

Supporting Information

Supported ionic liquid phase (SILP) facilitated gas-phase enzyme catalysis – CALB catalyzed transesterification of vinyl propionate

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Continuous e-SILP gas-phase reactor setup



Figure S1. Picture of the continuous gas-phase reactor for e-SILP catalyzed transesterification. (1) Carrier gas dosing, (2) liquid dosing, (3) saturator, (4) bypass, (5) reactor, (6) back-pressure

Calibration of online GC

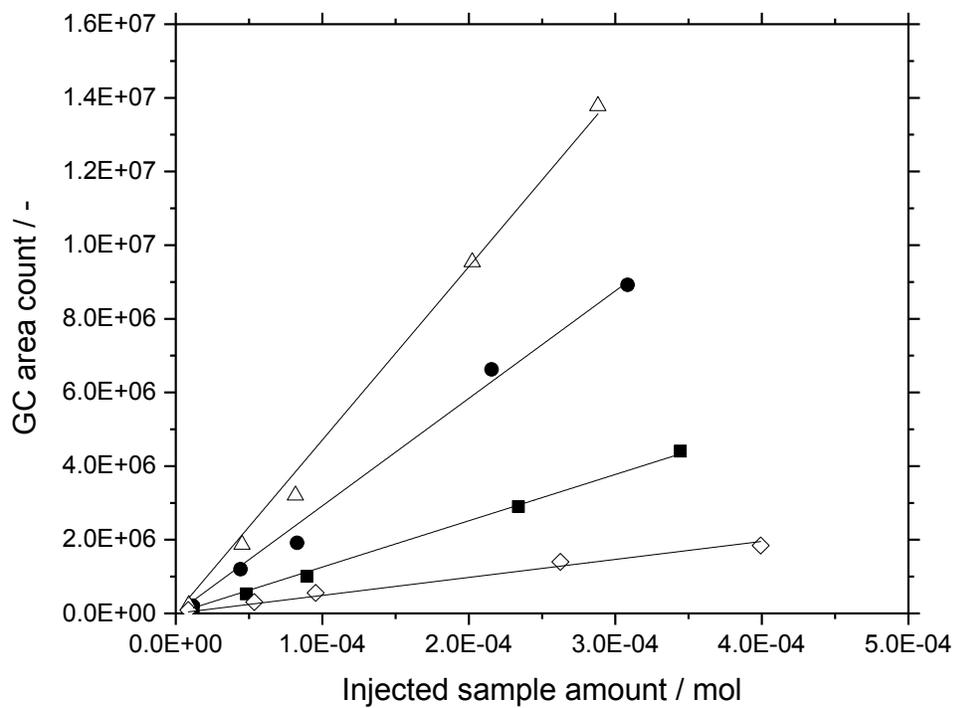


Figure S2. GC area count versus the injected sample amount in mol. Data for vinyl propionate (filled squares), 2-propanol (filled circles), 2-propylpropionate (open triangles) and acetaldehyde (open diamonds) are shown. The fitted lines all intersect in the origin.

Calibration of HPLC pump

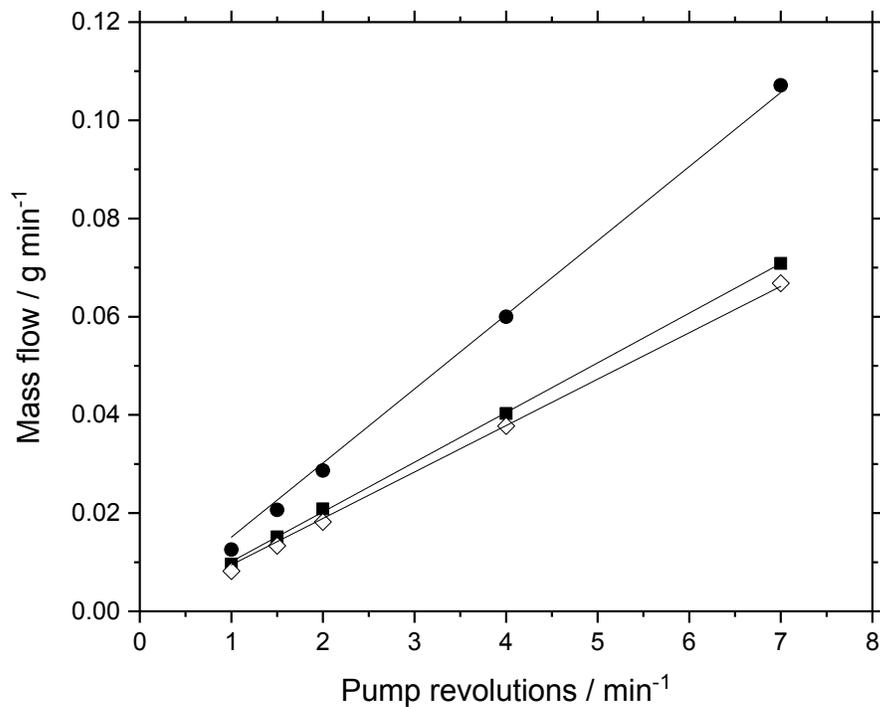


Figure S3. Measured mass flow as a function of HPLC pump revolutions. Data for vinyl propionate (filled squares), 2-propanol (filled circles) and a 1:1 molar mixture (open diamonds) are shown. The fitted lines all intersect in the origin.

Comparison between conversion calculated from bypass and cartridge data

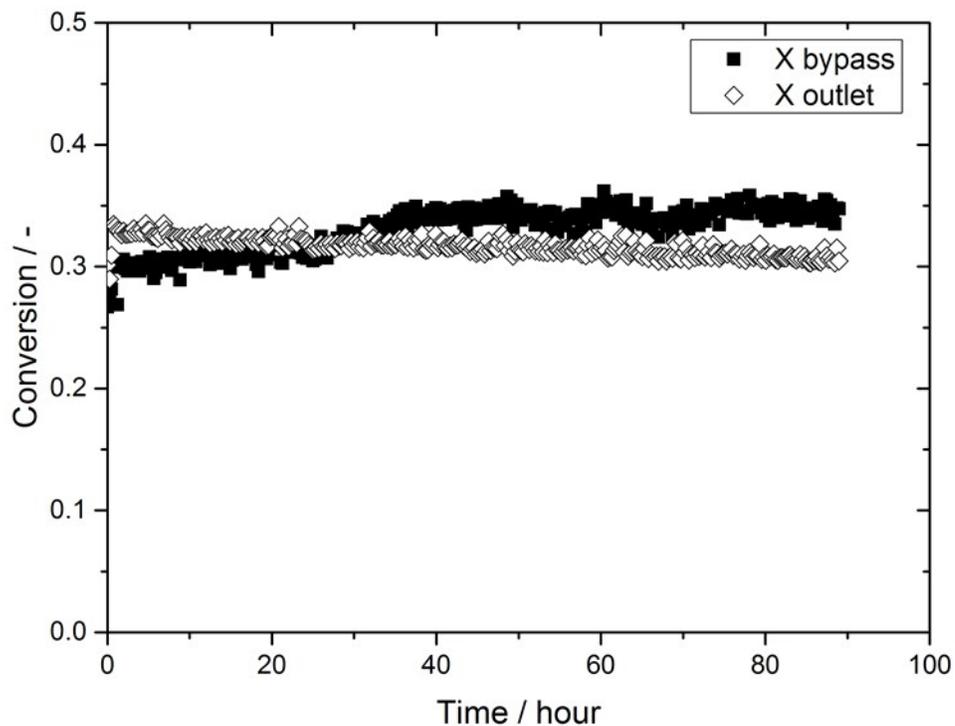


Figure S4. Conversion over time on stream for the CALB e-SILP catalyzed gas-phase transesterification of vinyl propionate with 2-PrOH. Comparison between bypass (filled squares) and cartridge (open diamonds) measurements. Reaction conditions: reactor set temperature 50°C, reactor pressure = 4 bar abs, saturator temperature = 40 °C, molar flow VP = 29.5 $\mu\text{mol min}^{-1}$, molar flow 2-PrOH = 29.5 $\mu\text{mol min}^{-1}$, molar flow N₂ = 3,6 $\mu\text{mol min}^{-1}$, residence time = 48 s.

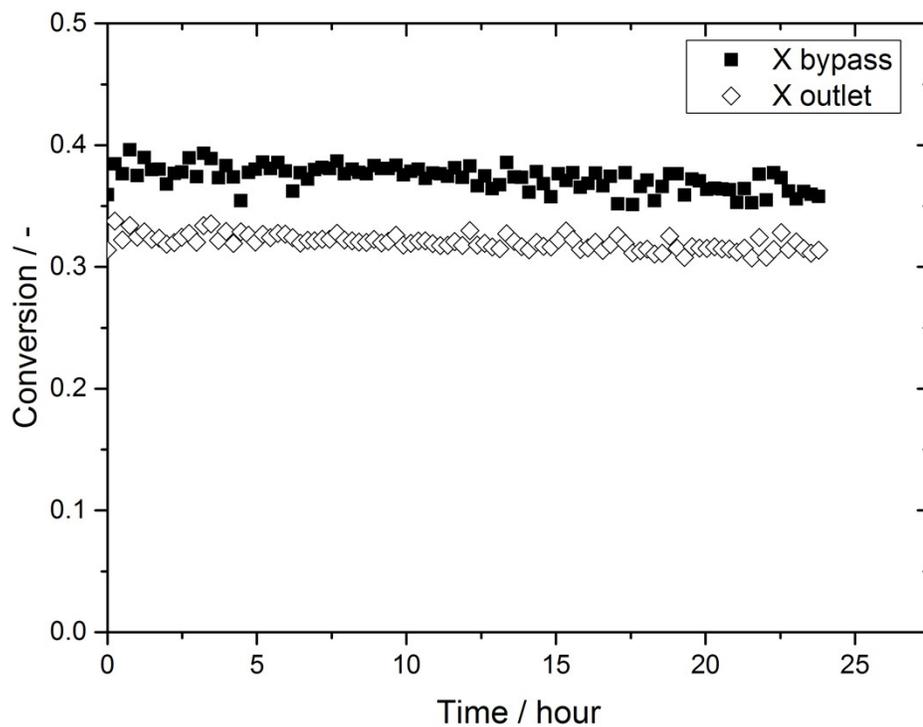


Figure S5. Conversion over time on stream for the CALB e-SILP catalyzed gas-phase transesterification of vinyl propionate with 2-PrOH. Comparison between bypass (filled squares) and cartridge (open diamonds) measurements. Reaction conditions: reactor set temperature 65°C, reactor pressure = 4 bar abs, saturator temperature = 40 °C, molar flow VP = 29.5 $\mu\text{mol min}^{-1}$, molar flow 2-PrOH = 29.5 $\mu\text{mol min}^{-1}$, molar flow N₂ = 3,6 $\mu\text{mol min}^{-1}$, residence time = 48 s.

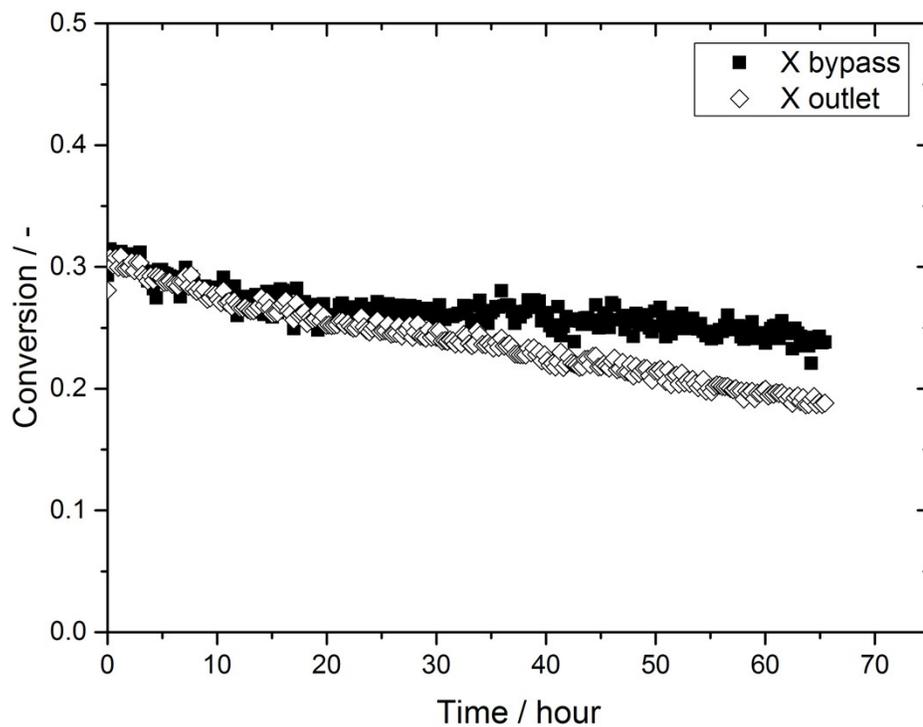


Figure S6. Conversion over time on stream for the CALB e-SILP catalyzed gas-phase transesterification of vinyl propionate with 2-PrOH. Comparison between bypass (filled squares) and cartridge (open diamonds) measurements. Reaction conditions: reactor set temperature 75°C, reactor pressure = 4 bar abs, saturator temperature = 40 °C, molar flow VP = 29.5 $\mu\text{mol min}^{-1}$, molar flow 2-PrOH = 29.5 $\mu\text{mol min}^{-1}$, molar flow N₂ = 3,6 $\mu\text{mol min}^{-1}$, residence time = 48 s.

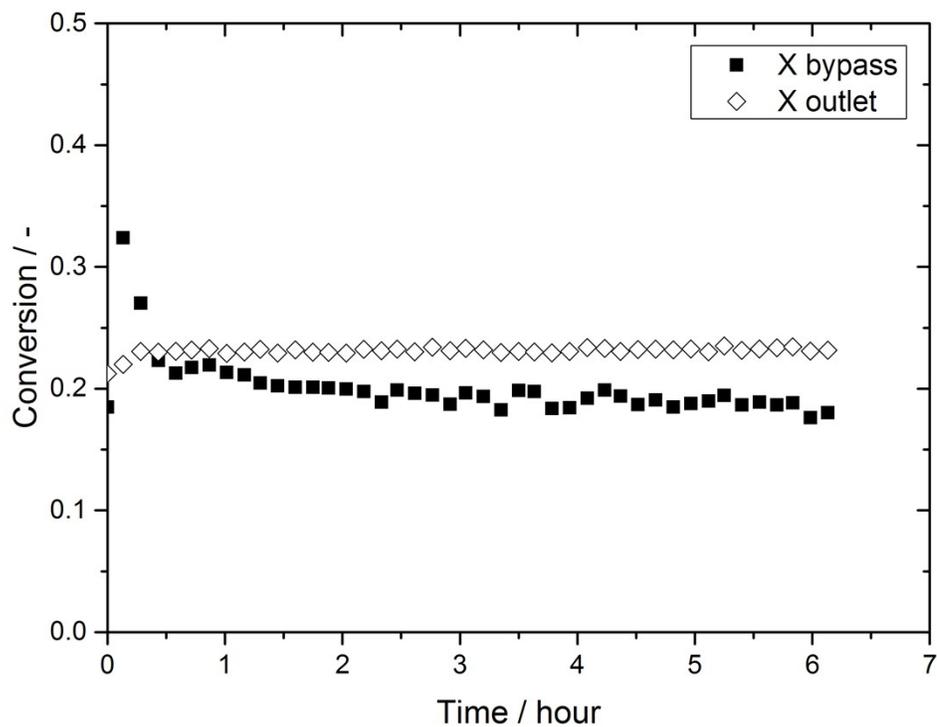


Figure S7. Conversion over time on stream for the CALB e-SILP catalyzed gas-phase transesterification of vinyl propionate with 2-PrOH for the **second cartridge**. Comparison between bypass (filled squares) and cartridge (open diamonds) measurements. Reaction conditions: reactor set temperature 55°C, reactor pressure = 4 bar abs, saturator temperature = 40 °C, molar flow VP = 29.5 $\mu\text{mol min}^{-1}$, molar flow 2-PrOH = 29.5 $\mu\text{mol min}^{-1}$, molar flow N₂ = 3,6 $\mu\text{mol min}^{-1}$, residence time = 48 s.

Effective activation energy for both e-SILP cartridges

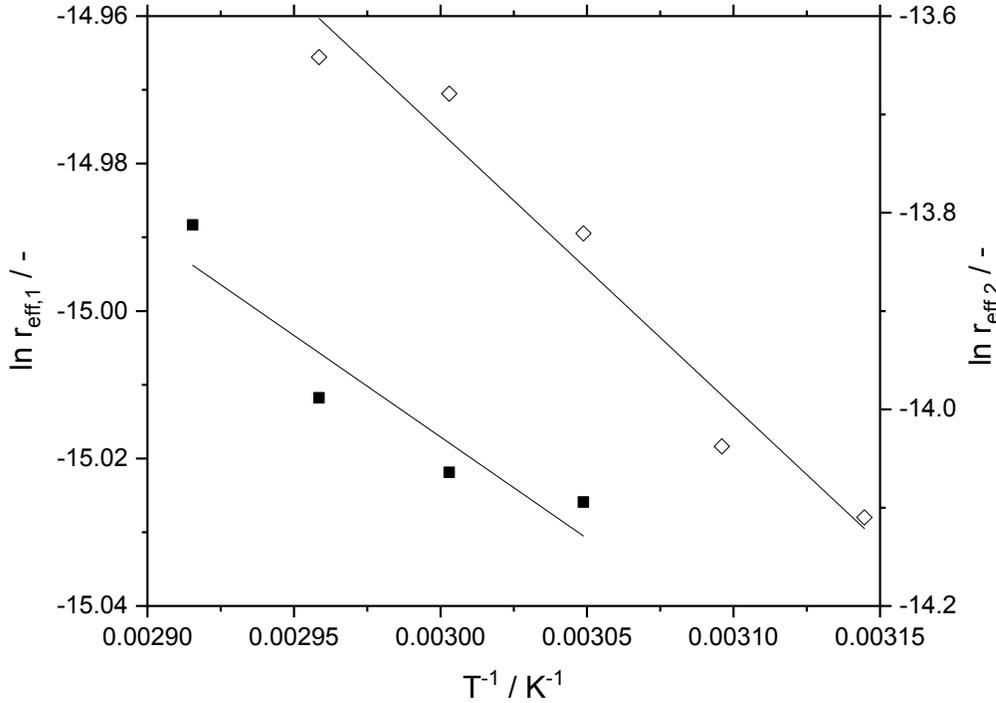


Figure S8. Arrhenius-type diagram for transesterification reaction using the first (filled squares) and second (open diamonds) e-SILP cartridge. Reactor pressure = 4 bar abs, saturator temperature = 40 °C, molar flow VP = 29.5 $\mu\text{mol min}^{-1}$, molar flow 2-PrOH = 29.5 $\mu\text{mol min}^{-1}$, molar flow N_2 = 3,6 $\mu\text{mol min}^{-1}$, residence time = 48 s.

Estimation of the Biot-number of mass for first e-SILP cartridge

The Biot number of mass Bi_m accounts for the relation between film diffusion around the pellet and effective diffusion inside the pellet.

$$Bi_m = \frac{k_f \cdot R}{D_{\text{eff}}} \quad (\text{S1})$$

The radius R of the microglobules was determined to be 2.1 μm . The binary diffusion coefficient D_{12} of 2-PrOH in N_2 was estimated according to the Chapman-Enskog theory to be $3.3 \cdot 10^{-2} \text{ m}^2 \text{ s}^{-1}$. The effective diffusion coefficient D_{eff} was estimated according to Equation (S2).

$$D_{eff} = \frac{\varepsilon \cdot D_{12}}{\tau} \quad (\text{S2})$$

The monolith porosity ε was determined to be 0.5 based on N_2 sorption data. The tortuosity τ was calculated from this porosity to be 2.7 using the Dumansky correlation shown in Equation (S3).

$$\frac{1}{\tau} = 1 - (1 - \varepsilon)^{0.67} \quad (\text{S3})$$

By Equation (S2) the D_{eff} was calculated to be $6.1 \cdot 10^{-3} \text{ m}^2 \text{ s}^{-1}$. In Equation (S1) the film diffusion coefficient k_f can be estimated from the Sherwood number according to Equation (S4).

$$Sh = \frac{k_f \cdot 2R}{D_{12}} \quad (\text{S4})$$

It was assumed that the packing of spherical microglobules inside the monolith allows the calculation of the Sherwood number Sh based on the following correlation (S5) that can be found in engineering textbooks.

$$Sh = 2 + 1.9(Re)^{0.5} (Sc)^{0.333} \quad (\text{S5})$$

The Reynold number Re for the packed-bed monolith was calculated from Equation (S6). The required kinematic viscosity ν of N_2 at 55 $^\circ\text{C}$ and 4 bar was taken from the literature to be $0.77 \text{ m}^2 \text{ s}^{-1}$ and the superficial gas velocity u was calculated from the total volume flow to be $1.55 \cdot 10^{-3} \text{ m} \text{ s}^{-1}$.

$$Re = \frac{2R \cdot u}{\nu \cdot (1 - \varepsilon)} \quad (\text{S6})$$

Thus, a Reynold number of $5.2 \cdot 10^{-9}$ results, indicate of a strong laminar flow regime. The required Schmidt number Sc was calculated from the relation between kinematic viscosity and binary diffusion coefficient to be 23.3 according to Equation (S7).

$$Sc = \frac{\nu}{D_{12}} \quad (S7)$$

Based on the extremely small value for Re , the Sherwood number was then calculated to be 2. This resulted in a film diffusion coefficient k_f of $1.55 \cdot 10^4 \text{ m s}^{-1}$. With this value, the Biot number of mass was calculated to be 5.4. As a rule of thumb, no film diffusion influence occurs when values of Bi_m are larger than 100. Thus, the reaction using the e-SILP monolith seems strongly limited by film diffusion.

Integral kinetic analysis for second e-SILP cartridge

Assuming a first order dependency of the effective reaction rate with substrate concentration, the power rate law in Equation (S8) applies.

$$r_{eff} = -\frac{dc_{VP}}{dt} = k_{eff} \cdot c_{VP} \quad (S8)$$

Integration of Equation (S8) yields the well-known form shown in Equation (S9).

$$\ln\left(\frac{c_{VP}}{c_{VP,0}}\right) = \ln(1 - X_{VP}) = -k_{eff} \cdot t \quad (S9)$$

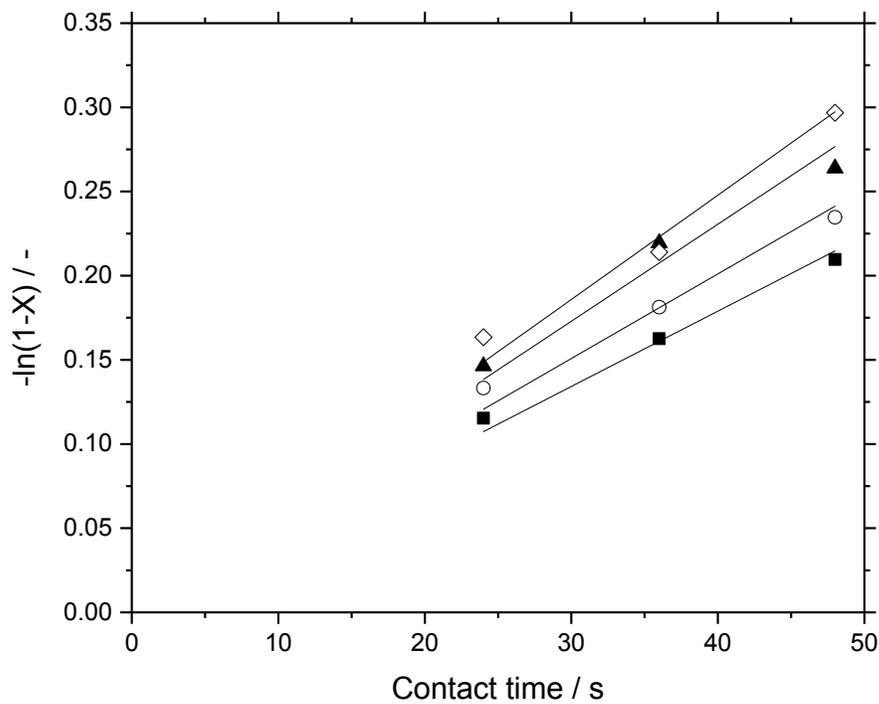


Figure S9. First order k-value determination of second e-SILP cartridge.

Plotting $-\ln(1-X_{VP})$ over the contact time t inside the e-SILP cartridge yields the effective reaction rate constants k_{eff} for each reaction temperature as shown in Figure S8. An Arrhenius-type diagram can be drawn by using these calculated effective reaction rate constants as shown in Figure S10.

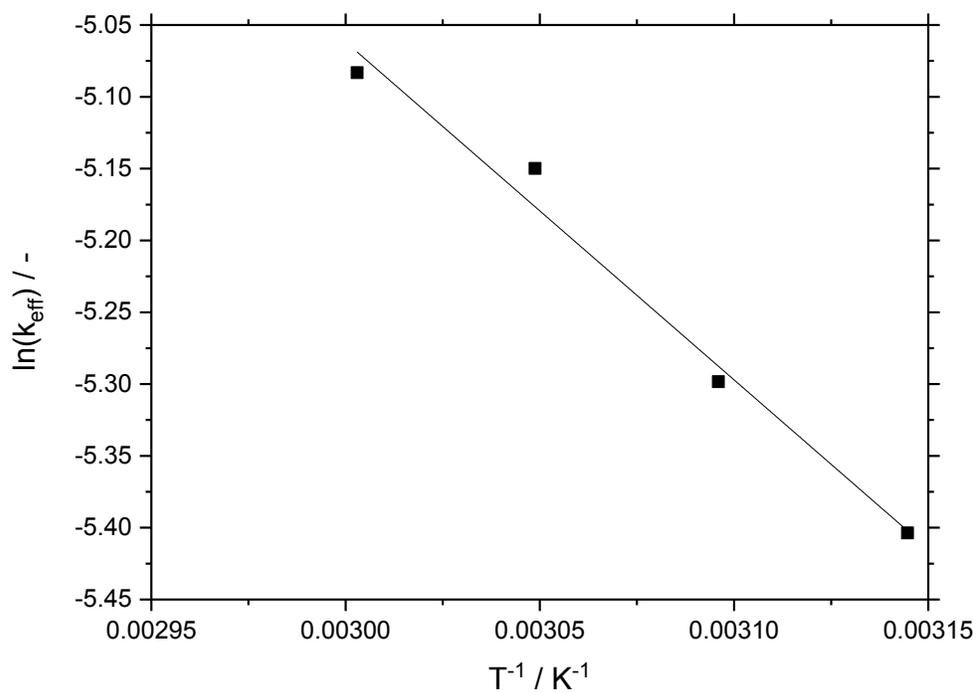


Figure S10. Arrhenius-type diagram for transesterification reaction using the second e-SILP cartridge.

Appearance of e-SILP cartridges after gas-phase reaction

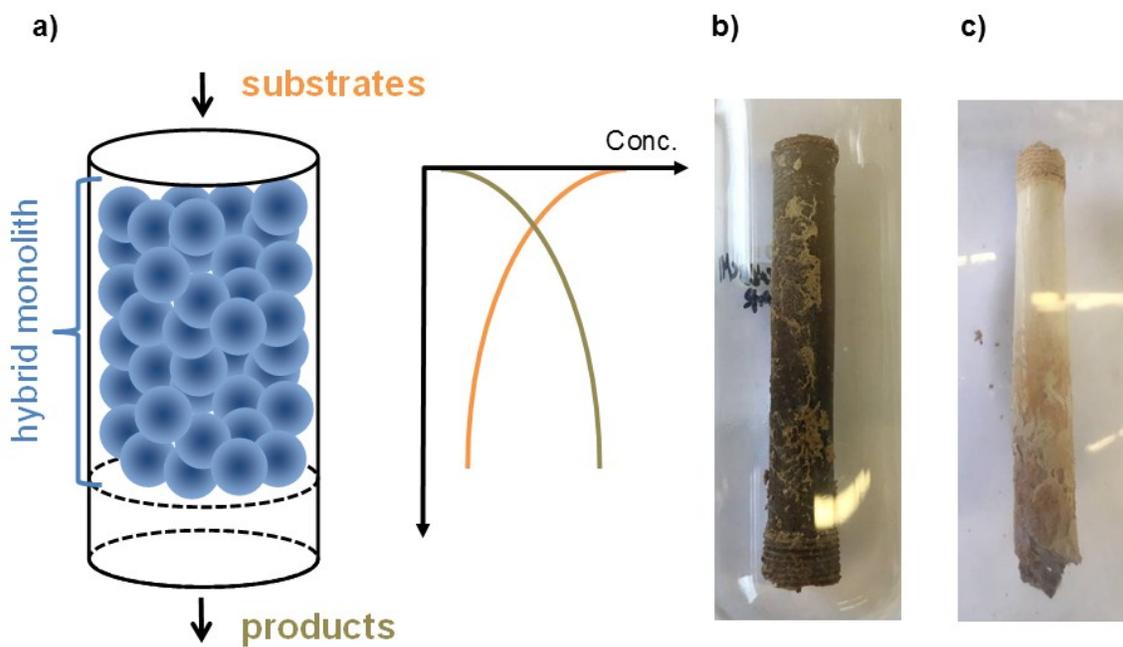


Figure S11. a) Schematic representation of the gas-phase transesterification and the resulting concentration profiles inside the e-SILP monolith; b) first e-SILP monolith after 320 h time on stream; c) second e-SILP monolith after 700 h time on stream.

Thermal stability analysis of the e-SILP cartridge

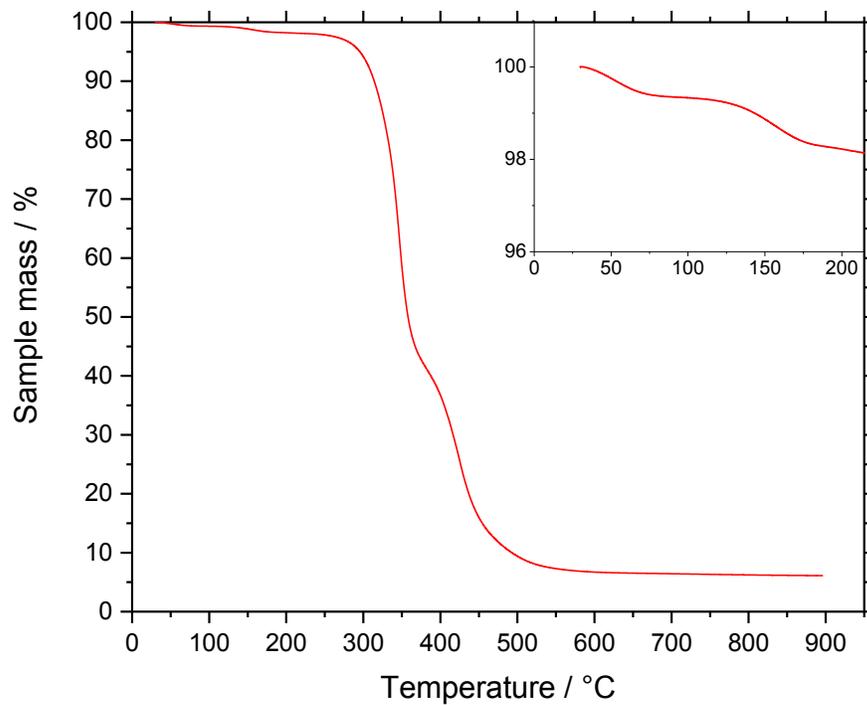


Figure S12. Thermal gravimetric analysis of the e-SILP cartridge. Heating rate $10\text{ }^{\circ}\text{C min}^{-1}$, air flow 50 mL min^{-1} . Insert shows mass loss from room temperature up to $200\text{ }^{\circ}\text{C}$.