

Experimental and model-based study of integrated reactor concepts for the dehydrogenation of propane

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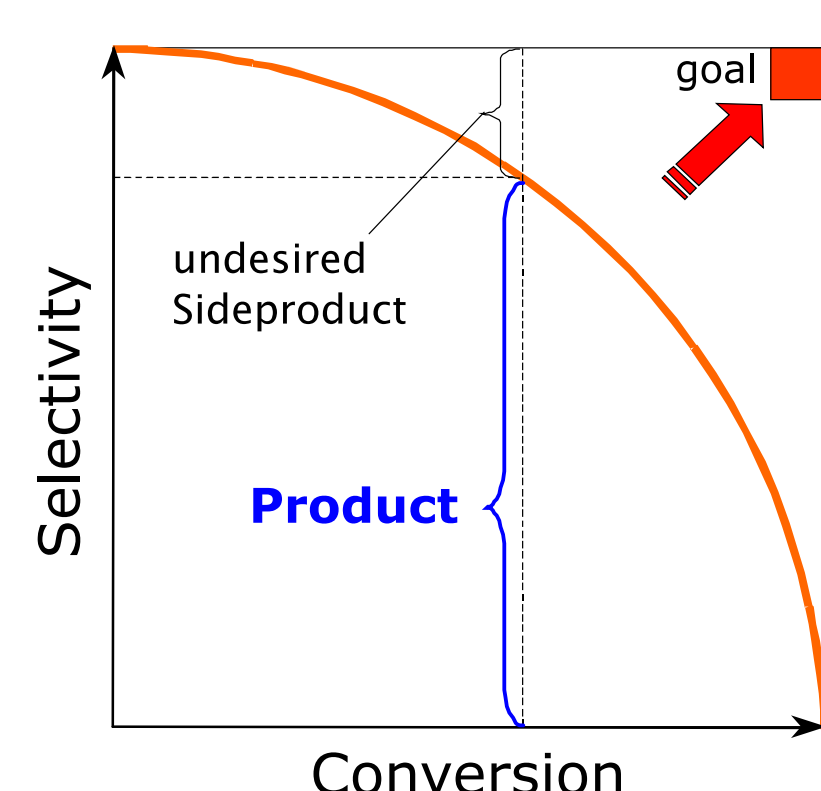
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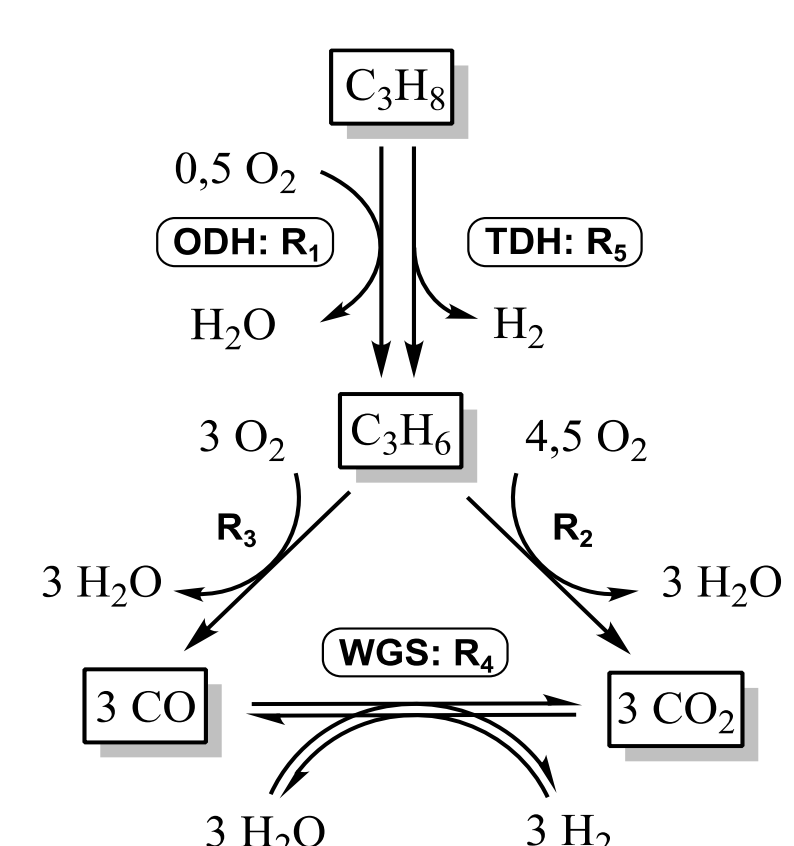
Motivation

- In the last 20 years demand of propylene derivatives, e.g. polypropylene, and propylene oxide, has significantly increased [1].
- The main part of the propylene production is gained as side product in crude oil refineries (FCC/RCC) and naphtha steam cracking.
- New innovative processes of propane dehydrogenation could be achieved by coupling of oxidative (ODH) and thermal dehydrogenation (TDH) in order to improve selectivity and yield [2 - 4].

➤ **Different process designs, integrations and operation modes are thinkable which have been studied theoretically and experimentally.**



Reaction Network



Enthalpy of reaction

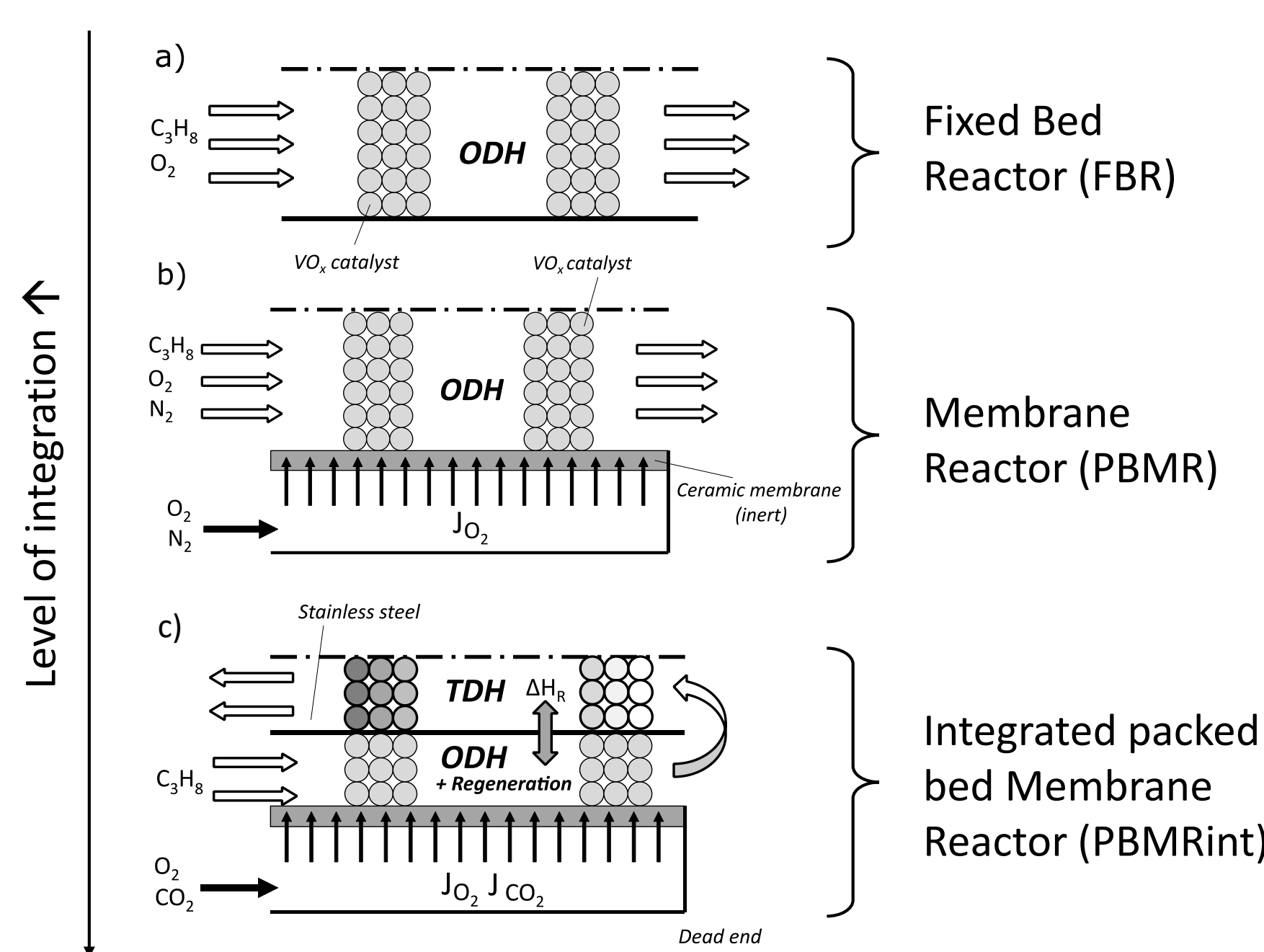
$$\text{ODH: } \Delta_R H_{r1} = -118 \text{ kJ mol}^{-1} \\
 \text{TDH: } \Delta_R H_{r5} = +124 \text{ kJ mol}^{-1}$$

Catalyst

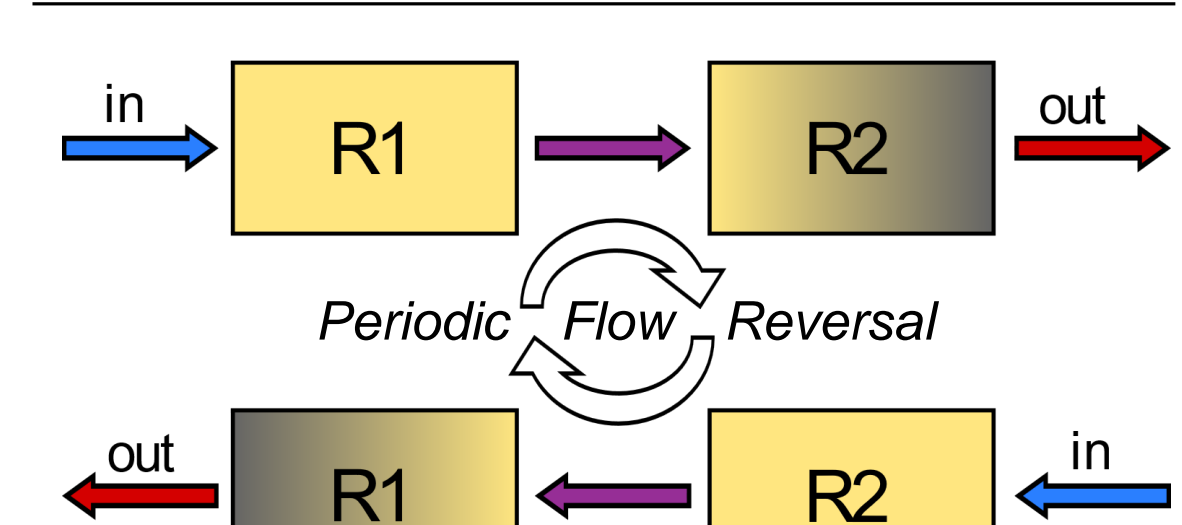
$$\text{ODH: VO}_x/\gamma\text{-Al}_2\text{O}_3, \\
 (\text{V: } 1.4\%, \text{ d}_p=1 \text{ mm});$$

- **ODH (R₁):** exothermic, less selective reaction
 ↳ **Problem:** Total and partial oxidation (R₂/R₃) as side reactions due to the presence of oxygen
- **TDH (R₅):** endothermic, highly selective reaction
 ↳ **Problem: Rapid coking of the catalyst**
 ⇒ **activity function a(t)** [2]

Reactor Concepts

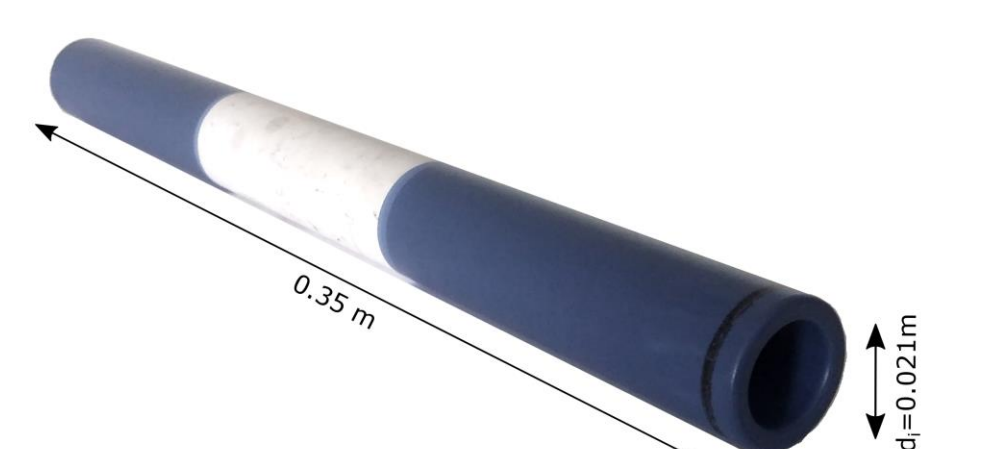


Reactor cascade with flow reversal

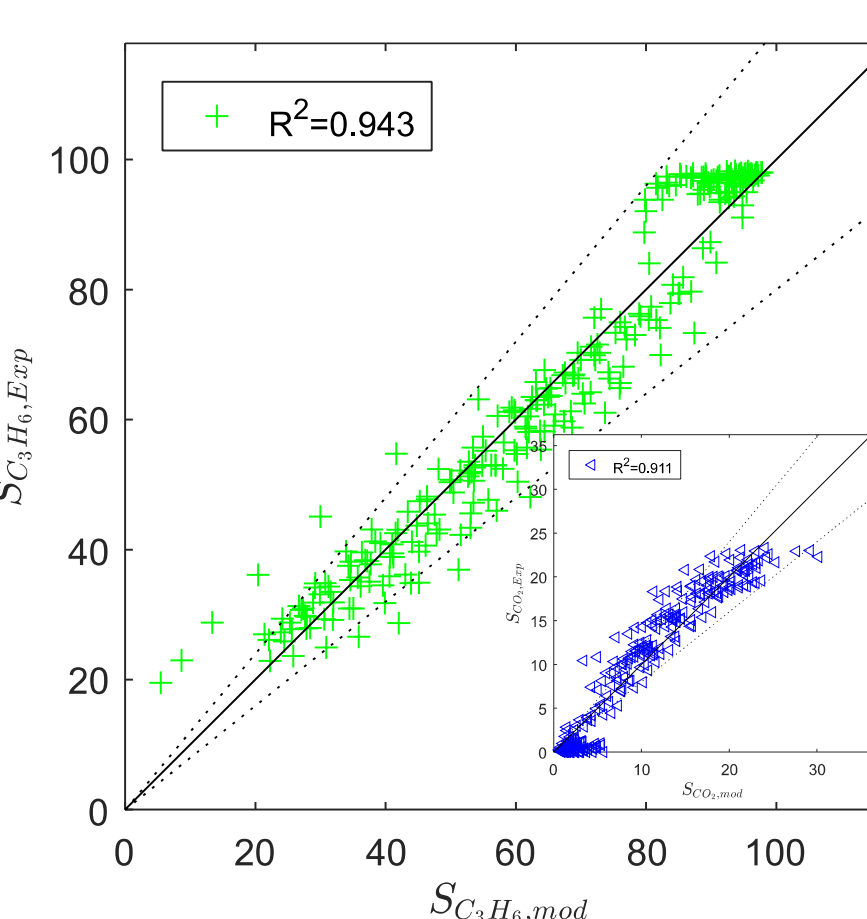
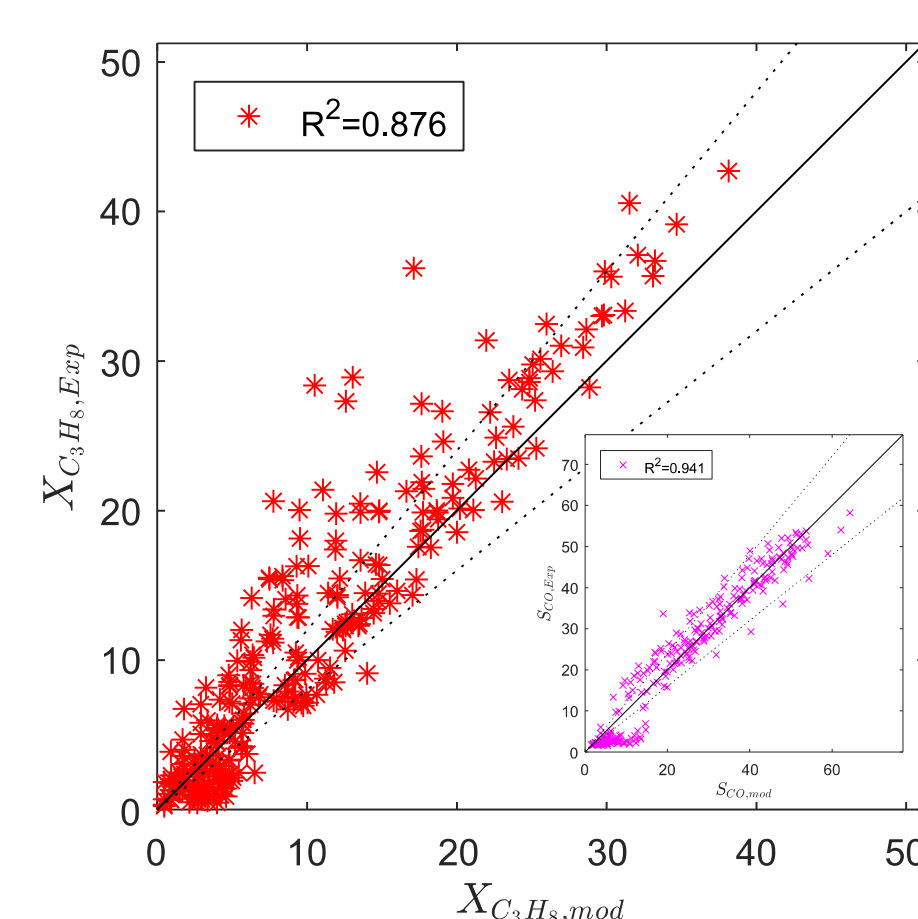


Membrane:

asymmetric, porous Al₂O₃ membrane; d_i/d_a=21/32mm, (Fraunhofer IKTS)



Kinetics: Main reactions



➤ Power Law Approach [2]:

$$\begin{aligned}
 r_1 &= k_1 \cdot p_{\text{C}_3\text{H}_8}^{a_1} \cdot p_{\text{O}_2}^{b_1} \\
 r_2 &= k_2 \cdot p_{\text{C}_3\text{H}_6}^{a_2} \cdot p_{\text{O}_2}^{b_2} \\
 r_3 &= k_3 \cdot p_{\text{C}_3\text{H}_6}^{a_3} \cdot p_{\text{O}_2}^{b_3} \\
 r_4 &= k_4 \left(\frac{p_{\text{H}_2\text{O}} p_{\text{CO}}}{K_{\text{WGS}}} - p_{\text{H}_2} p_{\text{CO}_2} \right) \\
 r_5 &= k_5 \cdot p_{\text{C}_3\text{H}_8}^{a_5}
 \end{aligned}$$

➤ Experimental Setup: Lab scale reactor

➤ Quartz glass, ID 6 mm

➤ Parameter Estimation: **Matlab (I-D)**

➤ Reactor model: **PFTR**, steady state, no deactivation

➤ Experimental Conditions:

➤ T = 350°C - 600°C

➤ TDH: C₃H₈ = 1/2/3/4/5%, c_{O₂} = 0%

➤ ODH: C₃H₈ = 0 - 1%, c_{O₂} = 0 - 1%

➤ WHSV = 100 - 400 (kg s)/m³

Kinetics: Coking, Deactivation and Regeneration

TG Analysis

➤ Netzsch STA 449 F5 Jupiter®

Modeled as **CSTR**

➤ Propene has been identified as main coke precursor in agreement with literature [3]

Monolayer Multilayer Coke Growth Model (MMCGM)

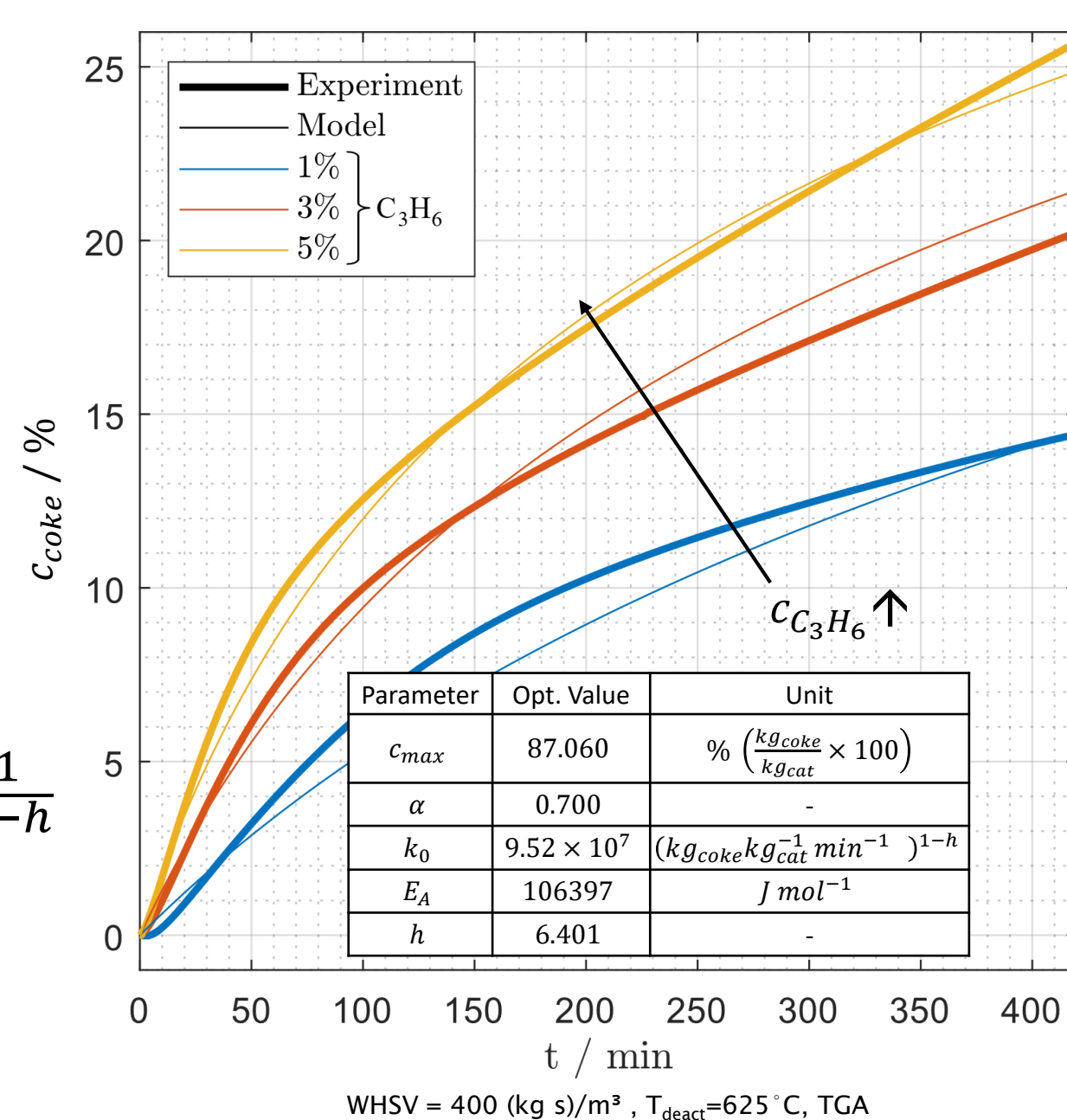
$$c_{\text{coke}} = c_{\text{max}} - \left((h-1) \cdot k_1 \cdot c_{\text{C}_3\text{H}_6}^L \cdot t + c_{\text{max}}^{1-h} \right)^{\frac{1}{1-h}}$$

➤ How is deactivation related to coking?
 ⇒ Approach of Dumez and Froment [3]

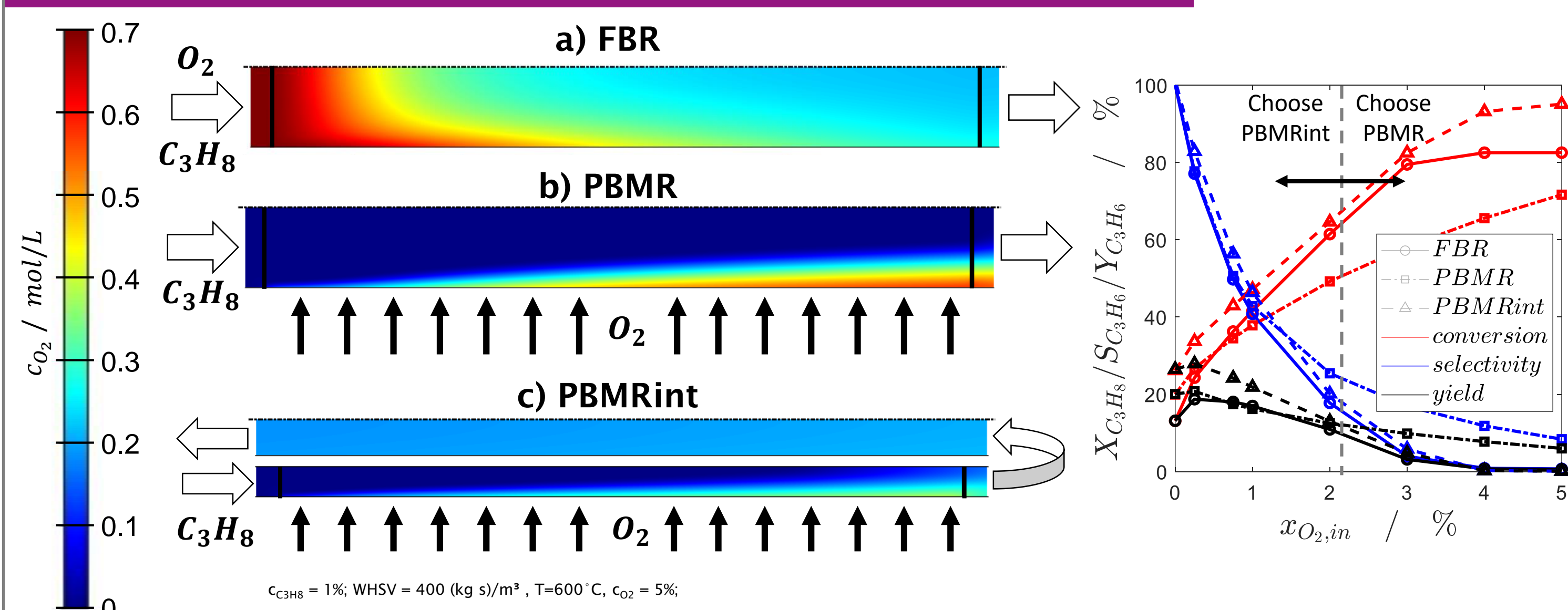
$$a_j = \frac{1}{1 + \zeta_j c_{\text{coke}}(t)}$$

$$r_j(t) = r_j^0 \cdot a_j(t)$$

Reaction	Parameter	Opt. Value	Unit	Confidence interval
R ₂	ζ ₂	0.2182	% ⁻¹	±2.6 × 10 ⁻³ %
R ₃	ζ ₃	0.1645	% ⁻¹	±3.3 × 10 ⁻³ %
R ₅	ζ ₅	1.1207	% ⁻¹	±0.5 × 10 ⁻³ %



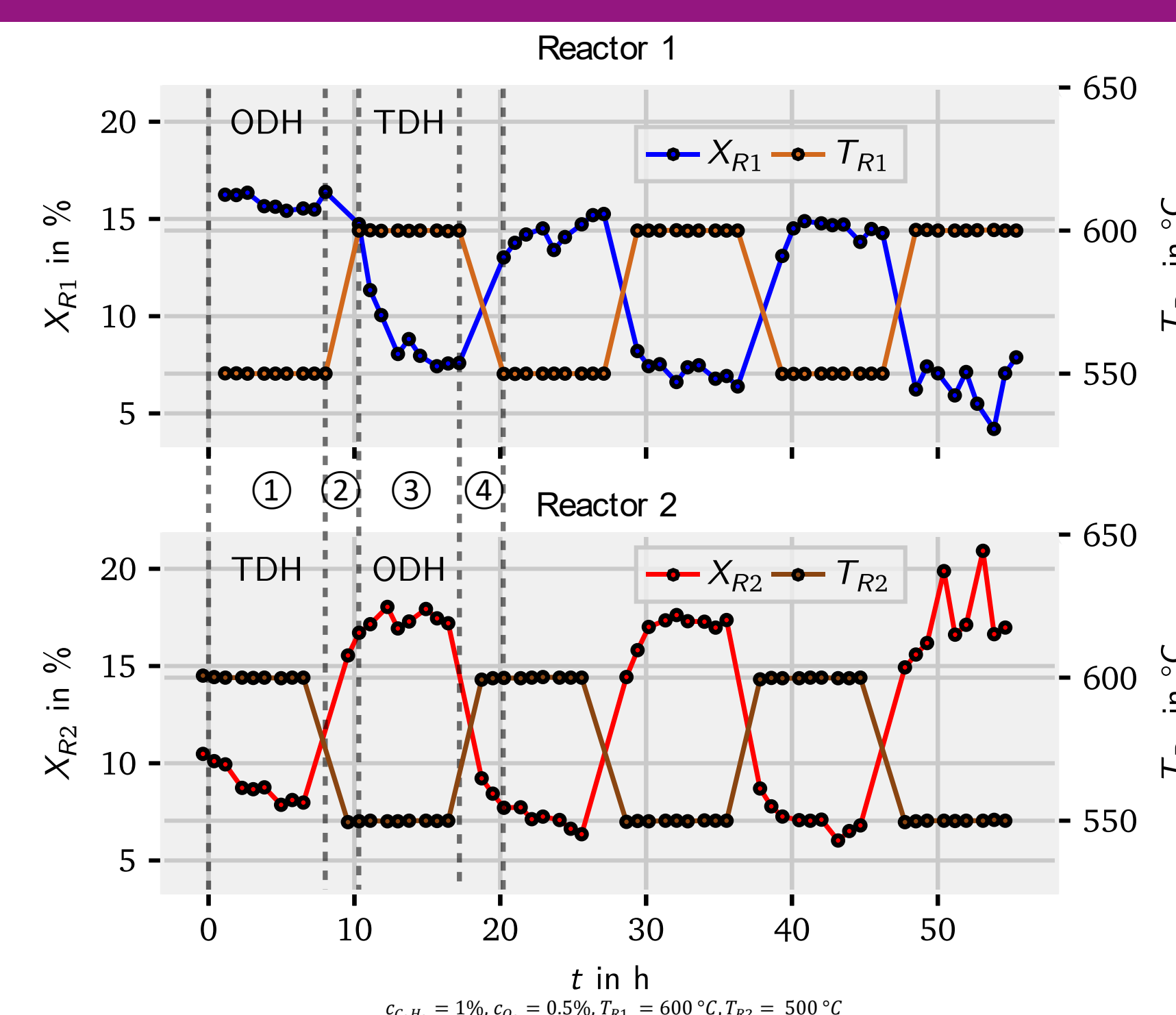
2D-Simulation: Integrated Reactor Concepts



➤ Distinct radial temperature and concentration gradients ⇒ Detailed 2D simulations needed for reactor concept evaluation

➤ Beneficial production regimes for different reactor setups can be identified

Outlook: Experiments in pilot scale



Phase ①
 Reactor 1: ODH
 Reactor 2: TDH

Phase ② + Phase ④
 Change of temperatures, switch of flow direction

Phase ③
 Reactor 1: TDH
 Reactor 2: ODH

➤ **Operando Regeneration by flow reversal: No deadtimes**

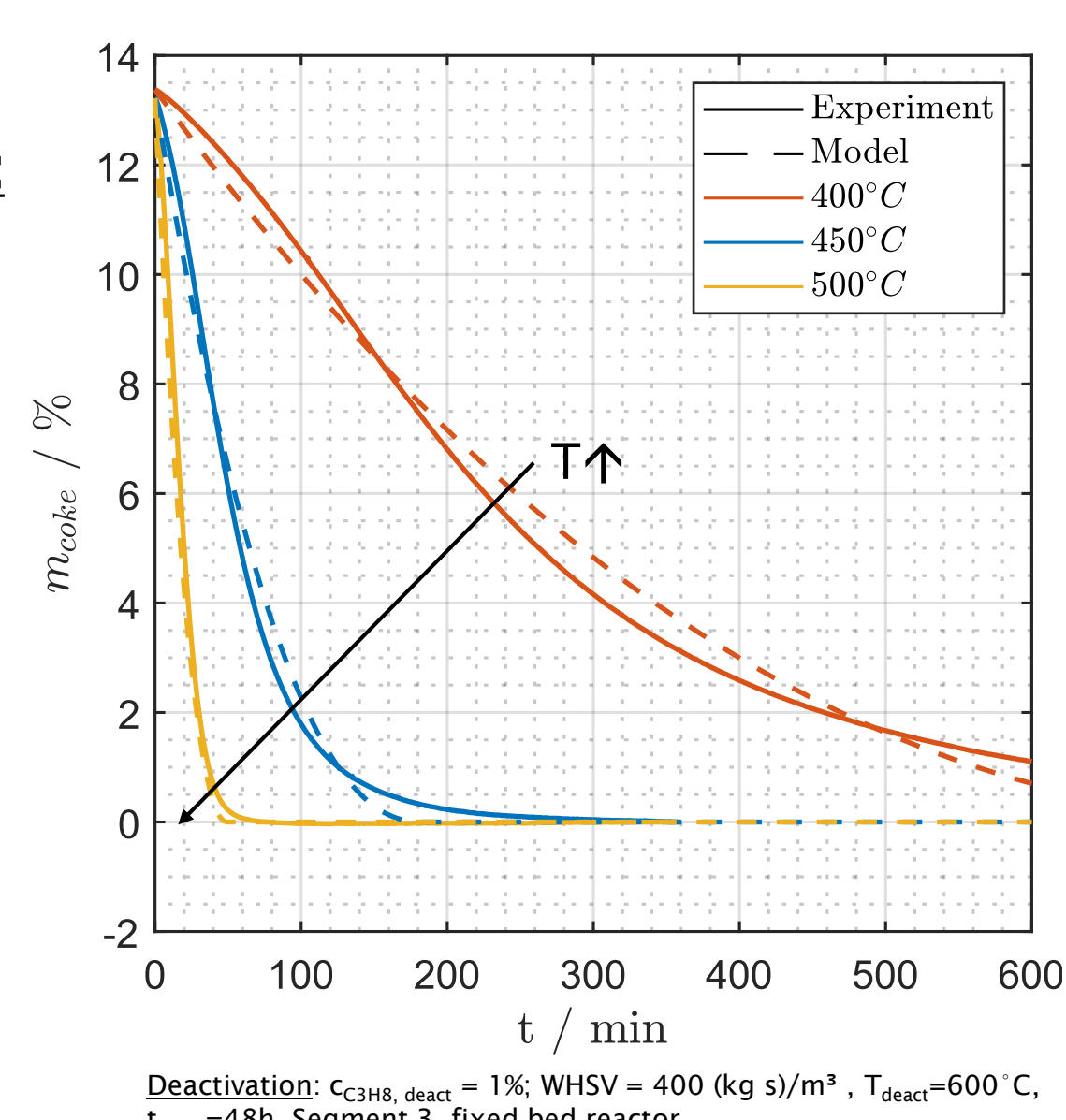
➤ **Less side reactions due to distributed oxygen dosing in membrane reactors**

Regeneration setup:

➤ TGA Netzsch STA 449 F5 Jupiter®

Deactivation setup:

➤ Glass reactor, 6mm ID, 1.5g catalyst, 3 segments



Power Law Approach

$$r = \frac{dm_c}{dt} = k \cdot m_c^\alpha \cdot \varphi_{\text{O}_2}^\beta$$

Optimization

Optimized Parameters

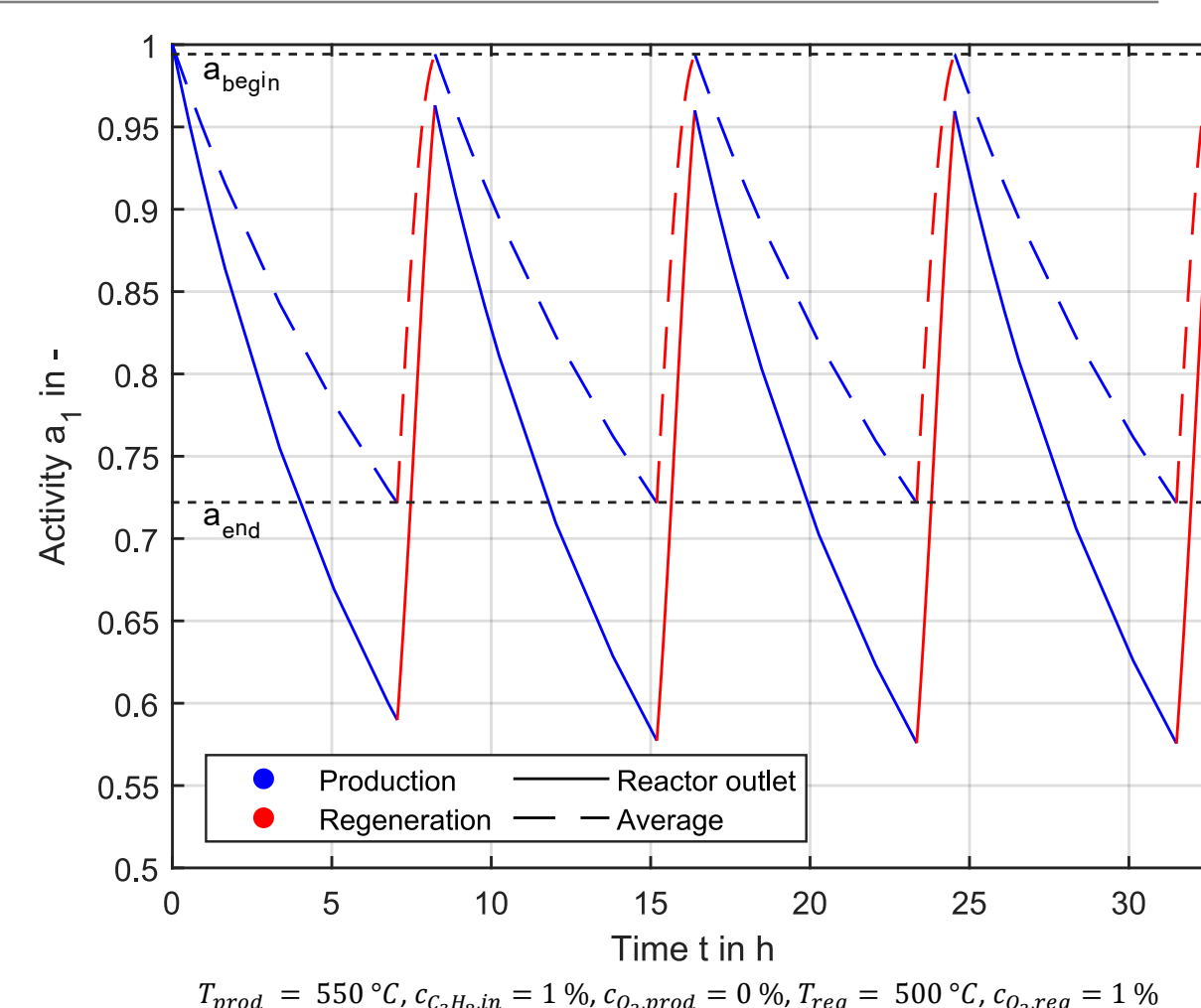
Parameter	Opt. value	Unit
k ₀	1.62 × 10 ⁸	% min ⁻¹
E _A	120835.9	J mol ⁻¹
α	0.5517	-
β	0.6859	-

Optimization of overall production process

➤ 1D reactor model (MATLAB)

➤ Production cycles including **incomplete** regeneration results in more efficient overall process

➤ **Consideration of regeneration phase in process design leads to more efficient processes**



Acknowledgement

DFG Project „Kontrolle und Intensivierung von Reaktionen durch Einsatz zyklisch betriebener Distributoren“, SE 568/23-1 / HA 6762/2-1

References

- [1] P. Eisele, R. Killpack, in *Ullmann's encyclopedia of industrial chemistry*, Vol. 82, Wiley, Chichester 2010.
- [2] A. Brune, A. Seidel-Morgenstern, C. Hamel, *Catalysts* 10 (2020) 1374. <https://doi.org/10.3390/catal10121374>.
- [3] J.P. Walter, A. Brune, A. Seidel-Morgenstern, C. Hamel, *Chem. Ing. Tech.* 93 (2021) 819-824. <https://doi.org/10.1002/cite.202000227>.
- [4] A. Brune, T. Wolff, A. Seidel-Morgenstern, C. Hamel, *Chem. Ing. Tech.* 56 (2019) 251. <https://doi.org/10.1002/cite.201800184>.