Real-time reaction control for solar production of chemicals under fluctuating irradiance

Citation for published version (APA):

Zhao, F., Cambié, D., Hessel, V., Debije, M. G., & Noël, T. (2018). Real-time reaction control for solar production of chemicals under fluctuating irradiance. *Green Chemistry*, 20(11), 2459-2464.
<https://doi.org/10.1039/C8GC00613J>

DOI:

[10.1039/C8GC00613J](https://doi.org/10.1039/C8GC00613J)

Document status and date:

Published: 07/06/2018

Document Version:

Accepted manuscript including changes made at the peer-review stage

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Real-time reaction control for solar production of chemicals under fluctuating irradiance

Fang Zhao,^{a,†} Dario Cambi,^{a,†} Volker Hessel,^a Michael G. Debije,^b and Timothy Nol^{*a}

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Arguably, one of the major practical barriers hampering a wider use of solar energy to promote photochemical reactions are the variations in sunlight intensity at different times of the day as well as the fluctuations caused by passing clouds. Herein, we present an automatically responsive reaction control system enabling solar photochemistry under vastly changeable irradiance conditions. While the luminescent solar concentrator photomicroreactor (LSC-PM) design converts solar light into a narrow and steady spectral distribution, this reaction control system, inspired by the Quality by Design approach, maintains the reaction conversion constant at a set target value by dynamically changing the residence time in the reactor. The superior efficiency of an LSC-PM equipped with this reaction control system is shown both with artificially generated light fluctuations and in outdoor experiments using sunlight.

Introduction

Solar energy, as well as renewable energy sources in general, are going to be increasingly important in the future,¹ not just to match the rising global energy demand but also to enable the production of fine chemicals.^{2, 3} Recently, photoredox catalysis has emerged as a versatile tool for solar synthesis as it allows the use of visible light, which constitutes over 40% of the solar radiation at ground level.⁴ With photoredox catalysis, photons can be used as a green and traceless reagent for a wide variety of chemical transformations.^{5–7} For example, the direct use of solar energy in the photocatalytic depolymerization of lignin might aid the transition from fossil to biomass-based feedstock.⁸ While the flask in the sun has long been the traditional approach to solar photochemistry, modern solutions need to be not only effective but also photon-efficient to balance the relatively dilute energy content of solar energy.^{2, 9, 10}

We have recently proposed a device, called a luminescent solar concentrator photomicroreactor (LSC-PM), as a solution for energy-efficient solar photocatalysis.^{11, 12} Our reactor exploits the ability of luminescent solar concentrators to harvest both direct and diffuse light, downconvert it to a narrow spectral range and deliver the luminescent photons to the embedded microflow channels.¹³ This approach is superior to optical

concentration solutions which can only use direct irradiation.^{14, 15} This results in a device that allows the direct use of solar energy for photochemical reactions, without any intermediate energy conversion. However, as a result of light scattering by clouds, solar light at ground level can significantly fluctuate in intensity.^{16–18} In particular, while seasonal and diurnal trends in solar irradiance can be described by astronomical relationships, local short-term fluctuations are mostly a function of stochastic parameters (including cloud frequency and height, atmospheric aerosol and turbidity, water vapour, and ground albedo).^{19–21} In Fig. 1A, the global horizontal radiation of a cloudy September day in Eindhoven, the Netherlands is presented as an example. It is clear that a control system capable of mitigating the impact of the fluctuating solar irradiance is needed to efficiently power a photochemical reaction with sunlight. Several flow-based reaction automation platforms have been developed in recent years.²² The most common solution is to employ on-line analytical techniques and to implement changes to the reaction conditions with a feedback loop.^{23, 24} However, this approach is ill-suited for a solar irradiance responsive system since the variations in the light intensity can be both frequent and significant.¹⁹ Furthermore, a delay between the variations and the analytical measurement would result in an erratic reaction conversion, especially with larger reactor volumes. Clearly, for any solar photochemical process, the irradiance variation constitutes a critical process parameter.²⁵ To manage the impact that this variability can have on the reaction performance in outdoor applications, process control technologies acting in real-time are needed.²⁶ Ideally, a reaction control system can be envisioned, capable of automatically adjusting the residence time of the reaction mixture based on the solar irradiance variation, resulting in a constant product quality.^{27, 28} In this way, inspired by the Quality by Design approach, the reaction conversion is kept constant and the

^a Department of Chemical Engineering and Chemistry, Micro Flow Chemistry and Process Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: t.noel@tue.nl

^b Department of Chemical Engineering and Chemistry, Functional Organic Materials and Devices, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

[†] These authors contributed equally to this work.

Electronic Supplementary Information (ESI) available: Materials and methods as well as detailed information for the construction of the reaction control system and the device source code. See DOI: 10.1039/x0xx00000x

selectivity can be maximized, thus simplifying the downstream processes.^{29, 30}

Fig. 1 Schematic overview of the real-time control system. A) The variation of global horizontal radiation during a cloudy September day in Eindhoven. The drastic reduction of the direct irradiation component of the solar spectrum associated with passing clouds is only partially compensated by the increase in diffuse radiation. B) The ability of LSC-PM to capture diffuse light and the relationship between the edge emission and the photon-flux received by the reaction channels. C) Schematic representation of the real-time reaction control system: the variation in solar irradiance is read through a light sensor placed at the edge of the device. Depending on the light intensity, the pump flow rate is adjusted. In order to quantify the reaction control performance, the conversion is monitored in-line with a spectrometer. D) The plot represents the correlation between the light sensor voltage and the edge photon flux. The light sensor voltage is measured as shown in the circuit scheme.

Results and discussion

To develop such a system, the reaction profile should first be investigated as a function of both the light intensity and spectral distribution. In the LSC-PM though, the photon flux received by the reactor channels is mostly (>85% according to ray-tracing simulations³¹) composed of luminescent photons emitted by the lightguide-embedded luminophore. Consequently, the spectral distribution can be considered constant regardless of the incident spectrum (see Fig. 1B). Therefore, if an LSC-PM design is used, the variation in the spectral distribution of the solar light can be ignored, vastly simplifying the requirements for the light sensing element of the reaction control system. Furthermore, given that in the LSC-PM the photon flux leaving the device at the edges is proportional to the photon flux experienced by the reaction mixture flowing in the microfluidic channels, it is enough to measure the photon flux at the reactor

edge to correct for the variation of solar irradiance.³¹ All of this results in a simple, inexpensive yet effective architecture for the reaction control system, constituted by a light sensor connected to a microcontroller that directly adjusts the pump (Fig. 1C).

As a light sensor, a simple and inexpensive silicon phototransistor was chosen to monitor the photon flux emitted at the LSC-PM edges.³² By including the phototransistor in a voltage divider electrical circuit, the light intensity becomes proportional to the voltage across a resistor connected in series. In Fig. 1D, the variation in the light sensor signal with the LSC-PM edge emission is presented. For our control system, the voltage drop measured in this way was used as an indirect measurement of the photon flux in the reactor channel. Information on the reaction profile under different light irradiance conditions is pivotal for the successful implementation of our reaction control system, as it links the measured edge emission with the required residence time for

Fig. 2 A) The model reaction studies. B) Reaction conversion vs. time at different light intensities and C) the resulting 3D surface correlating flow rate, conversion and light intensity.

Fig. 3 Effect of the system responsiveness on the ability to maintain the target conversion, clearly showing the advantage of real-time control versus feedback loops based strategies, which are characterized by a longer latency.

any conversion target. As a model reaction, the [4+2] photooxygenation of 1,9-diphenylanthracene with methylene blue as singlet oxygen photosensitizer was selected (Fig. 2A), as its kinetics is light limited, and because the conversion can be continuously analysed in-line with a UV-VIS spectrometer.³³ The continuous monitoring of the reaction performance was especially convenient in the development of our reaction control system as it allowed us to appreciate the relative impact of parameters such as the sampling interval or the employment of a conversion allowance. It should be noted that once the reaction profile has been obtained at different light intensities, no other analytical measurements are needed and the reaction control system (composed of the microcontroller and the light sensor) is fully autonomous.

The reaction conversions measured at different residence times and light intensities are reported in Fig. 2B. From the fitting of the experimental results, a 3D surface can be obtained correlating the three key parameters: conversion, residence time and light intensity, the latter described as light sensor voltage (Fig. 2C). The intersection between the 3D surface and each XY plane is a curve describing the relationship between the light sensor and the residence time required for the reaction conversion corresponding to the Z value of the XY plane. This

Fig 4 Impact of the reaction control system on the conversion in response to an arbitrary variation of irradiance intensity. The reaction control system reacts in real-time to the variation in light intensity by changing the pump flow rate, resulting in a stable conversion (set to 50% in this case). On the other hand, the reaction conversion in the reactor without microcontroller merely follows light intensity variations.

contour line is based only on the experimental results, with no assumptions on the relationship between reaction profile and light intensity. As such, this approach can be readily applied to any photochemical transformation, once the relevant reaction profiles at different light intensities have been elucidated.

To translate the light sensor voltage into a variation of the pump flow rate, an inexpensive Arduino-based control system was designed (see Supporting Information for details).^{34, 35} The voltage value is read as a 10-bit light level value (from 0 to 1023 for the 0-5V range) and the corresponding pump flow rate is calculated based on the previously performed kinetic

investigation. The flowrate is then set to the pump via a serial (RS-232) connection.

Within the architecture of the control system, the most important parameter is the sampling interval, that is, the time between two consecutive light intensity readings. Any delay between the light intensity change and the corresponding correction of the residence time can result in deviations from the target of conversion. Intuitively, an increase of light intensity that is not immediately compensated with an increase in the flow rate will result in an increase in the reaction conversion. Conversely, a delay in the response to an irradiance decrease would result in product conversions below the target value. It has been observed³⁶ that very few techniques are able to operate with a sampling frequency matching that of microflow devices. To achieve almost real-time responsiveness, we used a phototransistor, whose response time is less than a millisecond.

In the sampling rate timeframe, four events need to take place. First, the voltage in the light sensing circuit has to be read, then the microcontroller needs to calculate the corresponding flow rate and send the data to the pump and, finally, the pump updates the rotation speed of the stepper motor to match the set value. Among these four steps, the last one is by far the slowest. While a single voltage reading, calculating and sending the corresponding flow rate together takes few milliseconds, the shortest interval to which the syringe pump can respond to a flow rate change command is almost 500 ms. This short delay was deemed to be suitable to maintain the conversion stable within a 150 μ L reactor as reported here (see Fig. 3). Furthermore, this lower limit to the speed of the feedforward loop provides enough time to average between 4096 individual voltage readings for the light sensor circuit, resulting in a high accuracy (see Supporting Information). It is expected that, for larger reactor volumes, a longer sampling interval might be used resulting in similar performances.

For our experiments, a syringe pump powered by a stepper motor was used. With this type of motor, the lifetime of the pumping system is not affected by the continuous variations of the set flow rate, therefore, using the shortest delay possible for the control loop was not an issue. However, if the continuous variations in flow rate would constitute a concern for the pumping system, a conversion allowance can be set to skip the changes to the pump flow rate, which would result only in small conversion fluctuations. In this way, the flow rate would only be updated when the projected conversion exceeds a predefined limit value (see Supporting Information). Next, all the data was fed to a reaction control box comprising a microcontroller, a display showing the current light sensor voltage value and connections for the pump and the light sensor.

To evaluate the effectiveness of the reaction control system, we compared the ability of an LSC-PM reactor with and without reaction control to mitigate a programmed set of light irradiance fluctuations (Fig. 4, top). The target conversion was set at 50% since, at that conversion level, the reaction profile is still strictly dependent on the photon flux received. From the

results presented in Fig. 4, it is clear the reaction control system is able to maintain a stable conversion despite the dramatic fluctuations in the incident light irradiance. In particular, the conversion with reaction control varied in the 48–53% range, while without reaction control the reactor passively followed the programmed variations in light intensity with variations in reaction conversion between 26 and 66%. Finally, we moved toward testing the reaction control system under natural sunlight conditions. In this case, the conversion target was set to 90% as a more significant value from a production-oriented perspective. A setup was assembled and placed on a movable trolley (Fig. 5A) and tested outdoors on a day characterized by variable sky conditions (see Supporting Information for details). To compare the performance of two reactors under the same conditions, a 4-way valve was used to alternatively measure the conversion of each reactor with the in-line spectrometer. In particular, the LSC-PM with reaction control system was compared both to a simple LSC-PM (Fig. 5C) and to a traditional non-doped analogue (Fig. 5D). The flow rate of the reactors without reaction control was set at the beginning of the experiment to be equal to that of the reactor connected with the reaction control module. As is evident from the graph, the reaction control significantly improved the stability of the reaction conversion with respect to the solar irradiance variations (Fig. 5C and D). In particular, the reaction conversion in the LSC-PM with reaction control remained in the 86–93% range, while it spanned between 55 and 97% in the LSC-PM without reaction control and between 14 and 50% in the non-doped reactor. The variability in the conversion of the reactor with the reaction control system is mostly due to the fact that the variation in the pump flowrate do not immediately translate in a corresponding change of the residence time in the reactor due to elastic nature of the reactor material. Not surprisingly, the reaction conversion in the reactor without reaction control followed a very similar trend as the light intensity measured by

the light detector at the LSC-PM edge. This evidenced, once more, the need for a real-time reaction control system capable of correcting the process parameters to afford a constant quality in solar-based chemical production.

Conclusions

We have developed an inexpensive and efficient reaction control system capable of correcting in real-time the residence time of a photochemical reaction based on the variation in local irradiance. This system, requiring only an inexpensive microcontroller and a phototransistor, was designed taking advantage of the unique characteristics of the LSC-PM concept and can be used to automate the solar-powered photon-efficient production of chemicals via photochemistry, without the need for solar-tracking systems. Further investigations on the application of such a system on a large-scale solar photoreactor are currently underway in our research group.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We would like to thank Roland M.E. Valckenborg (TU/e) and Minnie de Jong (SEAC) for granting us access to their test facility for the outdoor experiment and providing the pyranometer data. This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 641861. Furthermore, this research was supported by a VIDI grant from the Dutch Science Foundation (NWO) to T.N. (SensPhotoFlow, No. 14150).

Notes and references

- 1 B. Obama, *Science*, 2017, 355, 126–129.
- 2 M. Oelgemoller, *Chem. Rev.*, 2016, 116, 9664–9682.
- 3 P. Esser, B. Pohlmann and H.-D. Scharf, *Angew. Chem., Int. Ed.*, 1994, 33, 2009–2023.
- 4 C. A. Gueymard, D. Myers and K. Emery, *Solar Energy*, 2002, 73, 443–467.
- 5 D. M. Schultz and T. P. Yoon, *Science*, 2014, 343, 1239176.
- 6 C. K. Prier, D. A. Rankic and D. W. C. MacMillan, *Chem. Rev.*, 2013, 113, 5322–5363.
- 7 N. A. Romero and D. A. Nicewicz, *Chem. Rev.*, 2016, 116, 10075–10166.
- 8 I. Bosque, G. Magallanes, M. Rigoulet, M. D. Kärkäs and C. R. J. Stephenson, *ACS Central Science*, 2017, 3, 621–628.
- 9 M. Oelgemöller, C. Jung, J. Ortner, J. Mattay and E. Zimmermann, *Green Chem.*, 2005, 7, 35–38.
- 10 A. M. Nauth, A. Lipp, B. Lipp and T. Opatz, *Eur. J. Org. Chem.*, 2017, 15, 2099–2103.
- 11 D. Cambié, F. Zhao, V. Hessel, M. G. Debije and T. Noël, *Angew. Chem., Int. Ed.*, 2017, 56, 1050–1054.
- 12 F. Zhao, D. Cambié, J. Janse, E. W. Wieland, K. P. L. Kuijpers, V. Hessel, M. G. Debije and T. Noël, *ACS Sustainable Chem. Eng.*, 2018, 6, 422–429.

Fig. 5 Validation of the reaction control system in an outdoor experiment. A) Photograph of the set-up B) Schematic representation of the experimental setup C) Comparison between LSC-PM with and without reaction control and D)

- 13 D. Cambié, C. Bottecchia, N. J. W. Straathof, V. Hessel and T. Noël, *Chem. Rev.*, 2016, 116, 10276-10341.
- 14 M. G. Debijs and V. A. Rajkumar, *Solar Energy*, 2015, 122, 334-340.
- 15 M. G. Debijs and P. P. C. Verbunt, *Adv. Energy Mater.*, 2012, 2, 12-35.
- 16 Thick, dark clouds can decrease the solar radiation at ground down to 1% of the extraterrestrial level.
- 17 H. Suehrcke and P. G. McCormick, *Solar Energy*, 1988, 40, 423-430.
- 18 J. Boland and B. Ridley, in *Modeling Solar Radiation at the Earth's Surface: Recent Advances*, ed. V. Badescu, Springer Berlin Heidelberg, Berlin, Heidelberg, 2008, DOI: 10.1007/978-3-540-77455-6_8, pp. 193-219.
- 19 A. Woyte, R. Belmans and J. Nijs, *Solar Energy*, 2007, 81, 195-206.
- 20 A. Madanchi, M. Absalan, G. Lohmann, M. Anvari and M. Reza Rahimi Tabar, *Solar Energy*, 2017, 144, 1-9.
- 21 G. M. Lohmann, A. H. Monahan and D. Heinemann, *Atmospheric Chemistry and Physics*, 2016, 16, 6365-6379.
- 22 B. J. Reizman and K. F. Jensen, *Acc. Chem. Res.*, 2016, 49, 1786-1796.
- 23 D. C. Fabry, E. Sugiono and M. Rueping, *Isr. J. Chem.*, 2014, 54, 341-350.
- 24 C. W. Coley, M. Abolhasani, H. Lin and K. F. Jensen, *Angew. Chem., Int. Ed.*, 2017, 56, 9847-9850.
- 25 Y. Su, K. P. L. Kuijpers, N. König, M. Shang, V. Hessel and T. Noël, *Chem. - Eur. J.*, 2016, 22, 12295-12300.
- 26 A. M. R. Hall, R. Broomfield-Tagg, M. Camilleri, D. R. Carbery, A. Codina, D. T. E. Whittaker, S. Coombes, J. P. Lowe and U. Hintermair, *Chem. Commun. (Cambridge, U. K.)*, 2017, DOI: 10.1039/c7cc07059d.
- 27 U.S. Department of Health and Human Services FDA, "Guidance for Industry PAT — A Framework for Innovative Pharmaceutical Development, Manufacturing, and Quality Assurance", September 2004.
- 28 T. Murphy, N. O'Mahony, K. Panduru, D. Riordan and J. Walsh, 2016 27th Irish Signals and Systems Conference (Issc), 2016, DOI: 10.1109/issc.2016.7528465, 1-7.
- 29 I. M. Mándity, S. B. Ötvös and F. Fülöp, *ChemistryOpen*, 2015, 4, 212-223.
- 30 J. M. Juran, *Juran on Quality by Design: The New Steps for Planning Quality Into Goods and Services*, Free Press, 1992.
- 31 D. Cambié, F. Zhao, V. Hessel, M. G. Debijs and T. Noël, *React. Chem. Eng.*, 2017, 2, 561-566.
- 32 One notable feature of our reaction control system is that the total cost price is only € 54 (See Supporting Information for more details), making it to the best of our knowledge the cheapest self-optimization system in the flow chemistry literature.
- 33 S. P. Pitre, C. D. McTiernan, W. Vine, R. DiPucchio, M. Grenier and J. C. Scaiano, *Sci. Rep.*, 2015, 5, 16397.
- 34 Arduino www.arduino.cc
- 35 D. E. Fitzpatrick, C. Battilocchio and S. V. Ley, *ACS Central Science*, 2016, 2, 131-138.
- 36 K. S. Elvira, X. C. i Solvas, R. C. R. Wootton and A. J. deMello, *Nat. Chem.*, 2013, 5, 905-915.