TRANSITIONING FROM CONVENTIONAL BATCH TO MICROFLUIDIC PROCESSES FOR THE EFFICIENT SINGLET OXYGEN PHOTOOXYGENATION OF METHIONINE

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CHEMICAL ENGINEERING

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Introduction

Development of photochemistry in macroscopic batch reaction vessels is hampered due to inherent limitations: superficial light penetration and poor heat exchange result in inhomogeneous irradiation. The recent implementation of **photochemical processes** in **microreactors under continuous-flow conditions** has emerged as an **alternative to batch processing** in $^1O_2$ photooxygenations through photosensitization of RB to obtain high-value added organic molecules.

Methionine sulfoxide (MetO) can be used in several applications such as organic synthesis, pharmaceutical sciences, biochemistry and material sciences. Intrinsic reaction kinetics were studied as a function of **RB concentration, light intensity and O$_2$ flow**. Apparent first-order kinetic constants, initial rates and space-time yields were calculated. Then, optimized reaction parameters were transposed to a microfluidic reactor for the photosensitized oxygenation of Met under continuous-conditions.
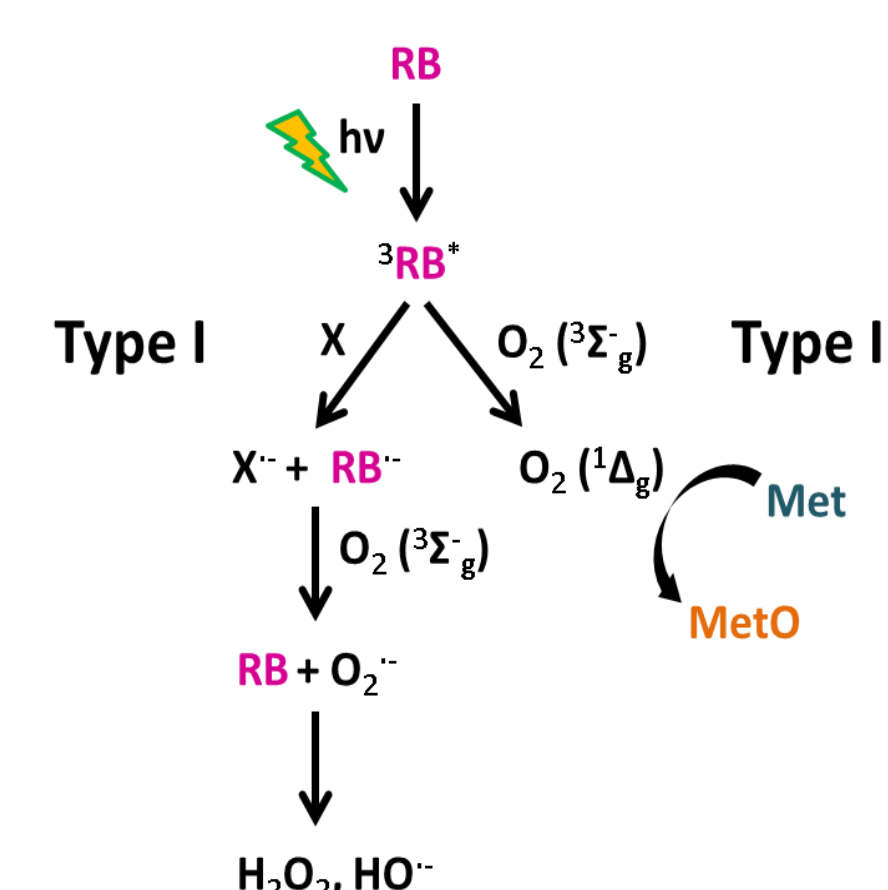

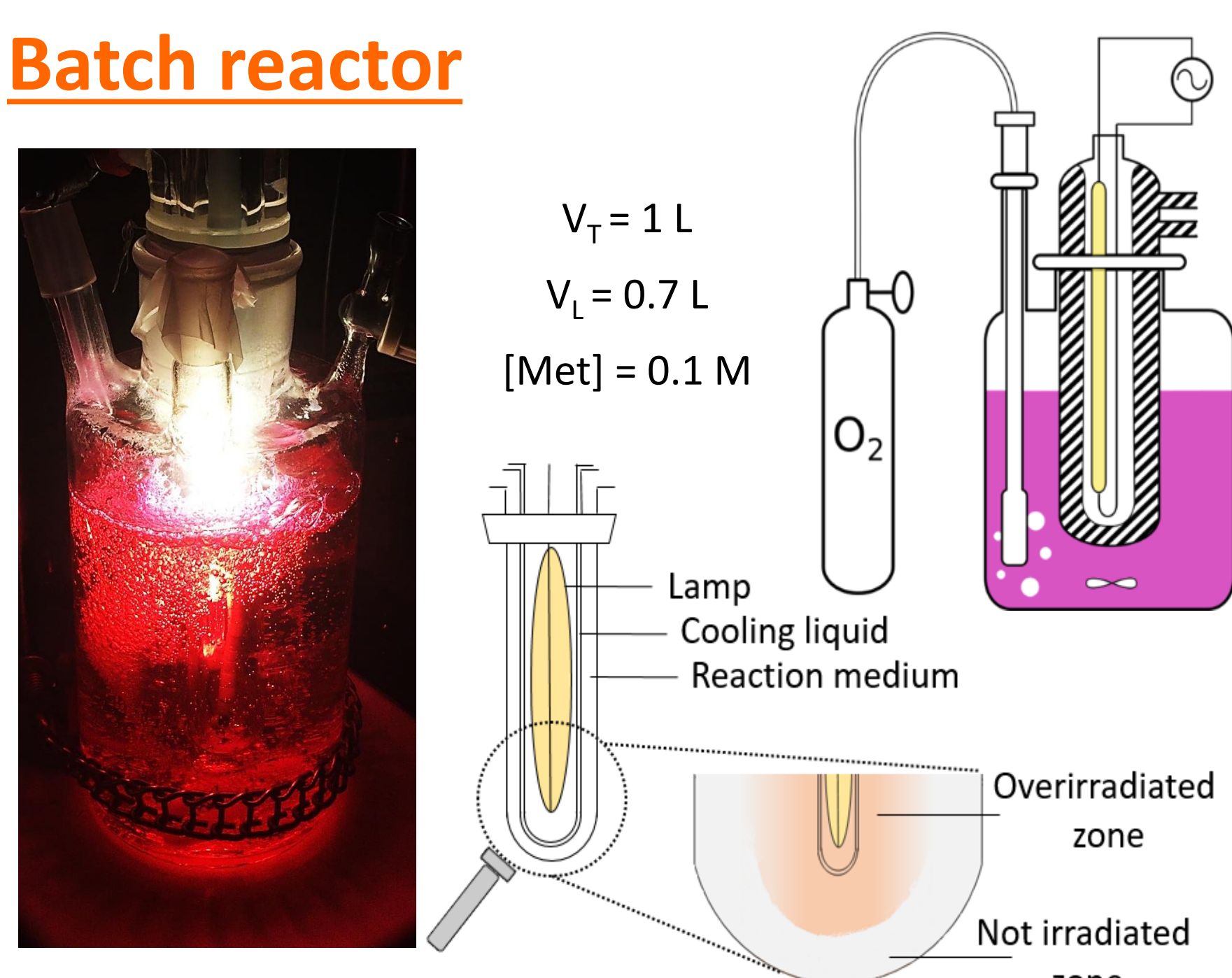Fig. 1. $^1O_2$ photooxygenation of Met

Batch reactor

$V_T = 1$ L
$V_L = 0.7$ L
[Met] = 0.1 M

Lamp
Cooling liquid
Reaction medium

Overirradiated zone
Not irradiated zone

Fig. 2. Batch reactor

Microreactor

Ø = 800 µm
P = 7 bar
[Met] = 0.1 M
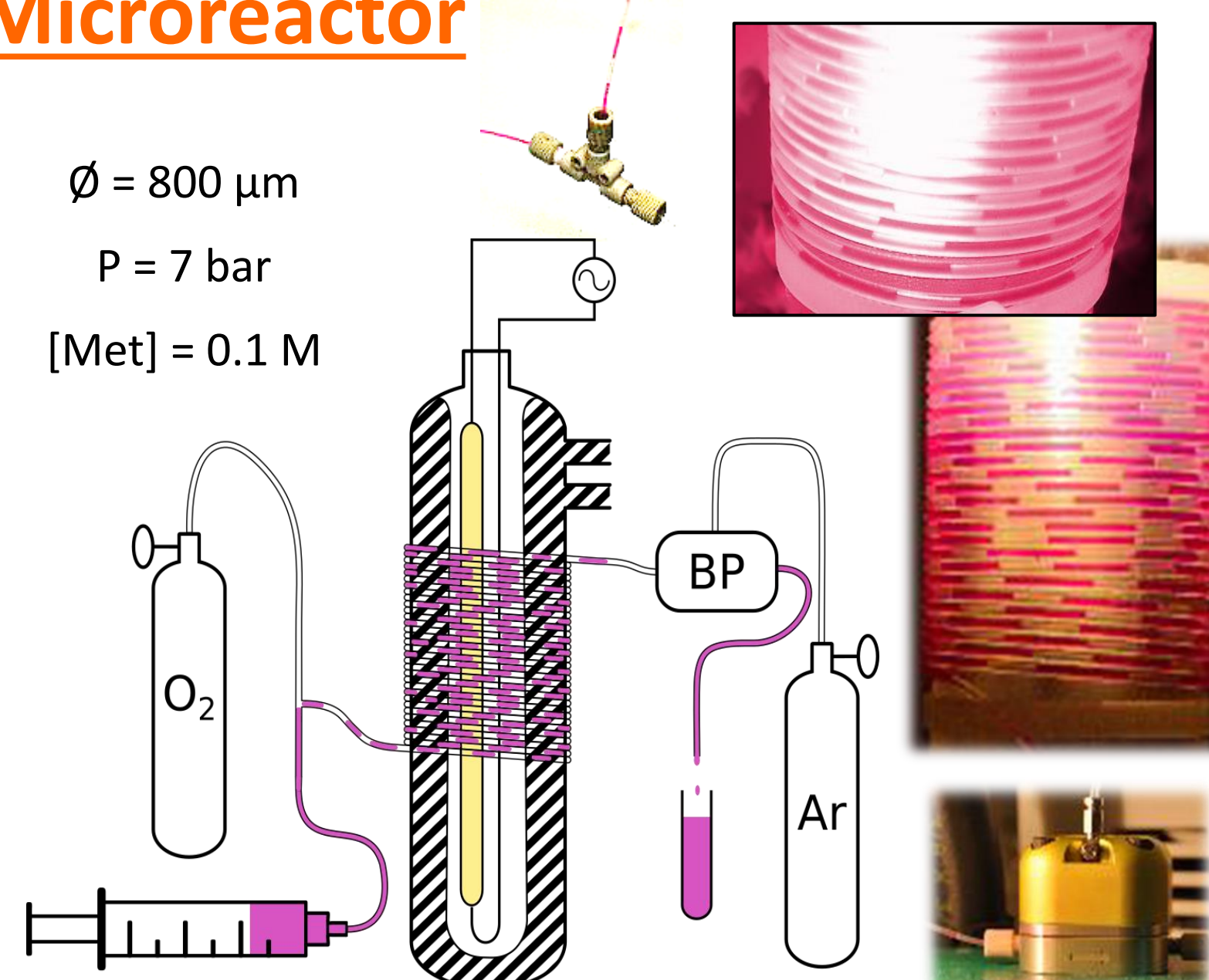
Fig. 3. Microreactor

¹H NMR
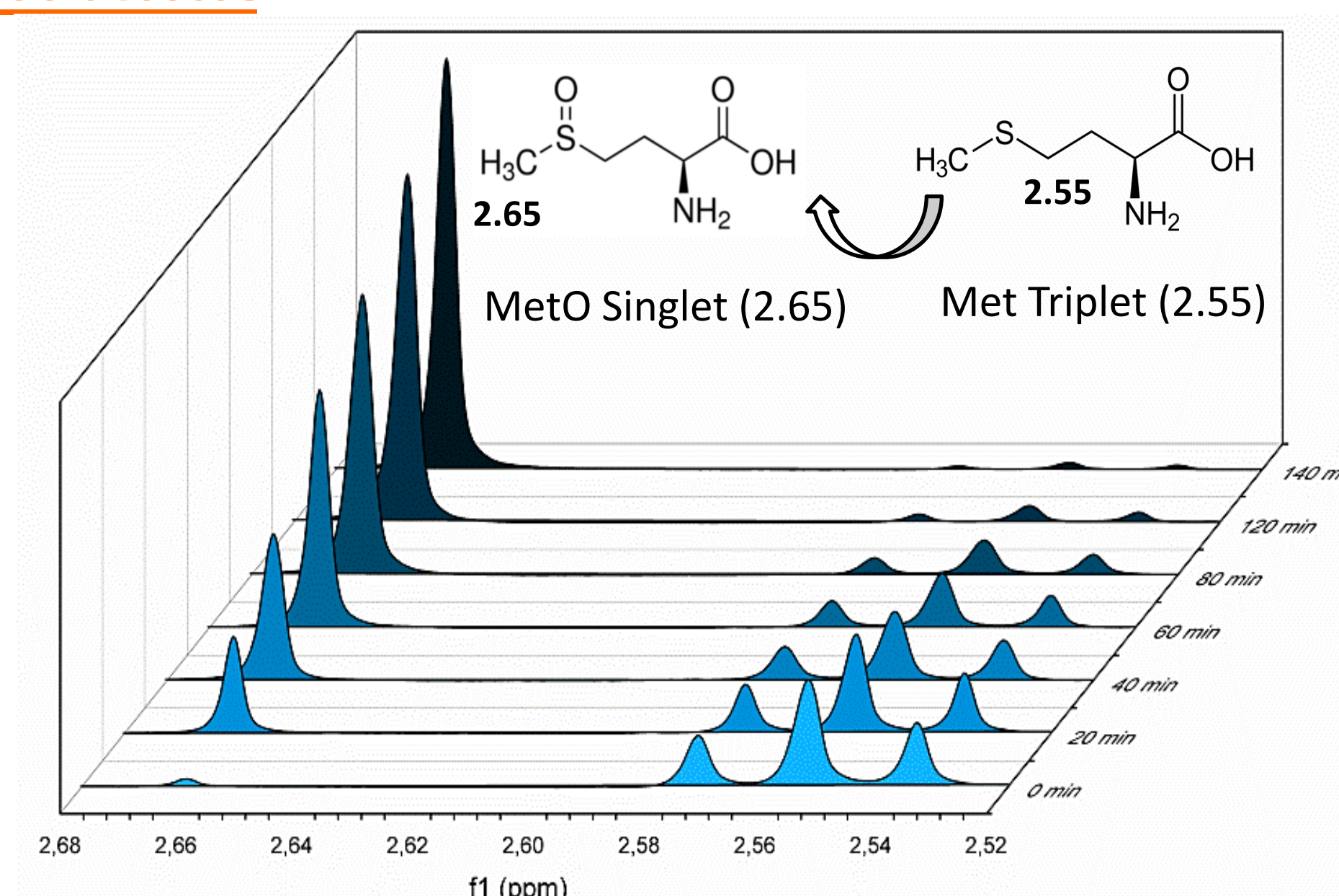

MetO Singlet (2.65)   Met Triplet (2.55)

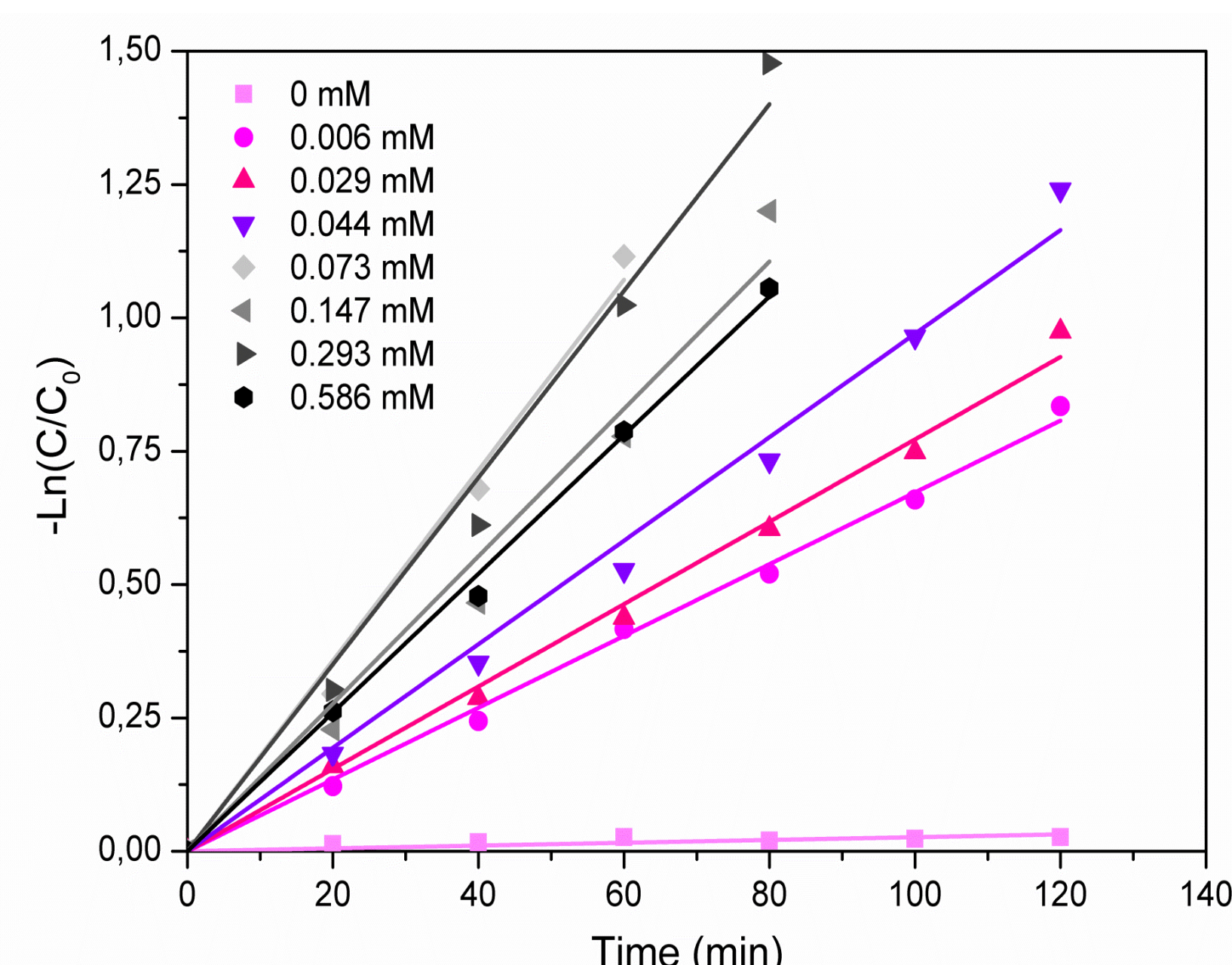Fig. 4. 1H NMR Spectra of the outlet vs. time in batch experiments

Photooxygenation of methionine in batch reactor

Fig. 5. Pseudo-first order relationship $-\ln([Met]/[Met]_0) = k_{app} \cdot t$ as a function of RB concentration
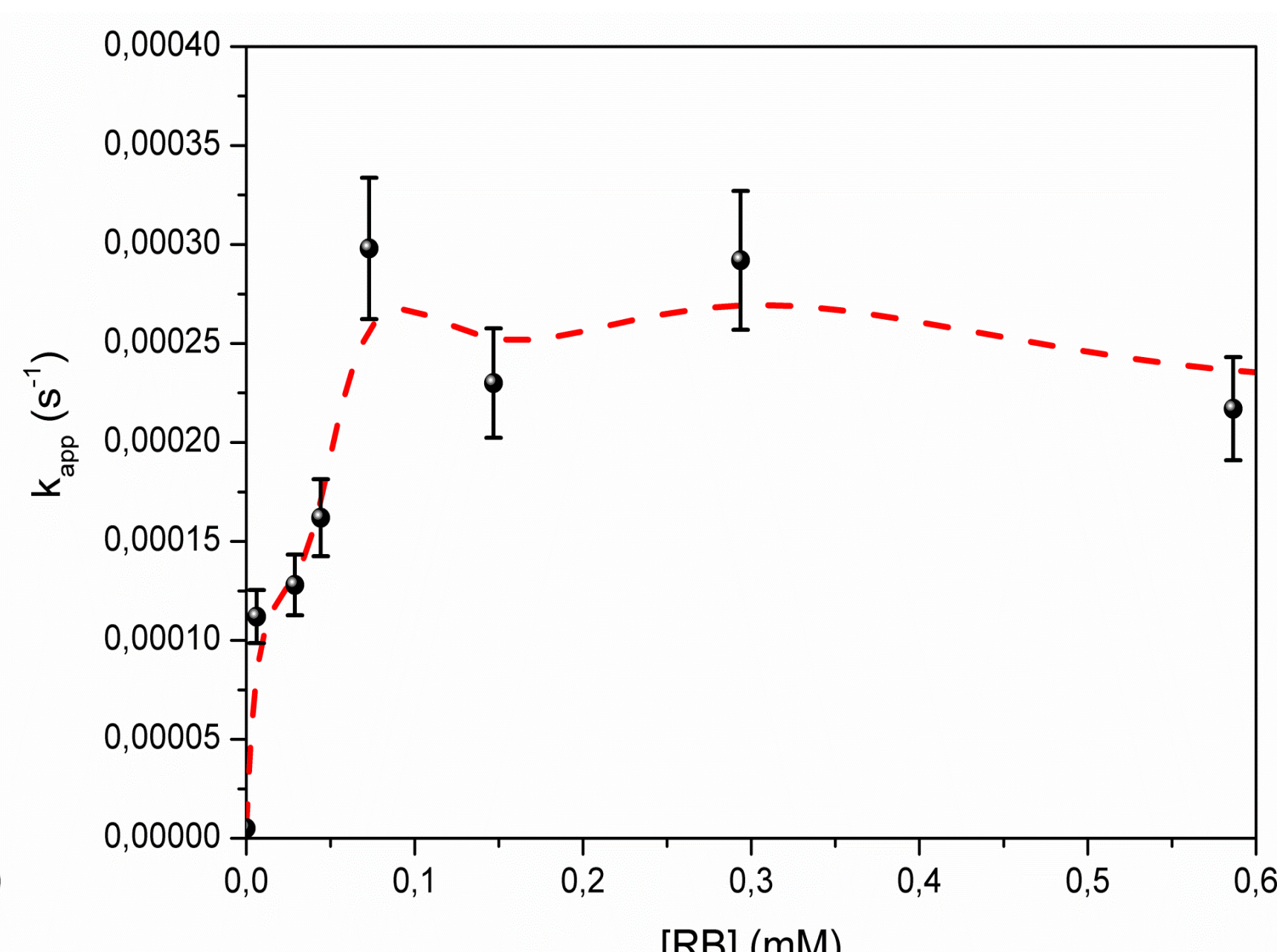
0 mM
0.006 mM
0.029 mM
0.044 mM
0.073 mM
0.147 mM
0.293 mM
0.586 mM

Fig. 6. k_{app} values as function of RB concentration

Fig. 7. Pseudo-first order relationship $-\ln([Met]/[Met]_0) = k_{app} \cdot t$ as a function of irradiance
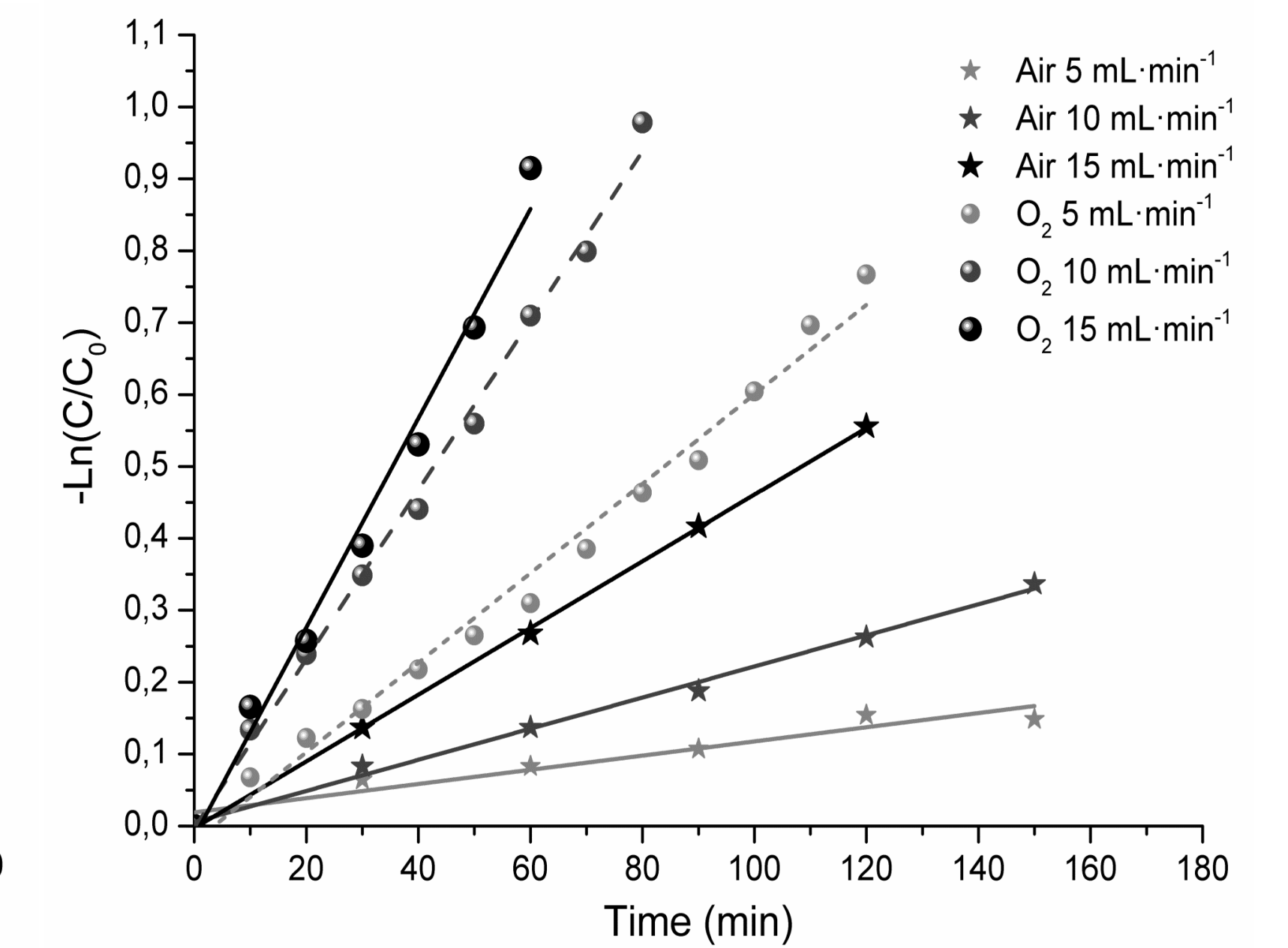
320 W/m²
1590 W/m²
3460 W/m²
5360 W/m²

Fig. 8. Pseudo-first order relationship $-\ln([Met]/[Met]_0) = k_{app} \cdot t$ as a function of O$_2$ flow

Air 5 mL·min⁻¹
Air 10 mL·min⁻¹
Air 15 mL·min⁻¹
O₂ 5 mL·min⁻¹
O₂ 10 mL·min⁻¹
O₂ 15 mL·min⁻¹

Comparison of photoreactors

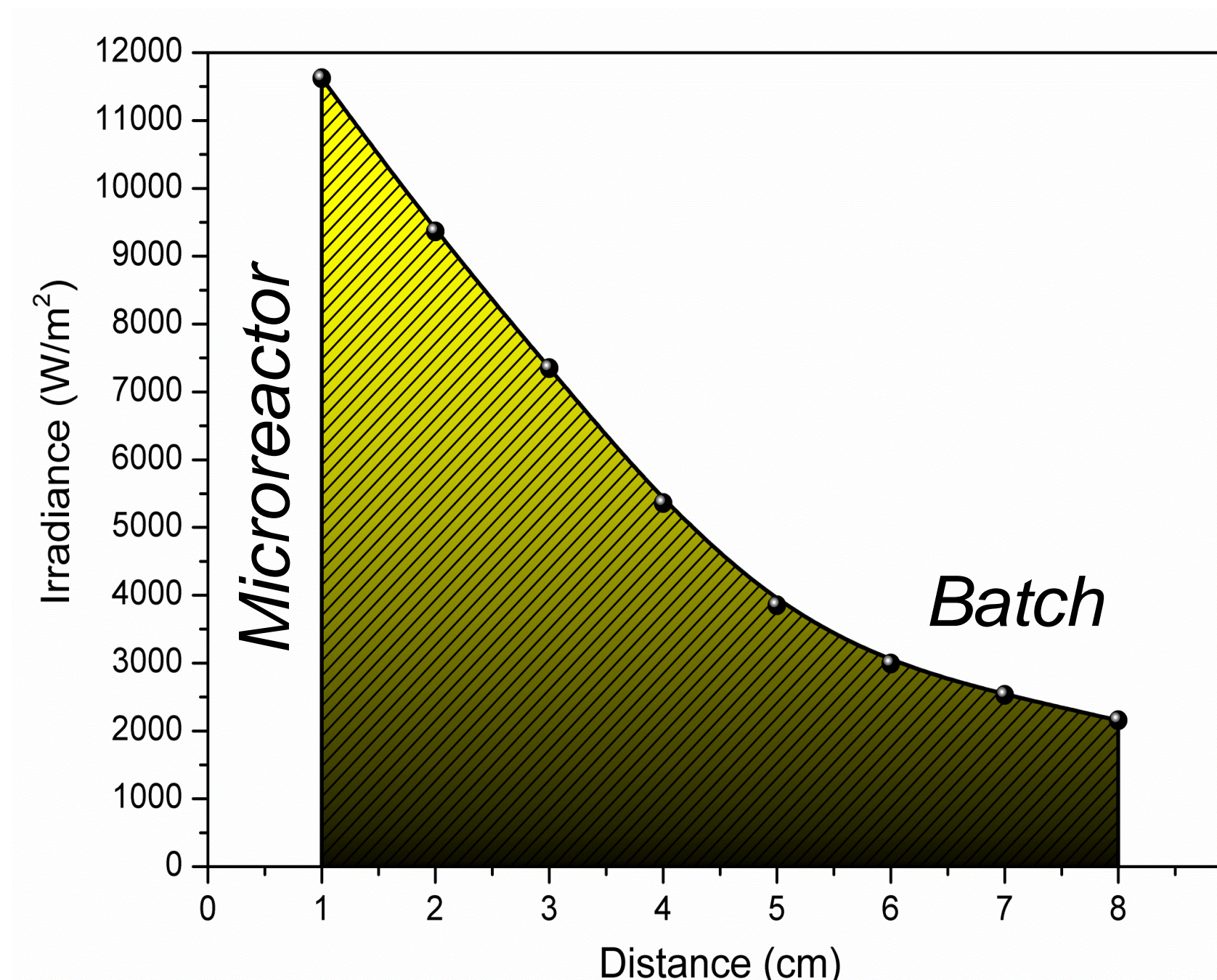| Parameters	Batch	Microreactor
Depth of light penetration (cm)	8	0.08
Irradiated area (cm²)	63	40
Irradiated volume (cm³)	700	1
Irradiated area/volume ratio (cm²·cm⁻³)	0.09	40
Photon flux density (einstein·m⁻³·s⁻¹)	0.0247	17.3
k_{app} (10^5 s⁻¹)	24.6	305.2
r_0 (10^5 mol·L⁻¹·s⁻¹)	2.4	29.3
STY (10^5 mol MetO·L·s⁻¹)	76.6	239

Fig. 9. Irradiance of the halogen lamp as a function of the distance

Conclusions

These results confirm the limitations of batch technologies in terms of light penetration and mass transfer when working with $^1O_2$-photosensitized oxygenations.

✍ RB concentration, light intensity and O$_2$ flow have been evaluated in batch reactor.

✍ Pseudo-first order kinetics and space-time yields have been also calculated in both technologies obtaining an enhancement of 12 and 3 fold for r_0 and STY, respectively when using when using continuous-flow microreactor.

Acknowledgements

References

[1] N. Emmanuel, Scalable photocatalytic oxidation of methionine under continuous-flow conditions. Org. Process. Res. Dev.
[2] C. Mendoza, Transitioning from conventional batch to microfluidic processes for the efficient singlet oxygen photooxygenation of methionine. J. Photochem. & Photobiol. A. Chemistry.
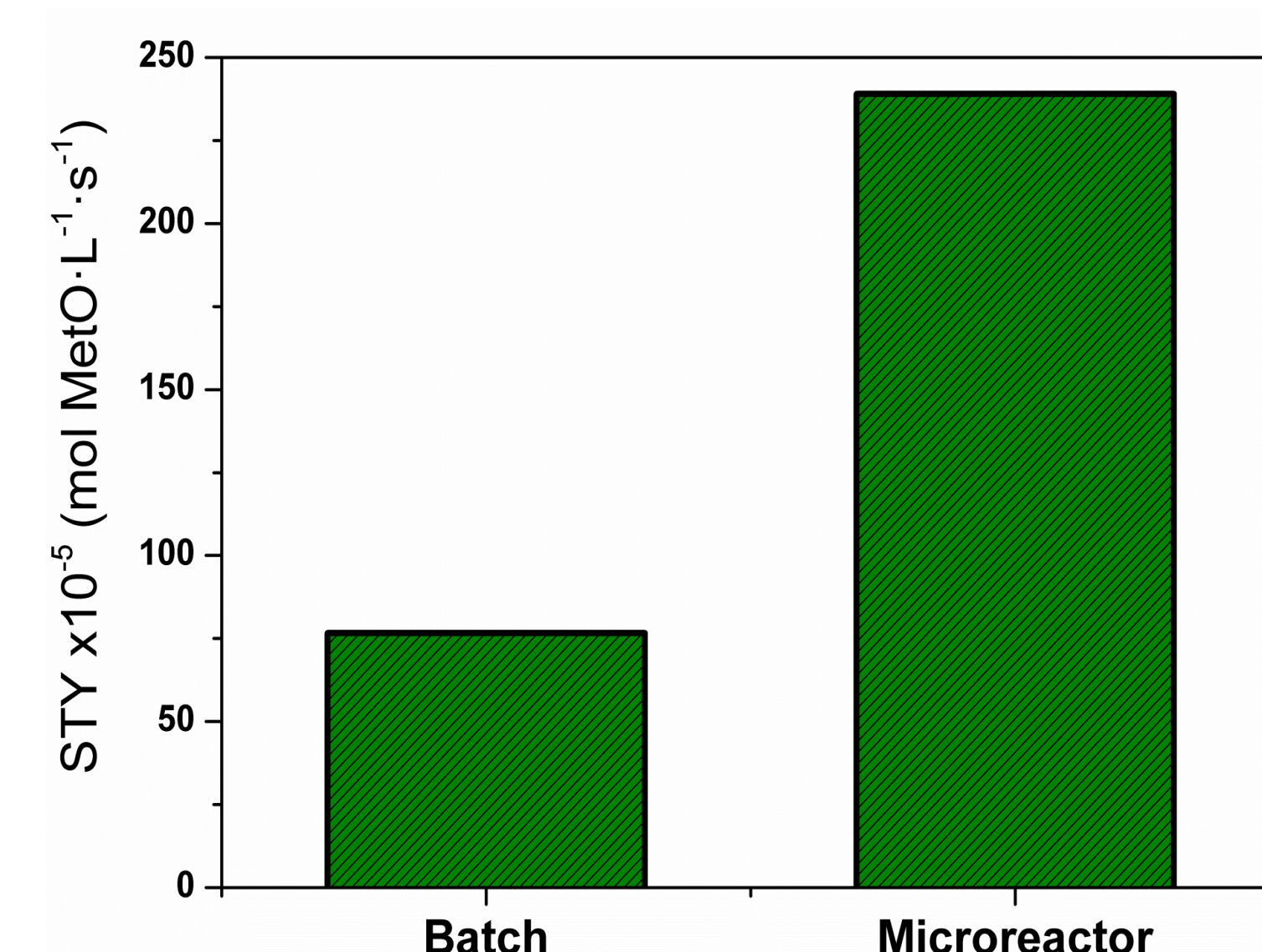
Fig. 10. Comparison between batch reactor and microreactor in terms of STY