Wireless µLED packed beds for scalable continuous multiphasic photochemistry

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Supplemental Information

Table of Contents

S1. Analytical Methods

GC Column type: 5Sil MS **FID column:** Rtx-5

 Thickness 0.25 mm, Diameter 0.25 μm, Length 30 m

Column Oven Temperature: Hold 90°C for 25 min then 8°C temp ramp until 260°C

Inlet: 160°C, 69.1 kPa

Total Flow: 54 mL min^{-1}

Column Flow: 1 mL min^{-1} Argon Carrier Gas

Linear velocity: 37 cm s^{-1}

Purge flow: 3 mL min^{-1}

Split Ratio: 50:1

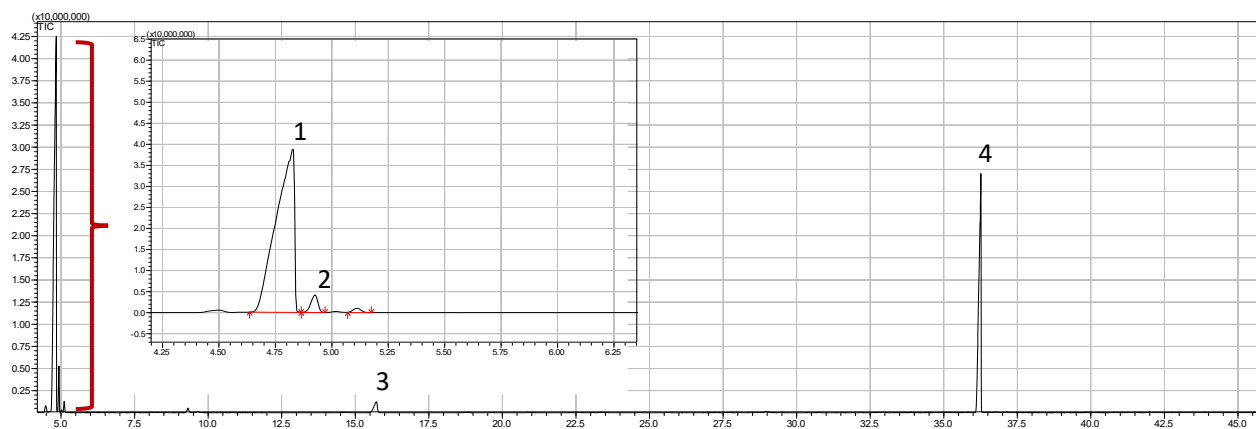**Internal standard:** Hexadecane

Figure S1. GC chromatogram for the oxidation of α-terpinene at liquid flowrate of 0.27 mL min^{-1} (τ=1.4 min)

Table S1. Retention time of molecule seen during the oxidation of α-terpinene

Chromatogram position	Retention time [min]	Molecule
1	4.640-4.838	α-terpinene
2	4.875-4.928	p-cymene
3	15.485-15.721	ascaridole
4	36.065-36.262	hexadecane

A 3 point linear calibration curve was developed using the ratio of FID peak area of α-terpinene to peak area of the internal standard hexadecane. Solutions were prepared in IPA.

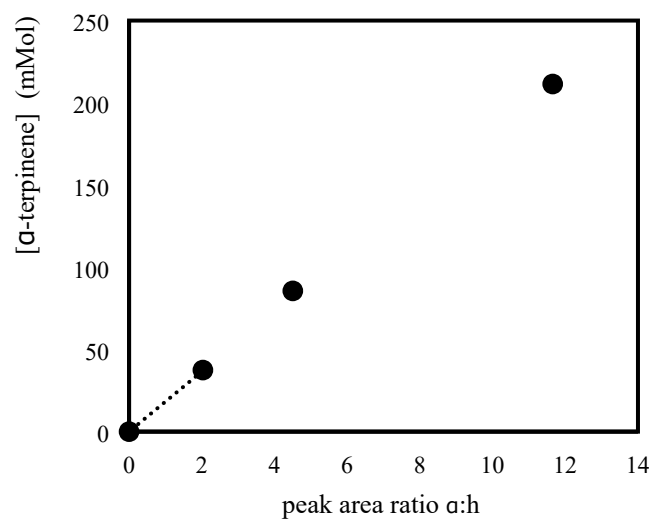Table S2. Concentration of α-terpinene and hexadecane and the resulting peak areas used to develop calibration curve.

Figure S2. Three point calibration curve used to determine the concentration of alpha-terpinene after reaction took place.
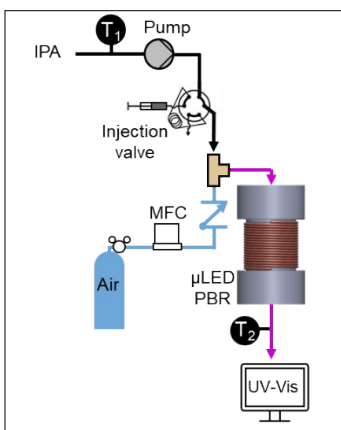
S2. Residence time distributions

Figure S3. Process flow diagram of the system configuration during RTD studies.

In Figure 3, reactor configuration including the six-port valve is displayed. 50 reactor volumes of IPA were pumped through the six port valve's bypass into the PBR. After the 50 reactor volumes the configuration was switched to pass through the sample loop and 0.05 mL of dye was injected. The reactor effluent was collected using transparent cuvettes and the transient absorbance relative to pure IPA at 548 nm was measured. Figure 4 contains the E curves of the 500 PBR at different liquid flow rates. The flowrate of air into the system was constant at 10 sscm during measurements. Matlab code used to deconvolute the reactor from the full system is available on request. In Table 3, the calculated residence time over the LED bed (reactor) is reported.
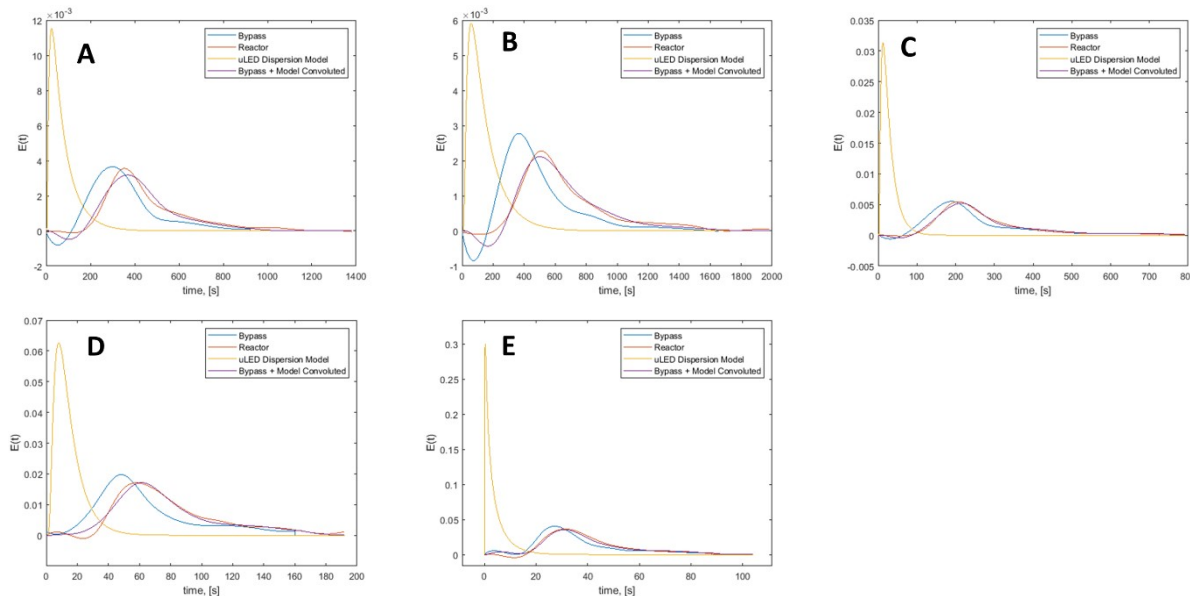

Figure S4 . E curves of the crushed glass bypass, μLED bed, , and deconvolution fits. A) Liquid flowrate: 10.8 mL min^{-1}. B) Liquid flowrate: 5.4 mL min^{-1}. C) Liquid flowrate: 1.35 mL min^{-1}.D) Liquid flowrate: 0.77 mL min^{-1}. E) Liquid flowrate: 0.54 mL min^{-1}.

Table S3. Residence times and dispersion determined using pulse injection RTD and a constant gas flow rate of 10 sccm

F_{liquid} [mL min^{-1}]	τ [min]	$\dfrac{D}{u\,L}$
10.8	0.02	1.39
5.4	0.17	0.22
1.35	0.29	0.32
0.77	0.66	0.49
0.54	1.4	0.37

S3. Flow Regime

The flow regime in a multiphasic packed bed reactor has been characterized by Charpentier and Favier and other authors [1]. Their regime maps, Carpentier diagrams, consider fluid characteristics in a ψ (Equation 1) and λ (Equation 2) term. The characteristics considered are critical surface tension of water (σ_c), surface tension of the liquid (σ_L), viscosity (μ), and density of the liquid, gas, or water ($\rho_{L,G}$), bed characteristics: porosity (ϵ), and operating conditions: gas superficial mass velocity (G) Equation 3,and liquid superficial mass velocity (**L**), Equation 4 which are both functions of the cross sectional area (A) of the reactor. The parameters are then used to determine position within a Charpentier diagram, where the horizontal position is a function of Equation 5 and the vertical positions is a function Equation 6. In Table 4 the fluid and reactor characteristics are listed. Solvent used in the system is (isopropyl alcohol) IPA and the gas is air, these materials will be used when determining the physical properties.

$$\psi = \frac{\sigma_{water}}{\sigma_L}\left[\frac{\mu_L}{\mu_{water}}\left(\frac{\rho_{water}}{\rho_L}\right)^2\right]^{\frac{1}{3}}$$
Equation 1

$$\lambda = \left[\frac{\rho_G \rho_L}{\rho_{air}\rho_{water}}\right]^{0.5}$$
Equation 2

$$G = F_G \cdot \frac{\rho_G}{A}$$
Equation 3

$$L = F_L \cdot \frac{\rho_L}{A}$$
Equation 4

$$\frac{G}{\lambda}$$
Equation 5

$$\frac{L\,\psi\,\lambda}{G}$$
Equation 6

Table S4. Values of physical properties used in calculating position on Charpentier diagram.

Property	Value
σ_c [kg/s²]	0.047
σ_{IPA} [kg/s²]	0.023
μ_{water} [kg/m/s]	0.001
μ_{IPA} [kg/m/s]	0.002
ρ_{water} [kg/m³]	1000
ρ_{IPA} [kg/m³]	785
ρ_{air} [kg/m³]	1.29

The λ and ψ are independent of the of operating conditions and were determined to be 0.88 and 2.98 respectively. This corresponds to horizontal position of 3E-4 on a Charpentier diagram.

The cross sectional area of the reactor was 7.99E-4 m². The flowrate of air was fixed at 10 sccm, G was determined to be 2.7E-4 kg m⁻¹ s⁻¹. The liquid flowrate ranged from 4.5E-9 to 1.8E-7 m³ s⁻¹, this corresponds to superficial mass velocities, **L**, ranging from 4.42E-3 to 0.17 kg m⁻¹ s⁻¹. This corresponds to a vertical position of with a minimum of 43 and 1730.

The vertical and horizontal positions fall within the trickle bed regime of an extrapolated Charpentier diagram [2].

S4. PSTY parameters

Table S5: Parameters used to calculate PSTY

Reactor	P_LED, [W]	V_L, [mL]	C_0 [mmol L^{-1}]	τ, [min]	X	Source
PBR-500	0.33	0.65	166	0.02	0.05	This
				0.17	0.05	work
				0.29	0.09	
				0.66	0.12	
				1.41	0.14	
PBR-250	0.16	0.32	162	0.02	0.04	This
				0.17	0.02	work
				0.29	0.05	
				0.66	0.09	
				1.41	0.11	
Batch-250	0.16	120	169	1	0.02	This
				5	0.02	work
				10	0.03	
				15	0.04	
				30	0.06	
				60	0.12	
Batch FL	18	50	25	15	0.79	[3]
				30	1	
				60	1	
FF FL	18	0.0430	50	0.53	0.57	[3]
		0.067		0.22	0.2	
		0.0930		0.12	0.1	
FF LED	3	0.0430	50	0.53	0.33	[3]
		0.067		0.22	0.12	
		0.0930		0.12	0.07	

S5. Selectivity

The selectivity of the reaction was calculated based on the on the GC-FID peak areas of the products formed as described in Equation 7. In Figure 5 at longer residence times the selectivity of the reaction in the packed bed reactor favored the formation of ascaridole.

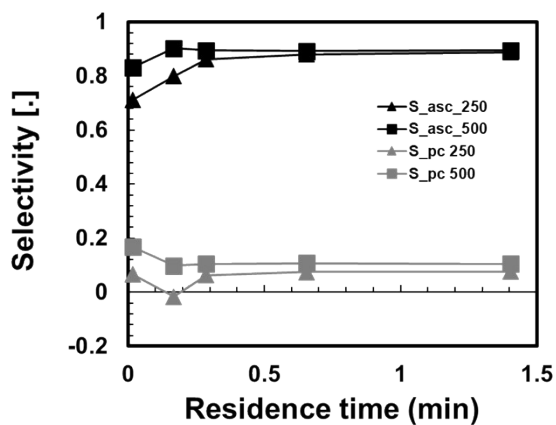$$S = \frac{A_i}{A_{asc.} + A_{p-cy.}}$$

Equation 7

Figure S5 Selectivity of the oxidation of alpha-terpinene to form ascaridole (asc) and p-cymene (pc) in the PBR .

SI References

[1]   A. Gianetto, G. Baldi, V. Specchia, and S. Sicardi, "Hydrodynamics and solid-liquid contacting effectiveness in trickle-bed reactors," *AIChE Journal,* vol. 24, no. 6, pp. 1087-1104, 1978, doi: 10.1002/aic.690240622.

[2]   F. Larachi, A. Laurent, N. Midoux, and G. Wild, "Experimental study of a trickle-bed reactor operating at high pressure: two-phase pressure drop and liquid saturation," *Chemical Engineering Science,* vol. 46, no. 5, pp. 1233-1246, 1991/01/01/ 1991, doi: https://doi.org/10.1016/0009-2509(91)85051-X.

[3]   O. Shvydkiv, K. Jähnisch, N. Steinfeldt, A. Yavorskyy, and M. Oelgemöller, "Visible-light photooxygenation of α-terpinene in a falling film microreactor," *Catalysis Today,* vol. 308, pp. 102-118, 2018/06/15/ 2018, doi: https://doi.org/10.1016/j.cattod.2017.11.009.