

Supporting Information to “Discriminating photochemical and photothermal effects in heterogeneous photocatalysis”

Kinetic derivation

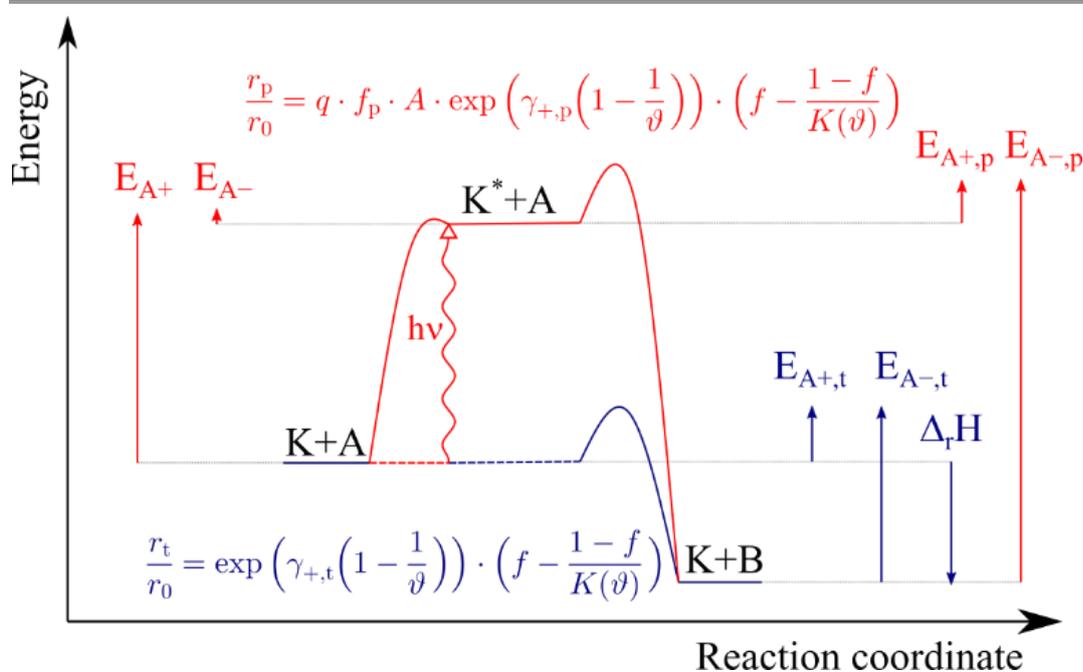


Fig S1: Schematic illustration of the chosen reaction network for the mere thermochemical path (blue) and the photochemical pathway (red).

As Figure S1 illustrates the considered reaction can occur via two routes, a conventional, thermochemical route and a second photochemical route. Via both pathways only one species A is converted into one species B on a catalyst site K. Both routes are described by different types of rate equations but are still governed by the same equilibrium constraints. The individual reactions are also illustrated in table S1.

Table S1: Overview of the assumed generic reactions.

reaction		description
$K + A \rightleftharpoons K + B$	(R1)	Thermochemical target reaction
$K + hv \rightarrow K^*$	(R2)	Excitation of the catalyst
$K^* \rightarrow K$	(R3)	Thermal relaxation of the catalyst
$K^* + A \rightarrow K + B$	(R4)	Photochemical target reaction

Thermochemical reaction rate

The thermochemical reaction is supposed to be affected by equilibrium between forward and backward reaction. For first order reaction kinetics one obtains:

$$r_t = k_{+,t} \cdot c_A + k_{-,t} \cdot c_B \quad (S1)$$

At the reference conditions for the temperature and a gas consisting only of species A this simplifies to

$$r_{t,0} = r_0 = k_{+,t,0} \cdot c_{A,0} + k_{-,t,0} \cdot c_{B,0} = k_0 \cdot c_{A,0} \quad (S2)$$

Assuming further a stoichiometry of one for the conversion of species A to B according to $A \rightarrow B$ eq. (S1) becomes eq. (S3).

$$r_t = k_{+,t} \cdot c_A + k_{-,t} \cdot (c_{A,0} - c_A) \quad (S3)$$

To yield a dimensionless rate, eq. (S3) is divided by eq. (S2) yielding an equation that uses the residual fraction f of species A as only measure for “concentration”.

$$\frac{r_t}{r_0} = \frac{k_{+,t}}{k_0} \cdot f + \frac{k_{-,t}}{k_0} \cdot (1 - f) \quad (S4)$$

The fractions of the kinetic constants for the forward reaction can be expressed with Arrhenius-Law eq. (S5) and converted into dimensionless form, eq. (S6).

$$\frac{k_{+,t}}{k_0} = \frac{k_{\text{ref}} \cdot \exp\left(-\frac{E_{A,+t}}{RT}\right)}{k_{\text{ref}} \cdot \exp\left(-\frac{E_{A,+t}}{RT_0}\right)} = \exp\left(\frac{E_{A,+t}}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right) \quad (S5)$$

$$\frac{k_{+,t}}{k_0} = \exp\left(\gamma_{+,t} \left(1 - \frac{1}{\vartheta}\right)\right) \quad (S6)$$

A similar approach for the backward reaction needs to take in the equilibrium constant, K, and its temperature dependence approximated with a constant heat of reaction, eq. (S7) before the dimensionless fraction of kinetic constants can be formulated, eq. (S8).

$$k_{t,-} = \frac{k_{+,t}}{K} = \frac{k_{t,\text{ref}} \cdot \exp\left(\frac{E_{A,+t}}{RT}\right)}{K_0 \cdot \exp\left(\frac{\Delta_R H}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right)\right)} \quad (S7)$$

$$\frac{k_{-,t}}{k_0} = \frac{k_{+,t}}{k_0 \cdot K} = \frac{\exp\left(\gamma_{+,t} \left(1 - \frac{1}{\vartheta}\right)\right)}{K_0 \cdot \exp\left(\frac{\Delta_R H \cdot c_0}{\rho c_p \cdot T_0} \cdot \frac{\rho c_p}{c_0 \cdot R} \left(\frac{T_0}{T} - \frac{T_0}{T_0}\right)\right)} = \frac{\exp\left((\gamma_{+,t} + \vartheta_{\text{ad}} \cdot C) \left(1 - \frac{1}{\vartheta}\right)\right)}{K_0} \quad (S8)$$

Equations (S6) and (S8) in (S4) lead to the desired dimensionless form on the thermochemical rate equation, eq. (S9).

$$\begin{aligned} \frac{r_t}{r_0} &= f \cdot \exp\left(\gamma_{+,t} \left(1 - \frac{1}{\vartheta}\right)\right) + \frac{(1-f)}{K_0} \cdot \exp\left((\gamma_{+,t} + \vartheta_{\text{ad}} \cdot C) \left(1 - \frac{1}{\vartheta}\right)\right) \\ &= \exp\left(\gamma_{+,t} \left(1 - \frac{1}{\vartheta}\right)\right) \left(f - \frac{(1-f)}{K_0} \exp\left(\vartheta_{\text{ad}} \cdot C \left(1 - \frac{1}{\vartheta}\right)\right)\right) \end{aligned} \quad (S9)$$

The first exponential term adjusts the rate according to the temperature, while the second difference term exhibits the driving potential for the reaction, namely the concentration difference towards equilibrium. Here the minuend is also a function of temperature to ensure a proper dependency of the equilibrium on the temperature.

Photochemical reaction rate

The photochemical rate can be derived from the local volumetric rate of photon absorption and the present concentration of reactant species plus an additional kinetic constant.

$$r_p = k_p \cdot \alpha \cdot \frac{E \cdot \lambda}{N_A \cdot h \cdot c_\lambda} \cdot c_A \quad (S10)$$

To further obtain a dimensionless form eq. (S10) is simply divided by the reference rate already used for the thermochemical reaction rate and expanded with a dimensionless fraction of some quantities.

$$\begin{aligned} \frac{r_p}{r_0} &= \frac{k_p \cdot \alpha \cdot E \cdot \lambda \cdot c_A}{r_0 \cdot N_A \cdot h \cdot c_\lambda} \\ &= \frac{k_p \cdot \lambda}{N_A \cdot h \cdot c_\lambda} \cdot \alpha \cdot \frac{E}{r_0} \cdot c_A \cdot \frac{T_0 \cdot \rho c_p \cdot c_{A,0} \cdot L}{T_0 \cdot \rho c_p \cdot c_{A,0} \cdot L} = \frac{k_p \cdot \lambda \cdot T_0 \cdot \rho c_p}{N_A \cdot h \cdot c_\lambda} \cdot \alpha \cdot L \cdot \frac{E \cdot c_{A,0}}{r_0 \cdot L \cdot T_0 \cdot \rho c_p} \cdot \frac{c_A}{c_{A,0}} \\ &= f_p(T) \cdot A \cdot q \cdot f \end{aligned} \quad (S11)$$

After some regrouping the rate depends on mainly four factors. The first one is still temperature dependent and the last of them is the residual fraction of species A, that does not yet include an equilibrium limitation of the rate.

Therefore, the equation is expanded with a similar term as in eq. (S9) for a temperature dependent driving potential, that includes the adherence towards equilibrium.

$$\frac{r_p}{r_0} = f_p \cdot A \cdot q \cdot \exp\left(\gamma_{+,p} \left(1 - \frac{1}{\vartheta}\right)\right) \left(f - \frac{(1-f)}{K_0} \exp\left(\vartheta_{ad} \cdot C \left(1 - \frac{1}{\vartheta}\right)\right)\right) \quad (S11)$$

Dimensionless parameters

This simulation study uses several dimensionless parameters that were based on several physical properties, which were assigned values of a realistic, expectable range. Only the absorption coefficient was deliberately chosen about an order of magnitude smaller than typical, which was done to yield less skewed results and more even profiles to improve visibility for discussion. This also only makes the behaviour more benign with respect to potential temperature rise. Eventually a further parameter variation includes significantly increased values for the absorbance and thus the absorption coefficient, which are then in line with expectable values. Table S1 shows all physical parameters used.

Table S2: Assumed physical properties of the catalyst, the reaction and additional parameters to define the model

	Symbol	Value	Unit	Description
General	R	8.31446	J mol ⁻¹ K	Universal gas constant
	N_A	6.0221 · 10 ²³	mol ⁻¹	Avogadro constant
	h	6.6261 · 10 ⁻³⁴	J s	Planck constant
	c_λ	2.9979 · 10 ⁸	m s ⁻¹	Speed of light
Reaction	r_0	100	mol m ⁻³ s ⁻¹	Thermochemical rate at gas-catalyst interface
	$E_{A,t}$	80 · 10 ³	J mol ⁻¹	Activation energy, thermochemical
	$E_{A,p}$	80 · 10 ³	J mol ⁻¹	Activation energy, photochemical
	$\Delta_r H$	200 · 10 ³	J mol ⁻¹	Enthalpy of reaction
Catalyst	ρ	1000	kg m ⁻³	Catalyst density
	c_p	1000	J kg ⁻¹ K ⁻¹	Isobaric specific heat capacity
	k	1	W m ⁻¹ K ⁻¹	Thermal conductivity of the catalyst
	D_{eff}	10 ⁻⁶	m ² s ⁻¹	Effective diffusion coefficient
	L	548 · 10 ⁻⁶	m	Thickness of the catalyst
Boundary	$c_{A,0}$	30	Mol m ⁻³	Surface concentration of reactant A
	T_0	500	K	Temperature of gas and wall
	h_{gas}	100	W m ⁻² K ⁻¹	Heat exchange coefficient at gas-catalyst interface
	h_{wall}	5 · 10 ⁴	W m ⁻² K ⁻¹	Heat exchange coefficient at catalyst-wall interface
	E_0	10 ⁴	W	Irradiance at gas-catalyst interface
Photo	λ	365	nm	Wavelength of light
	η_λ	1	-	Quantum efficiency
	α	7300	m ⁻¹	Absorption coefficient of the catalyst
	$k_{+,p,0}$	1.64 · 10 ⁻²	m ³ mol ⁻¹	Kinetic constant for the photochemical reaction

The assigned values were then selected to obtain dimensionless numbers for the reference case. In some case rounded values were used instead of the accurate number purely to yield more neat numbers. These are shown in table S2.

Table S3: Definition of the dimensionless numbers and the assumed values

Variable name	Equation	Reference Values
Thiele Modulus	$\Phi_0 = \sqrt{\frac{r_0}{D_{\text{eff}} \cdot c_{A,0}}} \cdot L$	$\Phi_0 = \sqrt{\frac{1000 \frac{\text{mol}}{\text{m}^3 \text{s}}}{1^{-6} \frac{\text{m}^2}{\text{s}} \cdot 30 \frac{\text{mol}}{\text{m}^3}}} \cdot 548 \mu\text{m} \approx 1$
Lewis number	$Le = \frac{k}{\rho \cdot c_p \cdot D_{\text{eff}}}$	$Le = \frac{1 \frac{\text{W}}{\text{mK}}}{1000 \frac{\text{kg}}{\text{m}^3} \cdot 1 \frac{\text{kJ}}{\text{kg K}} \cdot 10^{-6} \frac{\text{m}^2}{\text{s}}} = 1$
Biot number at gas boundary	$Bi_{\text{gas}} = \frac{h_{\text{gas}} \cdot L}{k}$	$Bi_{\text{gas,ref}} = \frac{100 \frac{\text{W}}{\text{m}^2 \text{K}} \cdot 548 \mu\text{m}}{1 \frac{\text{W}}{\text{mK}}} = 0.055 \approx 0.05$
Biot number at wall boundary	$Bi_{\text{wall}} = \frac{h_{\text{wall}} \cdot L}{k}$	$Bi_{\text{gas,ref}} = \frac{50000 \frac{\text{W}}{\text{m}^2 \text{K}} \cdot 548 \mu\text{m}}{1 \frac{\text{W}}{\text{mK}}} = 27.4 \approx 25$
Dimensionless adiabatic temperature increase	$\vartheta_{\text{ad}} = \frac{c_{A,0} \cdot (-\Delta_r H)}{T_0 \cdot \rho \cdot c_p}$	$\vartheta_{\text{ad}} = \frac{30 \frac{\text{mol}}{\text{m}^3} \cdot 200 \frac{\text{kJ}}{\text{mol}}}{500 \text{K} \cdot 1000 \frac{\text{kg}}{\text{m}^3} \cdot 1 \frac{\text{kJ}}{\text{kg K}}} = 0.012 \approx 0.01$
Arrhenius number	$\gamma_{+,t/p} = \frac{E_{A,+,t/p}}{RT_0}$	$\gamma = \frac{80 \frac{\text{kJ}}{\text{mol}}}{8.314 \frac{\text{J}}{\text{mol K}} \cdot 500 \text{K}} = 19.24 \approx 20$
Auxiliary thermodynamic constant	$C = \frac{\rho \cdot c_p}{R \cdot c_{A,0}}$	$C = \frac{1000 \frac{\text{kg}}{\text{m}^3} \cdot 1 \frac{\text{kJ}}{\text{kg K}}}{8.314 \frac{\text{J}}{\text{mol K}} \cdot 30 \frac{\text{mol}}{\text{m}^3}} = 4009.3 \approx 4000$
Dimensionless light intensity	$q_{\text{ref}} = \frac{E_0 \cdot c_{A,0}}{L \cdot r_0 \cdot T_0 \cdot \rho \cdot c_p}$	$q_{\text{ref}} = \frac{10^4 \frac{\text{W}}{\text{m}^2} \cdot 30 \frac{\text{mol}}{\text{m}^3}}{548 \mu\text{m} \cdot 100 \frac{\text{mol}}{\text{m}^3 \text{s}} \cdot 500 \text{K} \cdot 1000 \frac{\text{kg}}{\text{m}^3} \cdot 1 \frac{\text{kJ}}{\text{kg K}}} \approx 0.01$
Photo activity factor	$f_p = \frac{\lambda \cdot \eta_\lambda \cdot T_0 \cdot \rho \cdot c_p \cdot k_{+,p,0}}{N_A \cdot h \cdot c_\lambda}$	$f_p = \frac{365 \text{nm} \cdot 1 \cdot 500 \text{K} \cdot 1000 \frac{\text{kg}}{\text{m}^3} \cdot 1 \frac{\text{kJ}}{\text{kg K}} \cdot 1.639 \cdot 10^{-2} \frac{\text{m}^3}{\text{mol}}}{6.022 \cdot 10^{23} \frac{1}{\text{mol}} \cdot 6.625 \cdot 10^{-34} \text{Js} \cdot 2,998 \cdot 10^{-34} \frac{\text{m}}{\text{s}}} = 25$
Absorbance, optical thickness	$A_{\text{ref}} = \alpha \cdot L$	$A_{\text{ref}} = 7300 \frac{1}{\text{m}} \cdot 548 \mu\text{m} \approx 4$

Reaction rates of photo-active catalysts for a non-exothermal reaction

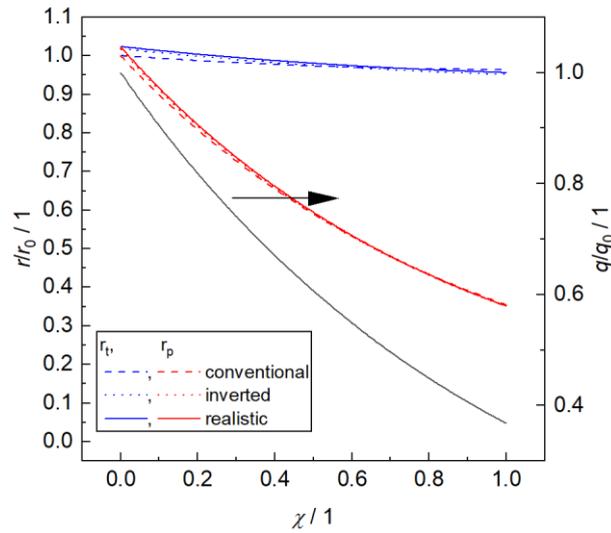


Fig. S2: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 0.25, \vartheta_{ad} = 0$

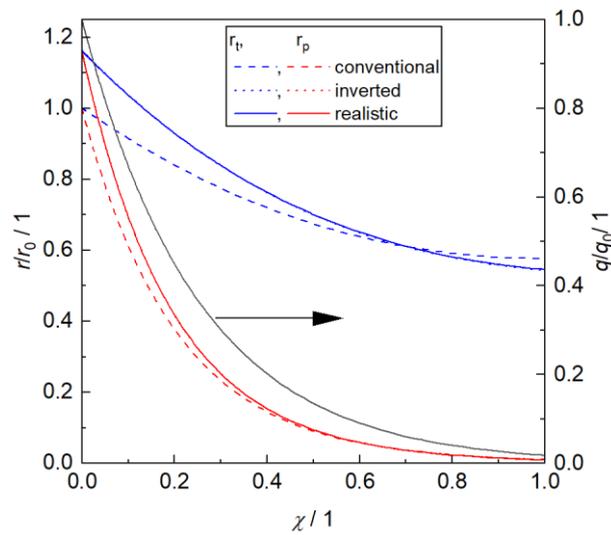


Fig. S3: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 1, \vartheta_{ad} = 0$

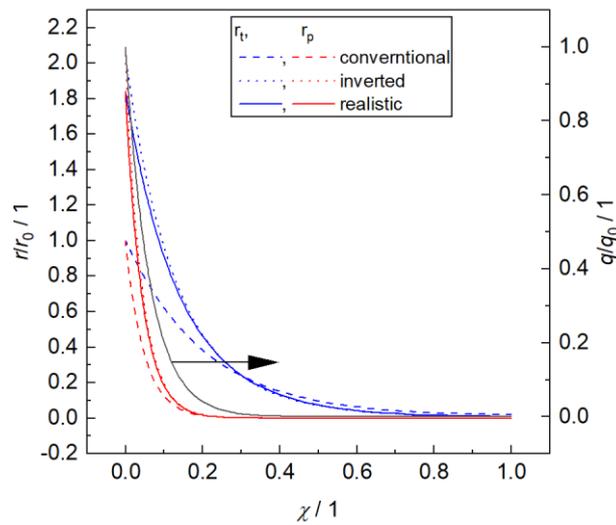


Fig. S4: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 4, \vartheta_{ad} = 0$

Reaction rates of photo-active catalysts for an exothermal reaction

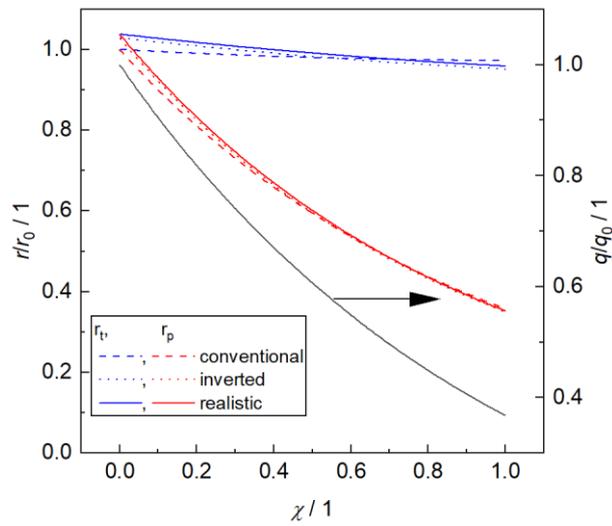


Fig. S5: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 0.25, \vartheta_{ad} = 0.01$

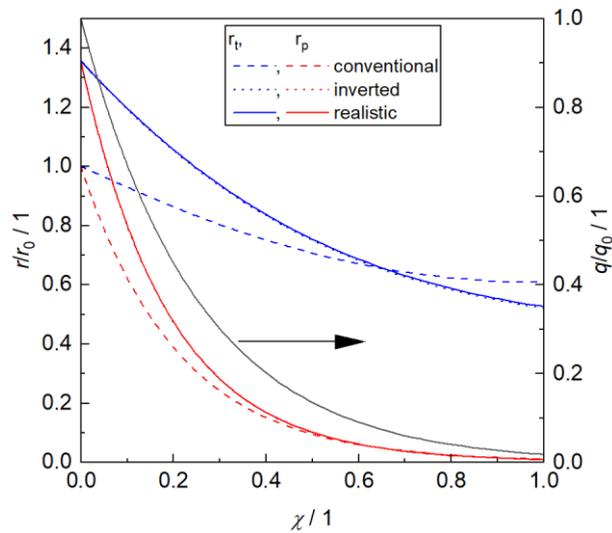


Fig. S6: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 1, \vartheta_{ad} = 0.01$

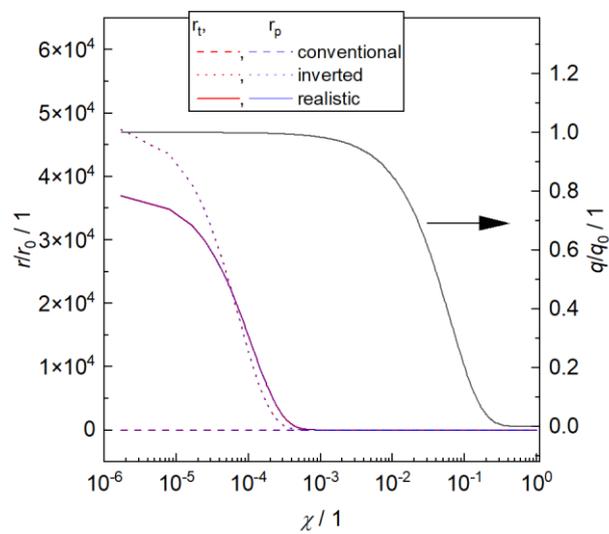


Fig. S7: Rates of thermochemical and photochemical reaction and relative light intensity as function of layer coordinate; $\Phi = 4, \vartheta_{ad} = 0.01$

Equilibrium values

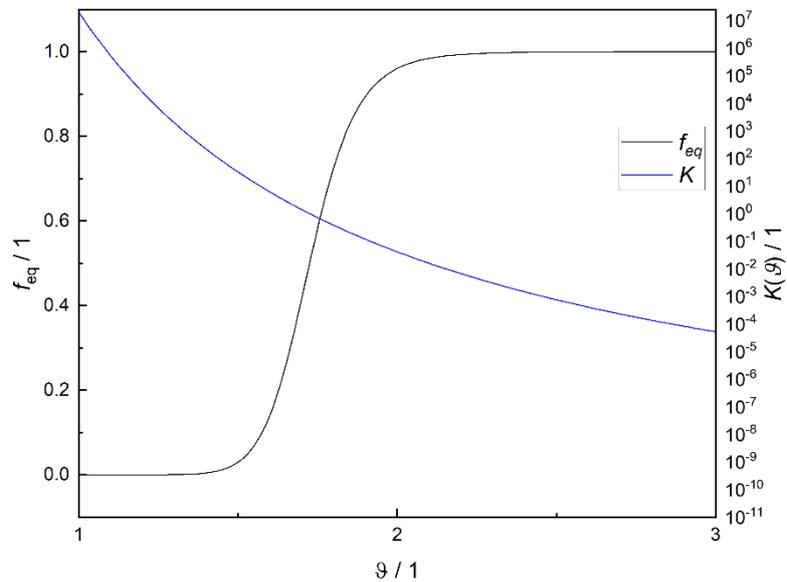


Fig. S8: Residual fraction in equilibrium and corresponding equilibrium constant as function of the dimensionless temperature.

Comparison of residual fraction and equilibrium value for a non-exothermal reaction

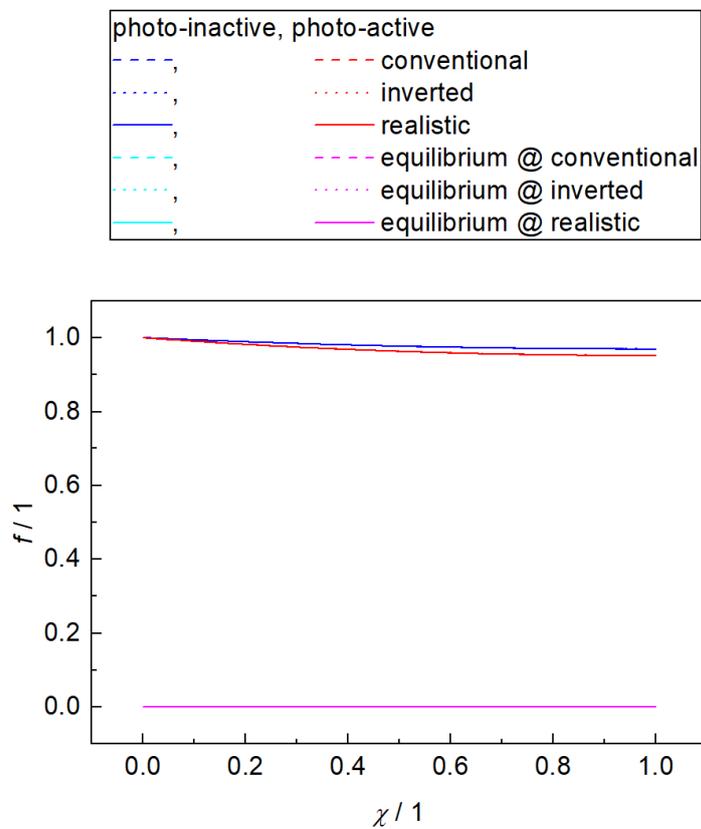


Fig. S9: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 0.25, \vartheta_{ad} = 0$

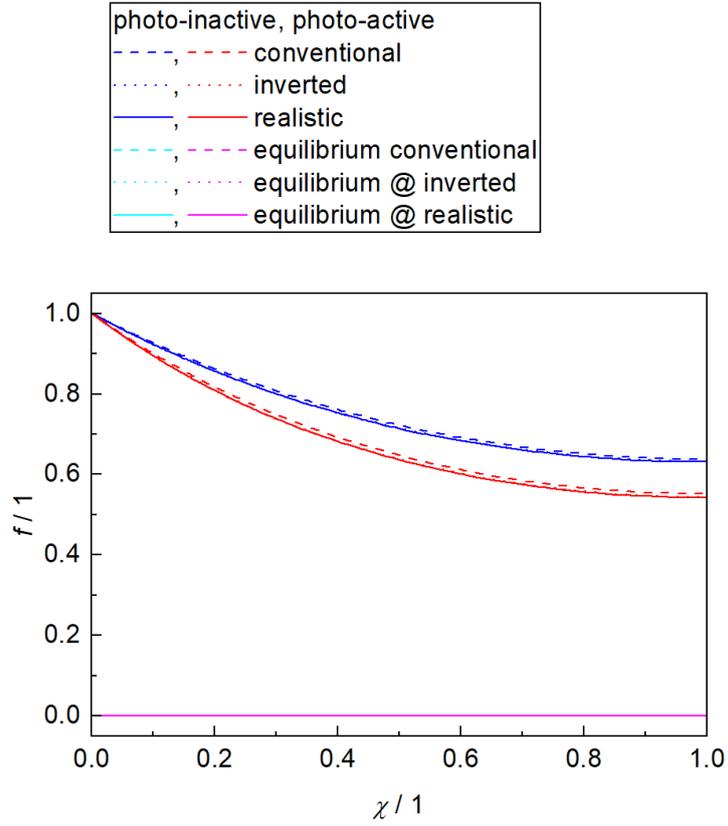


Fig. S10: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 1, \vartheta_{ad} = 0$

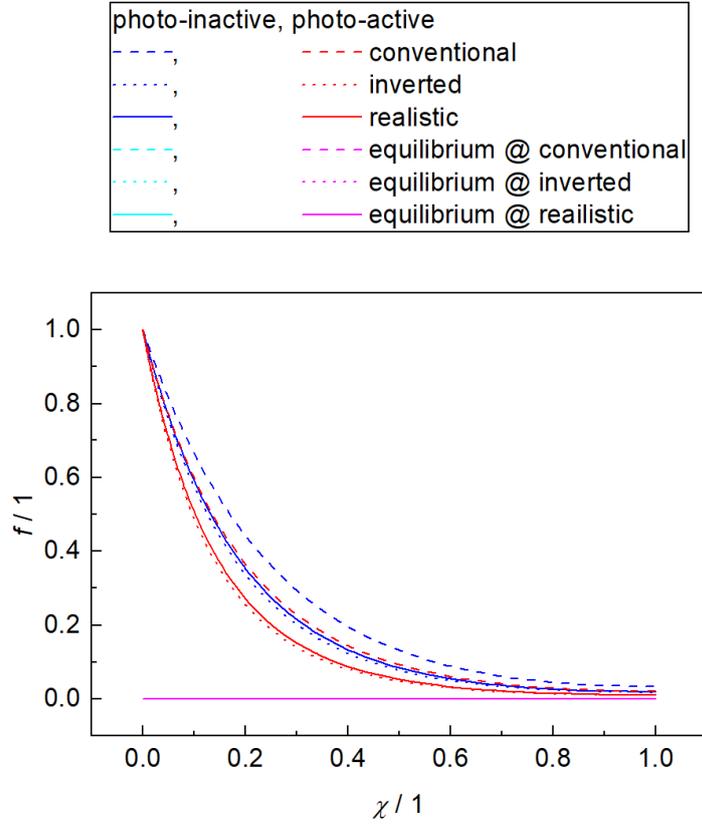


Fig. S11: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 4, \vartheta_{ad} = 0$

Comparison of residual fraction and equilibrium value for an exothermal reaction

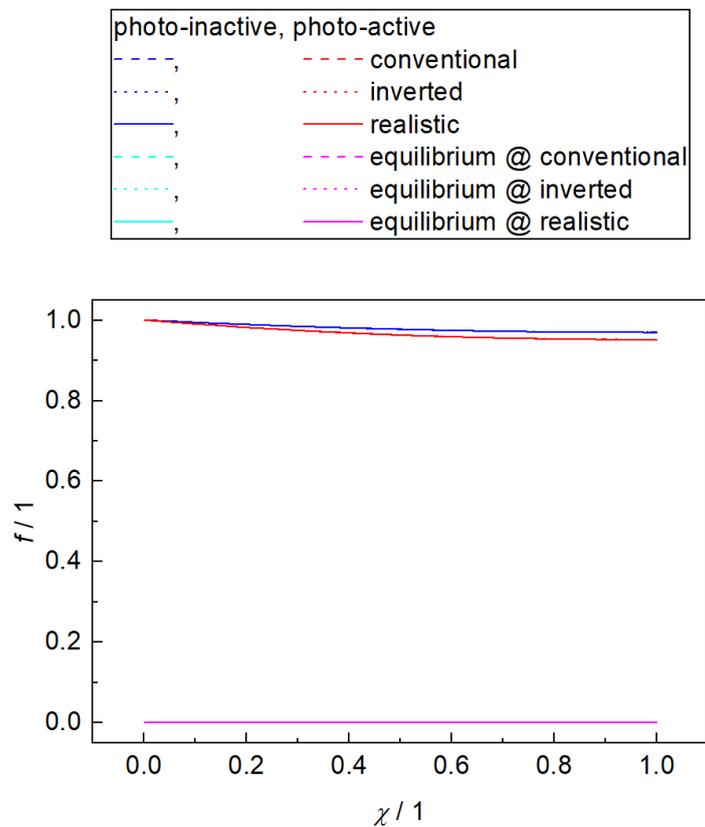


Fig. S12: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 0.25, \vartheta_{ad} = 0.01$

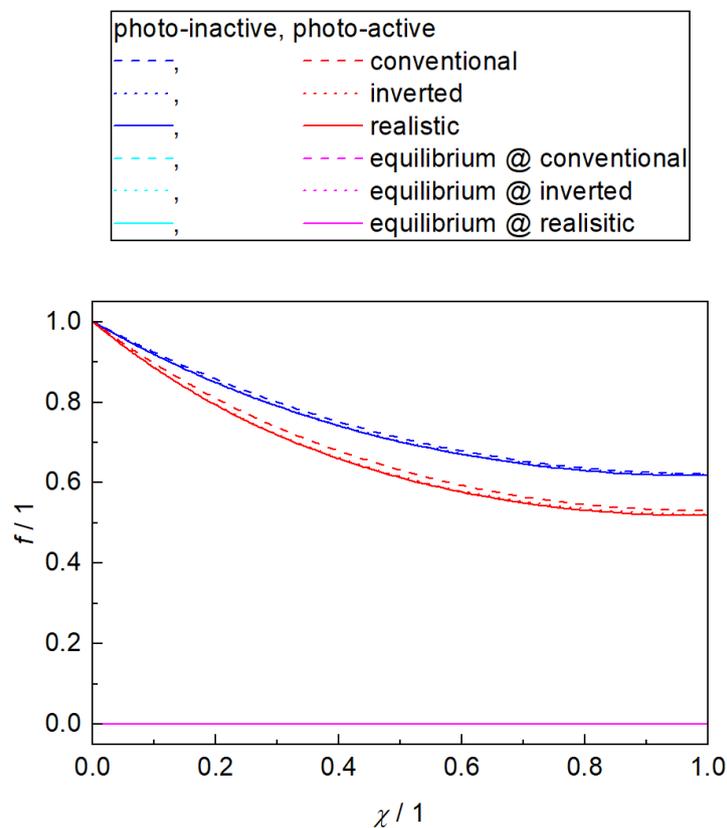


Fig. S13: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 1, \vartheta_{ad} = 0.01$

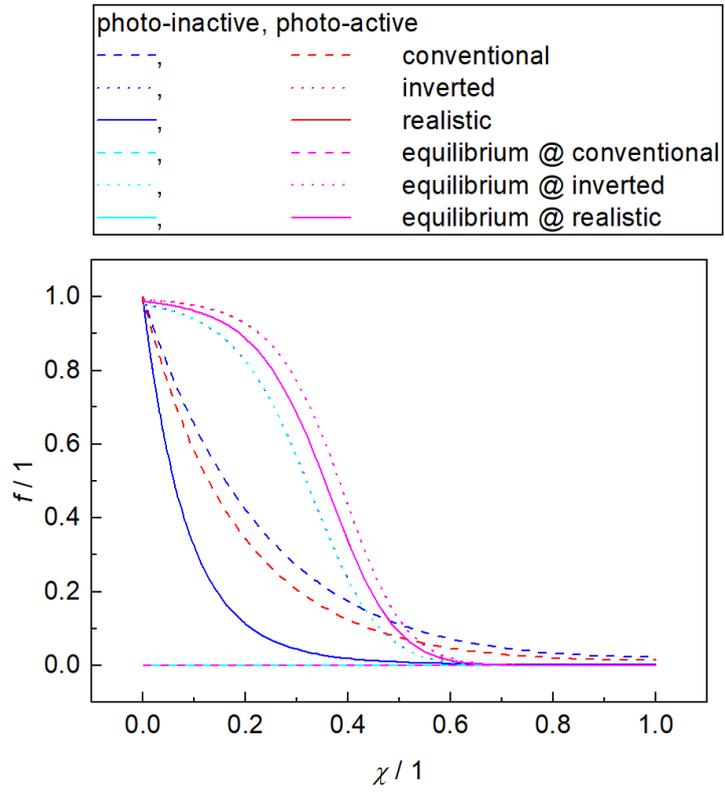


Fig. S14: Residual fraction and equilibrium value as function of layer coordinate; $\Phi = 4, \vartheta_{ad} = 0.01$

Integral Profiles – Variation of light intensity

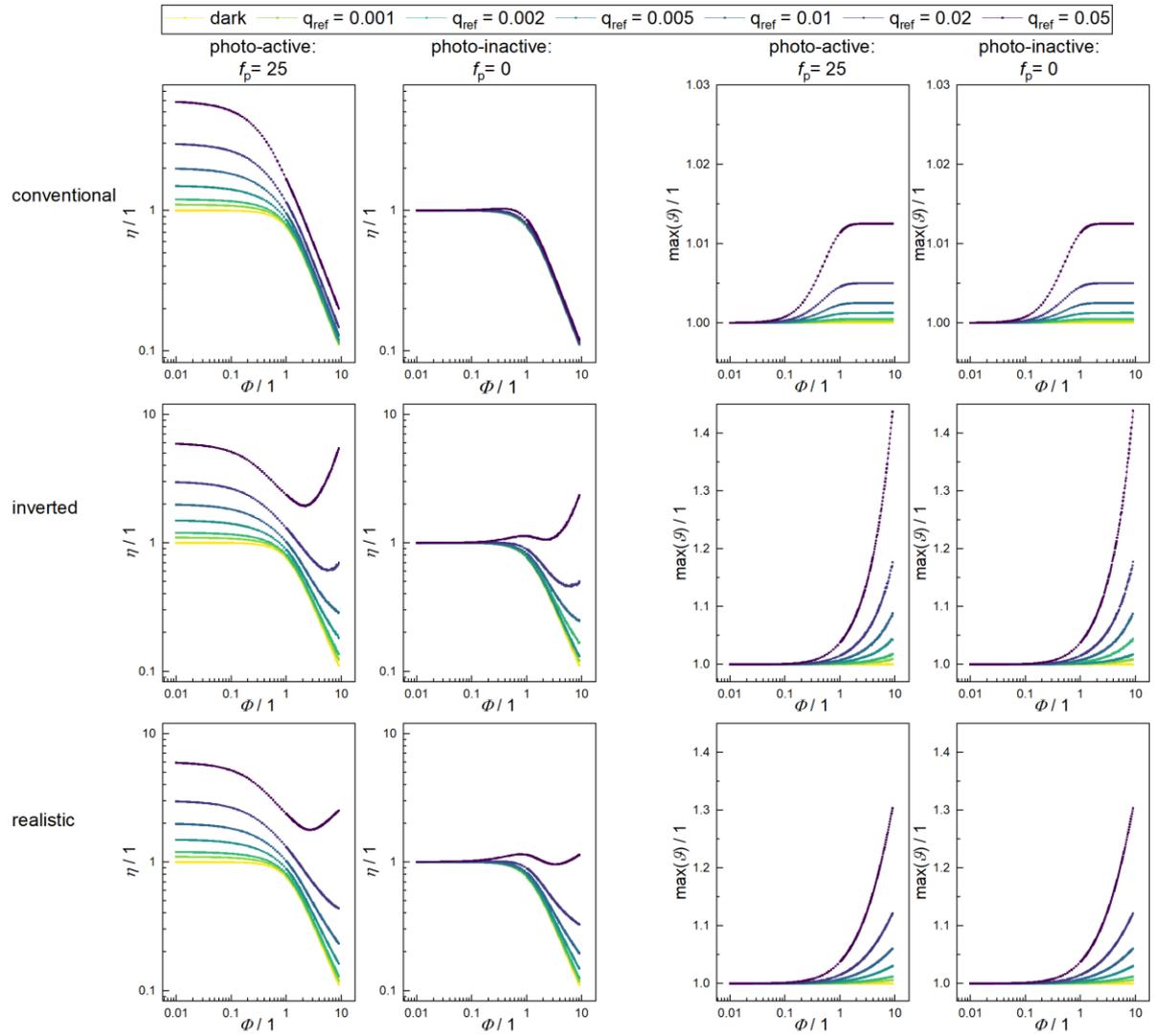


Fig. S15: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for conventional (top row), inverted (middle row) and realistic boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent various intensities of light; $\vartheta_{ad} = 0$.

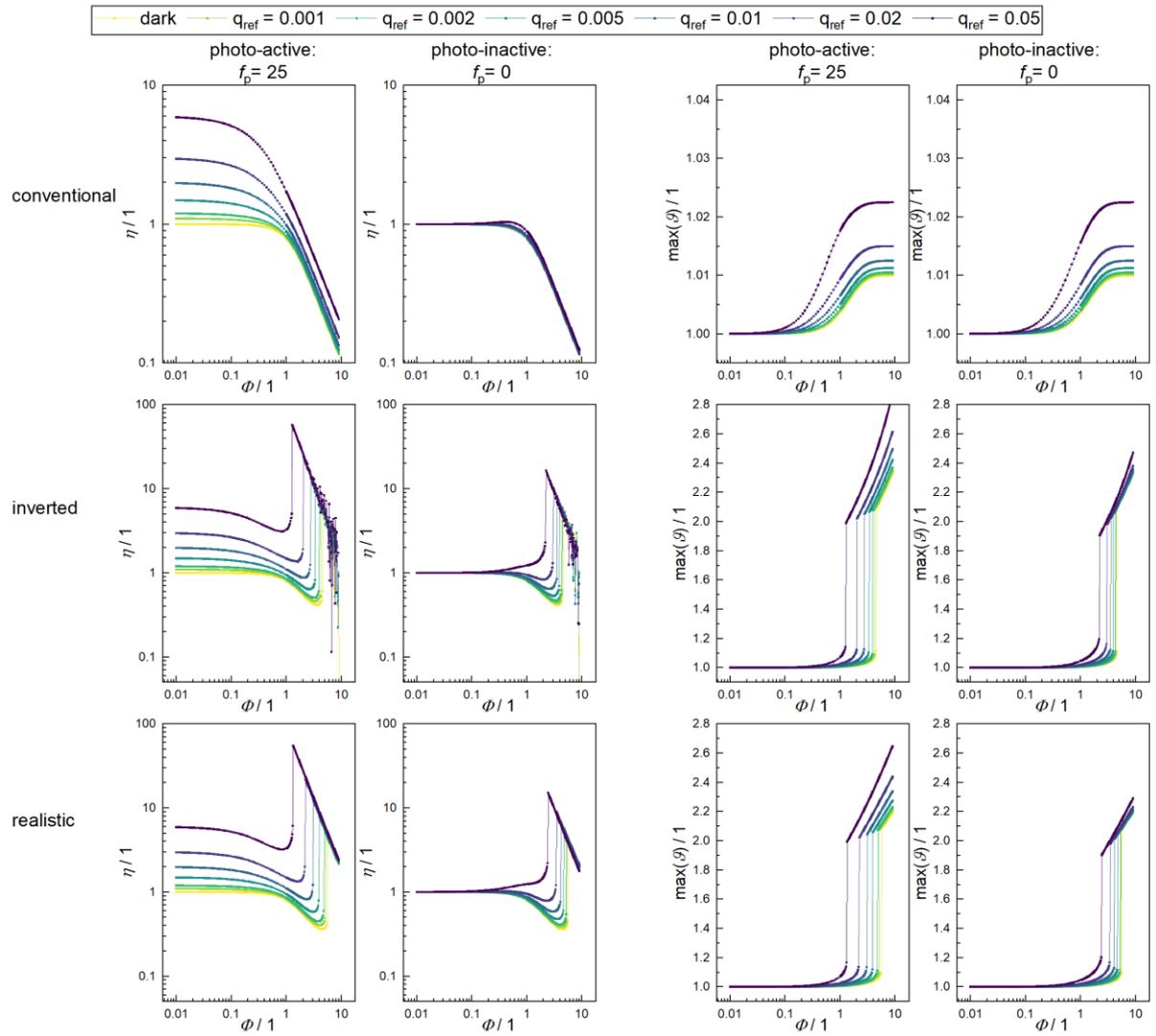


Fig. S16: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for conventional (top row), inverted (middle row) and realistic boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent various intensities of light; $\vartheta_{ad} = 0.01$.

Integral Profiles – Variation of light absorption

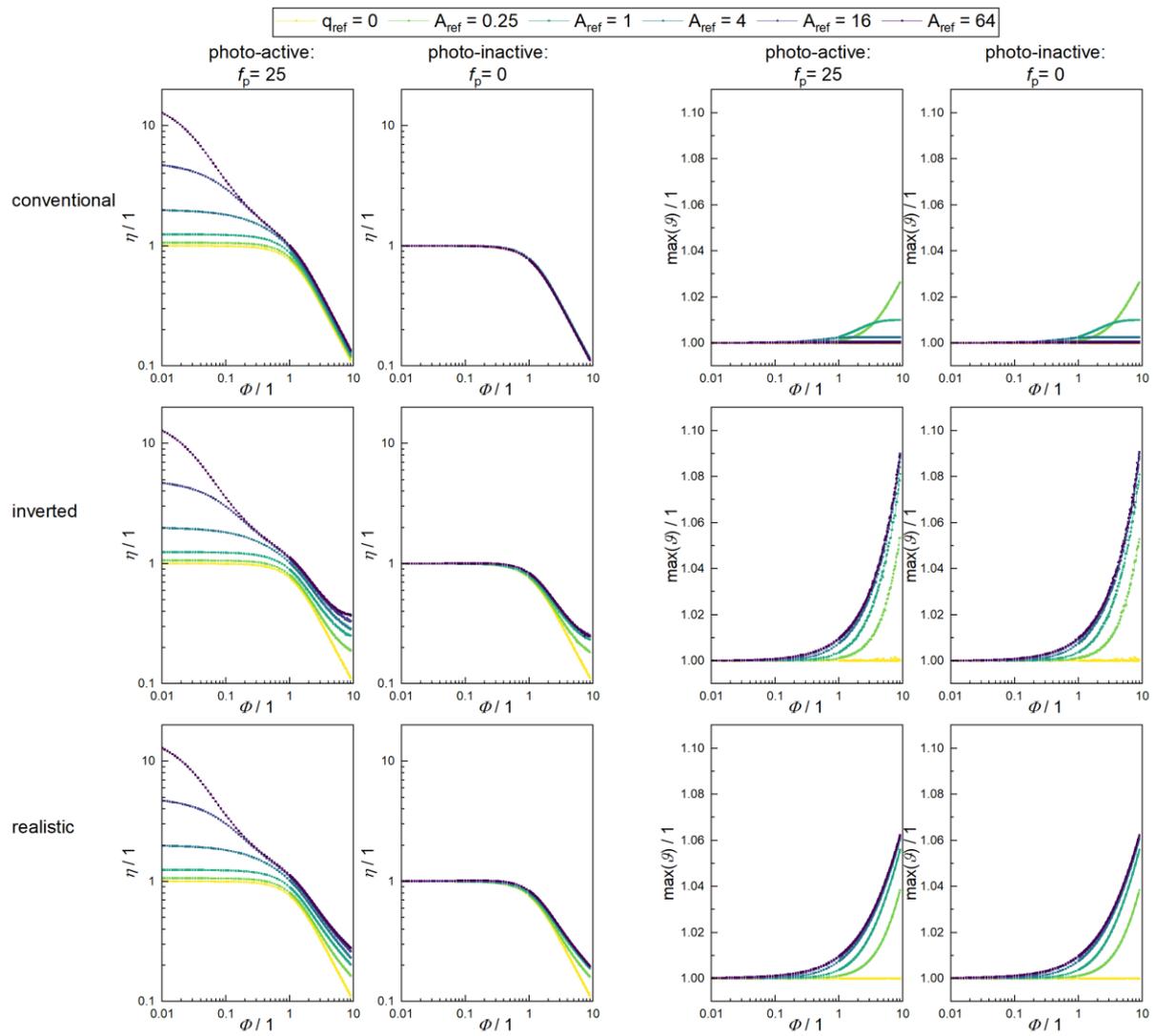


Fig. S17: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for conventional (top row), inverted (middle row) and realistic boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent various dimensionless absorption coefficients; $\vartheta_{\text{ad}} = 0$.

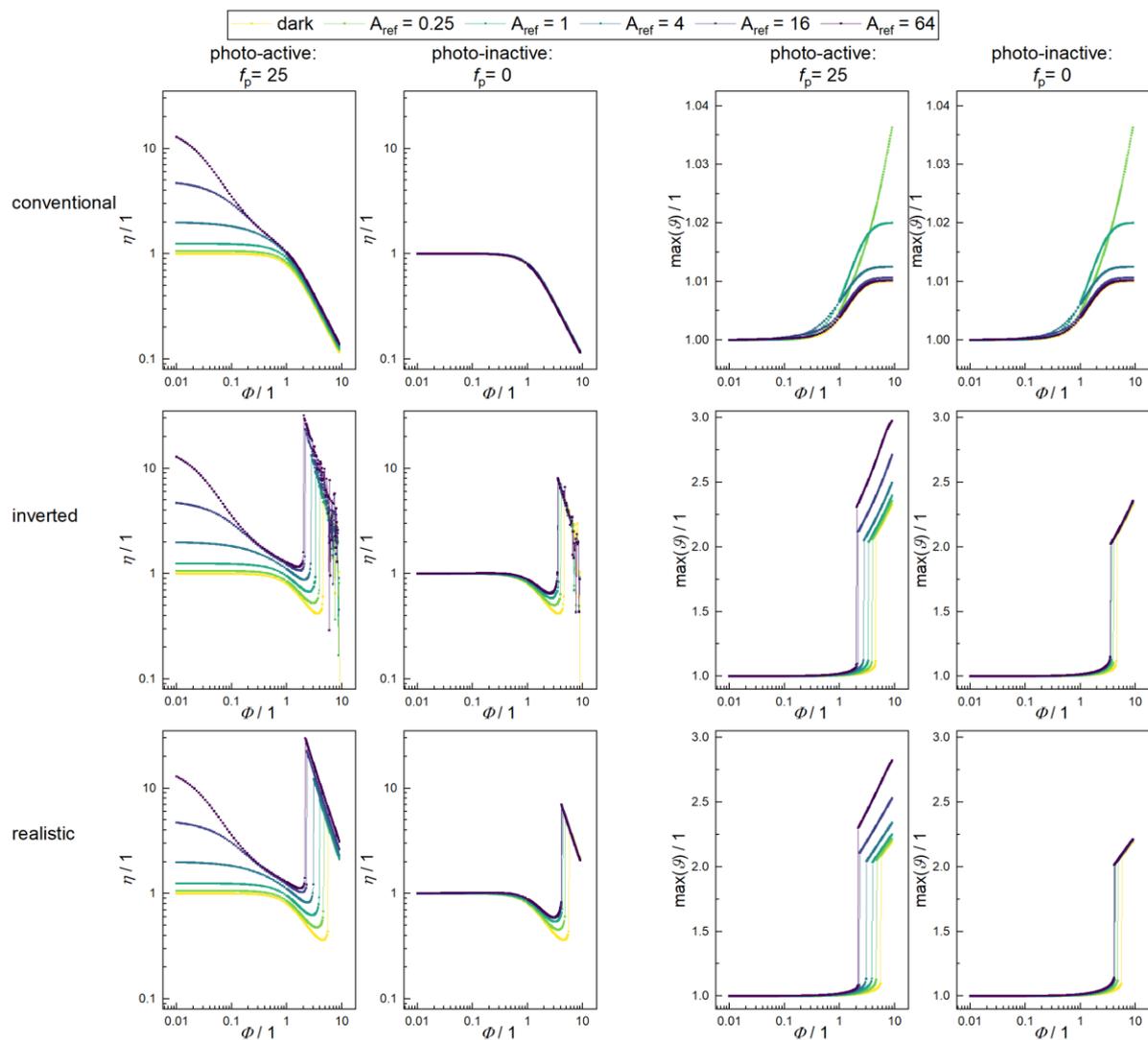


Fig. S18: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for conventional (top row), inverted (middle row) and realistic boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent various dimensionless absorption coefficients; $\vartheta_{ad} = 0.01$.

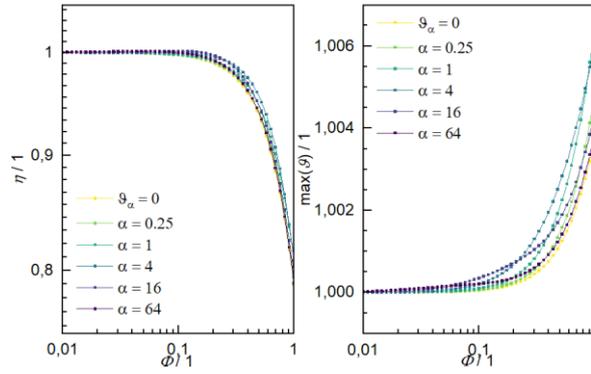


Fig. S19: Catalyst efficiency (left) and maximum observed temperature (right) as function of Thiele modulus, representing layer thickness, for conventional boundary conditions and a photo-inactive catalyst. Set of curves represent various dimensionless absorption coefficients; focus on low to medium values of Φ ; $\vartheta_{ad} = 0.01$.

Integral Profiles – Variation of the Lewis number

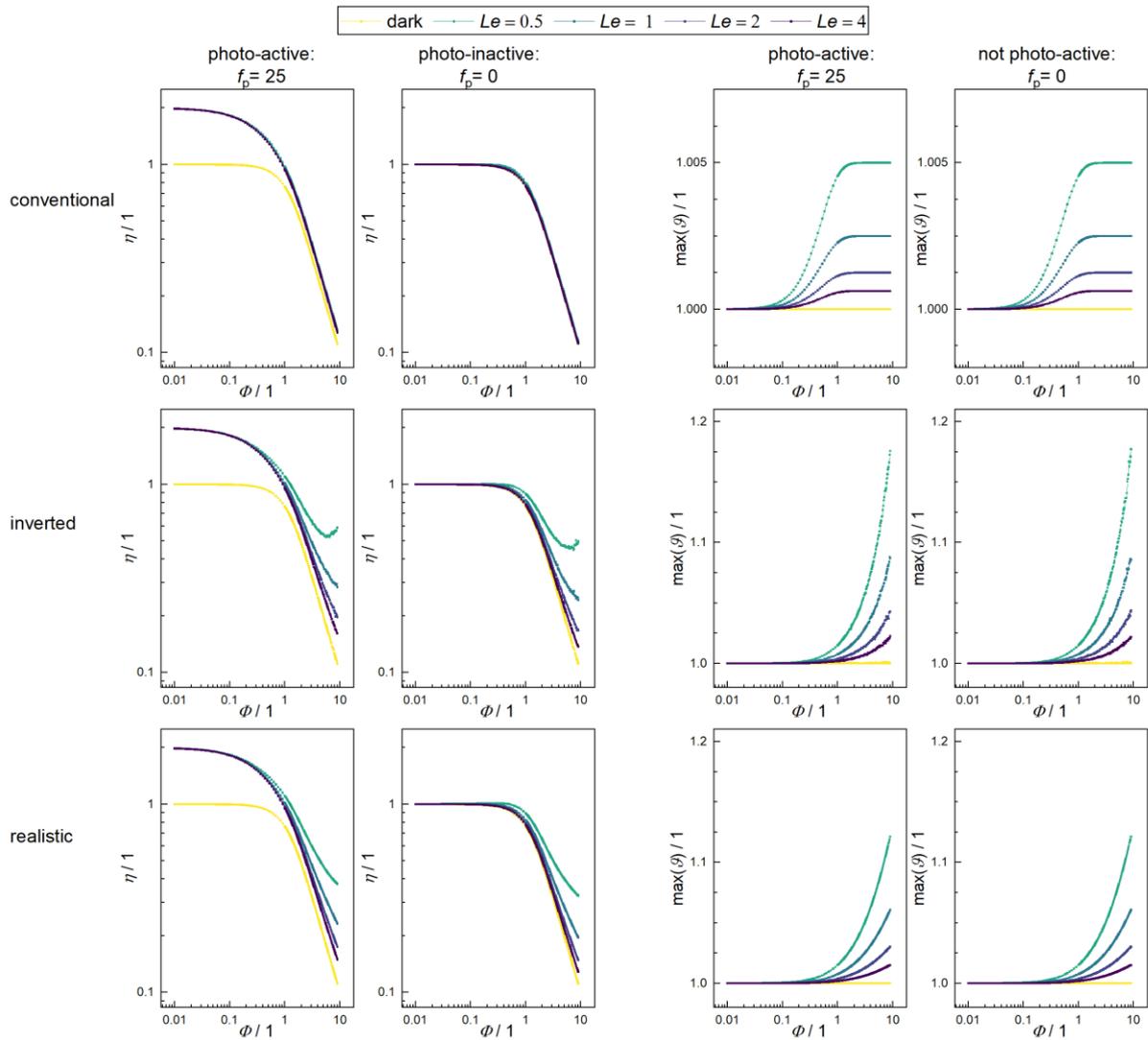


Fig. S20: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for realistic (top row) inverted (middle row) and conventional boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent different Lewis numbers; $\vartheta_{ad} = 0$.

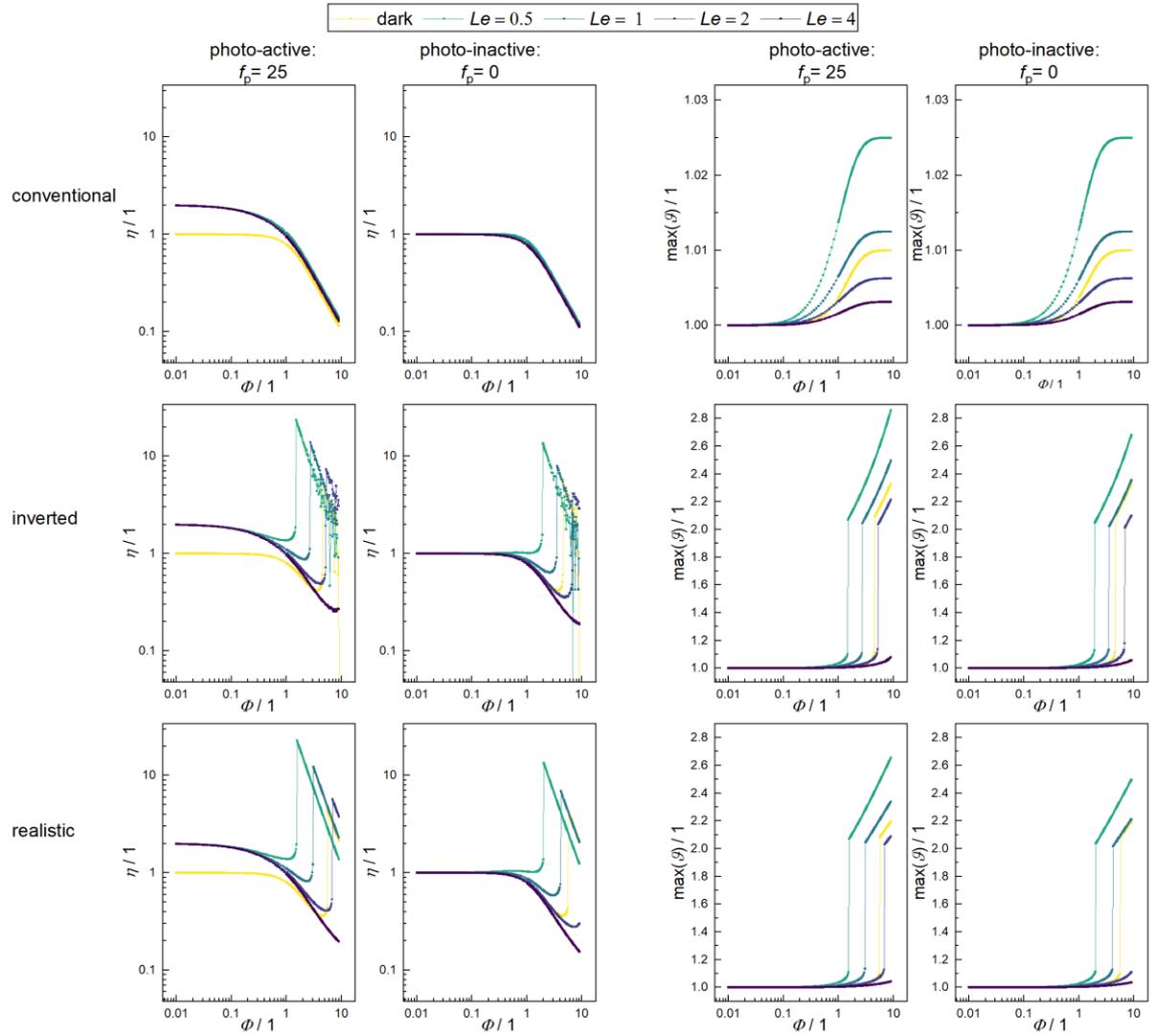


Fig. S21: Catalyst efficiency (left block) and maximum observed temperature (right block) as function of Thiele modulus, representing layer thickness, for realistic (top row) inverted (middle row) and conventional boundary conditions (bottom row) and either photo-active or photo-inactive catalysts. Set of curves represent different Lewis numbers; $\vartheta_{ad} = 0.01$.

Notation

Latin

A	absorbance, dimensionless
A_{ref}	reference absorbance at $\Phi = 1$, dimensionless
$Bi_{\text{gas,ref}}$	reference Biot number at the gas-catalyst interface for $\Phi = 1$, dimensionless
$Bi_{\text{wall,ref}}$	reference Biot number at the catalyst-wall interface for $\Phi = 1$, dimensionless
Bi_{gas}	Biot number at the gas-catalyst interface, dimensionless
Bi_{wall}	Biot number at the catalyst-wall interface, dimensionless
C	auxiliary constant, dimensionless
c_A	concentration of the reactant, mol m^{-3}
$c_{A,0}$	concentration of the reactant at the gas-catalyst interface, mol m^{-3}
c_B	concentration of the product, mol m^{-3}
$c_{B,0}$	concentration of the product at the gas-catalyst interface, mol m^{-3}
c_p	specific isobaric heat capacity of the catalyst, $\text{J mol}^{-1} \text{K}^{-1}$
c_λ	speed of light, m s^{-1}
D_{eff}	effective diffusion coefficient, $\text{m}^2 \text{s}^{-1}$
$E_{A,+,\text{p}}$	activation energy for photochemical forward reaction, J mol^{-1}
$E_{A,+,\text{t}}$	activation energy for thermochemical forward reaction, J mol^{-1}
E_0	irradiance at gas-catalyst interface, W m^{-2}
f	residual fraction of the reactant, dimensionless
h	Planck constant, J s
h_{gas}	heat exchange coefficient at the gas-catalyst interface, $\text{W m}^{-2} \text{K}^{-1}$
h_{wall}	heat exchange coefficient at the catalyst-wall interface, $\text{W m}^{-2} \text{K}^{-1}$
K	equilibrium constant, dimensionless
K_0	equilibrium constant at T_0 , dimensionless
k	thermal conductivity of the catalyst, $\text{W m}^{-1} \text{K}^{-1}$
$k_{-,t}$	kinetic constant for the thermochemical backward reaction, $\text{m}^3 \text{mol}^{-1}$
$k_{-,t,0}$	kinetic constant for the thermochemical backward reaction at T_0 , $\text{m}^3 \text{mol}^{-1}$
$k_{+,t}$	kinetic constant for the thermochemical forward reaction, $\text{m}^3 \text{mol}^{-1}$
$k_{+,t,0} = k_0$	kinetic constant for the thermochemical forward reaction at T_0 , $\text{m}^3 \text{mol}^{-1}$
$k_{+,p,0}$	kinetic constant for the photochemical forward reaction at T_0 , $\text{m}^3 \text{mol}^{-1}$
k_{ref}	pre-exponential factor for thermochemical forward reaction, $\text{m}^3 \text{mol}^{-1}$
L	catalyst thickness, m
Le	Lewis number, dimensionless
N_A	Avogadro constant, mol^{-1}
q	local light intensity, dimensionless
q_0	light intensity at the gas-catalyst interface, dimensionless
$q_{0,\text{ref}}$	reference light intensity for $\Phi = 1$ at the gas-catalyst interface, dimensionless
R	universal gas constant, $\text{J mol}^{-1} \text{K}^{-1}$
r	total reaction rate, $\text{mol s}^{-1} \text{m}^3$
r_p	reaction rate due to photon absorption, $\text{mol s}^{-1} \text{m}^{-3}$
$r_{p,0}$	reaction rate due to photon absorption at T_0 and q_0 , $\text{mol s}^{-1} \text{m}^{-3}$
r_t	thermochemical reaction rate, $\text{mol s}^{-1} \text{m}^{-3}$
$r_{t,0} = r_0$	thermochemical reaction rate at T_0 , $\text{mol s}^{-1} \text{m}^{-3}$
T_0	temperature of gas and wall, K
x	lateral coordinate, m

Greek

α	linear absorption coefficient of the catalyst, m^{-1}
$\gamma_{-,p}$	activation energy for the photochemical forward reaction, dimensionless
$\gamma_{-,t}$	activation energy for the thermal backward reaction, dimensionless
$\gamma_{+,p}$	activation energy for the photochemical forward reaction, dimensionless
$\gamma_{+,t}$	activation energy for the thermal forward reaction, dimensionless
$\Delta_r H$	enthalpy of reaction, J mol^{-1}
η	catalyst efficiency, dimensionless
η_λ	quantum efficiency, dimensionless
θ	time, dimensionless
ϑ	temperature, dimensionless

ϑ_{ad}	adiabatic temperature increase, dimensionless
λ	wavelength of light, m
ρ	density of the catalyst, kg m^{-3}
Φ	Thiele modulus, dimensionless
χ	lateral coordinate, dimensionless