including the competitive side-product, are evacuated from the light source, thus reducing their influence. Considering both lower and higher concentration experiments, it can be concluded that co-current illumination performs the best as it can cope well with competitive absorbance products and side-products. Counter-current illumination is more useful for niche applications where there is absolutely no competitive absorbance by formed products and by-products. Furthermore, it was noted that for higher concentrations, cross-current illumination becomes more efficient as more light can be absorbed, leading to higher conversion, which was also predicted by the model. Regarding the current photochemical reactor set-ups in operation, they can in fact benefit from increasing the concentration of the light absorbing compound to significantly boost the performance of their reactor. Lastly, it was shown that only a single batch degradation experiment is required to allow the model to estimate the performance of a flow system accurately.

Acknowledgments

Glen Meir thankfully acknowledges FWO-Flanders for a SB PhD fellowship (1SA6219N). Mumin Enis Leblebici thankfully acknowledges FWO-Flanders for a postdoctoral fellowship (39715). The authors would like to extend their gratitude to Senne Fransen for his help regarding model derivations and to Kenneth Simoens for his help regarding HPLC measurements and analysis.

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Table 1: Simplified equations to model cross-, co- and counter-current illumination which will be used in this work. The equations include complex flow regimes via residence time distribution (in red), with initial conditions (I.C.).⁶

Technique	Equation(s)	I.C.
Cross	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \left(1 - 10^{-(A_{A,\text{avg}}(1-X(\zeta)))}\right) \partial \zeta \textcolor{red}{E(\theta)} \partial \theta$ $\int_0^1 \iota(\zeta) d\zeta = 1 \quad \iota(\zeta) = 1 \text{ (homogeneous illumination)}$	$X(\zeta = 0) = 0$ $\iota(0) = \iota$
Co	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \ln(10) A_{A,\text{avg}} (1 - X(\zeta)) \partial \zeta \textcolor{red}{E(\theta)} \partial \theta$ $\iota(\zeta) = \int_0^1 -\iota(\zeta) \ln(10) (A_{A,\text{avg}} (1 - X(\zeta))) \partial \zeta$	$X(\zeta = 0) = 0$ $\iota(\zeta = 0) = 1$
Counter	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \ln(10) A_{A,\text{avg}} (1 - X(\zeta)) \partial \zeta \textcolor{red}{E(\theta)} \partial \theta$ $\iota(\zeta) = \int_0^1 \iota(\zeta) \ln(10) (A_{A,\text{avg}} (1 - X(\zeta))) \partial \zeta$	$X(\zeta = 0) = 0$ $\iota(\zeta = 1) = 1$

$X[-]$ the conversion, $\iota[-]$ the dimensionless light fraction with respect to incident light flux, $\phi [\text{mol einstein}^{-1}]$ the quantum yield, $\rho [\text{einstein mol}^{-1}]$ the photon balance, $\theta [-]$ the normalized residence time, $A [-]$ the absorbance, $\zeta [-]$ the normalized axial reactor coordinate, and $E(\theta)[-]$ residence time distribution. Note that (ζ) signifies a dependency regarding the axial coordinate of the reactor and is placed between brackets after the respective parameter. The index A refers to the reagent species.

Table 2. Specific absorbance values of reagent, product and one of the expected side-products in the wavelength range emitted by the co-and cross-current LEDs. These values are different for each LED, due to the slightly different spectral distribution.

	ϵ_{avg} (co-current) [L mol ⁻¹ cm ⁻¹]	ϵ_{avg} (cross-current) [L mol ⁻¹ cm ⁻¹]
2-Chloroacetophenone (reagent)	5.61	6.59
Phenylacetic acid (product)	0.0562	0.0577
Acetophenone (side product)	0.735	0.918

Table 3: Simplified equations to model cross-, co- and counter-current illumination with the addition of competitive absorbance by formed products (in green). The equations include complex flow regimes via residence time distribution (in red), with initial conditions (I.C.).⁶

Technique	Equation(s)	I.C.
Cross	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \left(1 - 10^{-(A_{A,\text{avg}}(1-X(\zeta)) + S_B A_{B,\text{avg}} X(\zeta))} \right) \frac{A_{A,\text{avg}}(1-X(\zeta))}{A_{A,\text{avg}}(1-X(\zeta)) + S_B A_{B,\text{avg}} X(\zeta)} \partial \zeta \textcolor{red}{E(\theta) \partial \theta}$ $\int_0^1 \iota(\zeta) d\zeta = 1 \quad \iota(\zeta) = 1 \text{ (homogeneous illumination)}$	$X(\zeta = 0) = 0$ $\iota(0) = \iota$
Co	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \ln(10) A_{A,\text{avg}} (1 - X(\zeta)) \partial \zeta \textcolor{red}{E(\theta) \partial \theta}$ $\iota(\zeta) = \int_0^1 -\iota(\zeta) \ln(10) (A_{A,\text{avg}} (1 - X(\zeta)) + S_B A_{B,\text{avg}} X(\zeta)) \partial \zeta$	$X(\zeta = 0) = 0$ $\iota(\zeta = 0) = 1$
Counter	$X(\zeta) = \int_0^\infty \int_0^1 \phi_{\text{avg}} \iota(\zeta) \rho \theta \ln(10) A_{A,\text{avg}} (1 - X(\zeta)) \partial \zeta \textcolor{red}{E(\theta) \partial \theta}$ $\iota(\zeta) = \int_0^1 \iota(\zeta) \ln(10) (A_{A,\text{avg}} (1 - X(\zeta)) + S_B A_{B,\text{avg}} X(\zeta)) \partial \zeta$	$X(\zeta = 0) = 0$ $\iota(\zeta = 1) = 1$

Figure 1: Graphical presentation of the experimental setup, with the reactor tube (1) in borosilicate glass held between two aluminum support pieces (2). The reactor is illuminated radially by a series of 10 LEDs for cross-current illumination, mounted to a heat sink (3), and illuminated axially by an LED mounted to a bigger heat sink (4).

Figure 2: Synthesis of phenylacetic acid from 2-chloroacetophenone via a photo-favorskii rearrangement, after 10

Figure 3: UV absorbance spectrum of 2-chloroacetophenone measured in acetonitrile (orange) via Lambda 365 (Perkin Elmer). Normalized intensity distribution of cross-current LEDs (by Roithner, green) and the co-axial LED (by Mightex, blue).

Figure 4: Cross-current LEDs calibration per LED. The diamonds indicate the total light flux emitted by the LED, the circles indicate the received light flux in the reactor (OD 15 mm, ID 11 mm, borosilicate) with a distance of 2 mm between LEDs and reactor. The triangles indicate the validation of the simulation data by actinometry, two replicates are performed.

Figure 5: Coaxial LED calibration. The circles indicate the total light flux emitted by the LED, the triangles indicate the received light flux in the reactor with an aperture of 11 mm. The triangles indicate the received light flux, determined by a scaling factor via actinometry. The diamonds are the actinometry results used to scale down the total emitted light flux to the absorbed light flux due to reflection and reduction in aperture.

Figure 6: Conversion of 10 mM 2-chloroacetophenone in a 60 mL batch reactor with a path length of 4 cm (a), the model fit is based on the average quantum yield ($\phi=0.364\pm0.022$) as determined by the experiments. Selectivity towards product (phenylacetic acid) and quantum yield of the reaction for the batch degradation of 2-chloroacetophenone is calculated based on conversion (b).

Figure 7: Conversion of 25 mM 2-chloroacetophenone in a 60 mL batch reactor with a path length of 4 cm (a), the model fit is based on the average quantum yield ($\phi=0.275\pm0.021$) as determined by the experiments. Selectivity towards product (phenylacetic acid) and quantum yield of the reaction for the batch degradation of 2-chloroacetophenone are based on the measured conversion (b).

Figure 8: Validation of cross-current model (using RTD data, red) to predict conversion by photochemical reactor using a series of cross-current LEDs and experimental data (blue) for variation of flow rate (Q , 10-1.4 mL min⁻¹), in blue diamonds) and light flux (q_0 , $1.9-16 \times 10^{-6}$ einstein s⁻¹), in blue circles) for a concentration of 10 mM 2-chloroacetophenone.

161x90mm (600 x 600 DPI)

Figure 9: Validation of co-current model (using laminar flow, crosses, (a)) and counter-current (using laminar flow, crosses, (b)) to predict conversion by photochemical reactor using a collimated co-axial LED at a constant flow rate (10 mL min^{-1}) and variable light flux ($1.3\text{--}8.3 \times 10^{-6} \text{ einstein s}^{-1}$) for a concentration of 10 mM 2-chloroacetophenone.

Figure 10: Validation of cross-current model (using RTD data, red crosses) to predict conversion by photochemical reactor using a series of cross-current LEDs and experimental data for variation of flow rate (Q , 4-0.5 mL min⁻¹, blue diamonds) and light flux (q_0 , 1.9×10^{-6} einstein s⁻¹, blue circles) for a concentration of 25 mM 2-chloroacetophenone.

Figure 11: Validation of co-current model (using laminar flow, crosses, a) and counter-current model (using laminar flow, crosses, b) to predict conversion by photochemical reactor using a collimated co-axial LED at a constant flow rate (10 mL min^{-1}) and variable light flux ($1.3\text{--}8.3 \times 10^{-6} \text{ einstein s}^{-1}$) for a concentration of 25 mM 2-chloroacetophenone.

Figure 12: Comparison of experimental data for cross-, co- and counter-current based on energy scale ($\rho\phi$) (a) and conversion (X) (b) versus PSTY for an initial concentration of 10 mM 2-chloroacetophenone.

Figure 13: Comparison of cross-, co- and counter-current based on energy scale ($\rho\phi$) (a) conversion (X) (b) and PSTY for a concentration of 25 mM 2-chloroacetophenone.