Operation Range Extension via Hot Spot Control for Fixed-Bed CO_2 Methanation Reactors

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A   Supplementary Material

A.1   Heat transport correlations

Jacket

The heat transport coefficient for the reactor jacket k_{jac} in eqn (15) is obtained via

$$k_{jac} = \left(\frac{1}{\lambda_{jac}} \ln((R + \delta_{jac})/R) \right)^{-1},$$

to compensate radial mismatch between inner and outer jacket surface. Its impact on the overall heat transport is illustrated in Fig. A.6.

Cooling channel

The heat transport inside the cooling channel (considered as an annular gap) is calculated via the correlations from Gnielinski [Gni10]. As heat transfer medium we selected the synthetic oil *Marlotherm SH* and used the corresponding thermo-physical properties as described in [Pre10]. Fig. A.1 illustrates our results for the coolant Nusselt number over a broad coolant Reynolds number range and for different technically relevant coolant temperatures.

Furthermore, we assume technically relevant values for coolant velocity and hydraulic cooling channel diameter as:

$$v_{cool} = 1\text{--}2\,\frac{m}{s} \quad \text{and} \quad d_h = 0.01\text{--}0.02\,m.$$

The resulting cooling regime in Fig. A.1 relevant for our study is shaded in red. Consequently, two limiting cases can be identified to estimate a reasonable range for the coolant heat transfer coefficient α_{cool}:

Max. case:

$T_{cool} =$	573	K	$\Delta p_{cool} =$	0.3	bar
$d_h =$	0.02	m	$\dot{V}_{cool} =$	2.1	l/s
$v_{cool} =$	2	m/s			

$$\text{Re}_{cool} = 8.9 \times 10^4 \Rightarrow \text{Nu}_{cool} = 560$$
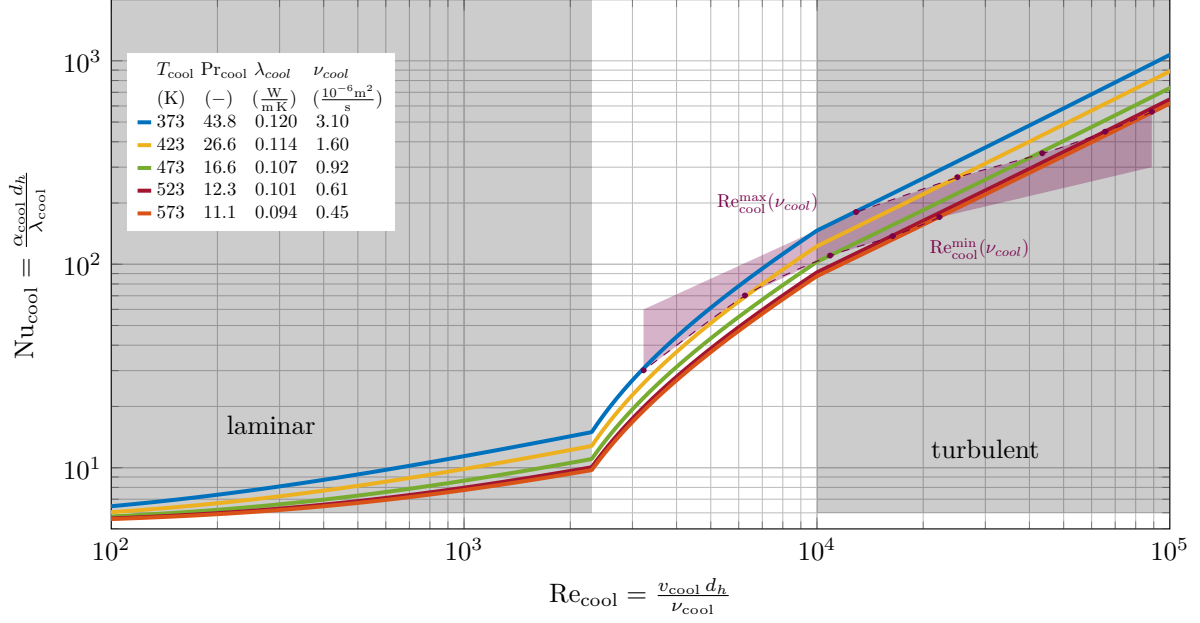
$$\Rightarrow \alpha_{cool} = 2632\,\frac{W}{m^2\,K},$$

Figure A.1: Nu-Re-dependency for the heat transfer medium *Marlotherm SH*; $d_h = 0.01\,m$ and $L = 2.5\,m$; thermo-physical data from [Pre10].

Min. case:

$T_{\text{cool}} =$	373	K	$\Delta p_{\text{cool}} =$	0.04	bar
$d_h =$	0.01	m	$\dot{V}_{\text{cool}} =$	0.45	l/s
$v_{\text{cool}} =$	1	m/s			

$$\text{Re}_{\text{cool}} = 3.2 \times 10^3 \Rightarrow \text{Nu}_{\text{cool}} = 30$$

$$\Rightarrow \alpha_{\text{cool}} = 360 \, \frac{\text{W}}{\text{m}^2\,\text{K}}.$$

Thus, the reference heat transfer coefficient α_{cool} of 500 W/m^2 K used in this study is relatively moderate, so that the coolant supply is rather not a limiting factor of our proposed control approach.

A.2   Rate expressions

The rate expressions used in our model are adapted from Xu and Froment [Xu89] and Koschany et al. [Kos16], which have been implemented via the following correlations.

Xu and Froment

Xu and Froment [Xu89] considered three rate equations including the water-gas-shift (WGS) reaction:

$$r_1 = \frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1} \right) \bigg/ \text{DEN}^2, \tag{A.1}$$

$$r_2 = \frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2} \right) \bigg/ \text{DEN}^2, \tag{A.2}$$

$$r_3 = \frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right) \bigg/ \text{DEN}^2, \tag{A.3}$$

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where p_α is the partial pressure of the respective component in bar and DEN is a dimensionless parameter defined as

$$\text{DEN} = 1 + K_{CO}\, p_{CO} + K_{H_2}\, p_{H_2}$$
$$+ K_{CH_4}\, p_{CH_4} + \frac{K_{H_2O}\, p_{H_2O}}{p_{H_2}}.$$

K_α is the respective adsorption constant for CH_4, CO, H_2O and H_2 and b_β are rate coefficients exponentially depending on temperature via:

$$K_\alpha = \mathcal{A}_\alpha \exp\left(-\frac{\Delta H_\alpha}{\mathcal{R}T}\right),$$
$$k_\beta = \mathcal{A}_\beta \exp\left(-\frac{E_\beta}{\mathcal{R}T}\right).$$

$\mathcal{A}_\beta$, E_β, $\mathcal{A}_\alpha$, ΔH_α are constant kinetic parameters stated in Tab. A.1.

Table A.1: Kinetic parameters for Eqs. (A.1) to (A.3); each pre-exponential factor contains a multiplier of 1.225 (see Xu and Froment [Xu89])

α	Formula	$\mathcal{A}_\alpha$	$[\mathcal{A}_\alpha]$	ΔH_α	$[\Delta H_\alpha]$	β	$\mathcal{A}_\beta$	$[\mathcal{A}_\beta]$	E_β	$[E_\beta]$
1	CH_4	8.15×10^{-4}	bar^{-1}	-38.28	$\frac{\text{kJ}}{\text{mol}}$	1	5.176×10^{15}	$\frac{\text{kmol\,bar}^{0.5}}{\text{kg}_{\text{cat}}\,\text{h}}$	240.10	$\frac{\text{kJ}}{\text{mol}}$
2	CO	10.08×10^{-5}	bar^{-1}	-70.65	$\frac{\text{kJ}}{\text{mol}}$	2	2.395×10^{6}	$\frac{\text{kmol}}{\text{kg}_{\text{cat}}\,\text{h\,bar}}$	67.13	$\frac{\text{kJ}}{\text{mol}}$
4	H_2O	2.17×10^{5}		88.68	$\frac{\text{kJ}}{\text{mol}}$	3	1.250×10^{15}	$\frac{\text{kmol\,bar}^{0.5}}{\text{kg}_{\text{cat}}\,\text{h}}$	243.90	$\frac{\text{kJ}}{\text{mol}}$
5	H_2	7.50×10^{-9}	bar^{-1}	-82.90	$\frac{\text{kJ}}{\text{mol}}$					

The temperature dependent equilibrium constants K_1, K_2 and K_3 are based on the Gibbs reaction energy (STP) as shown in Poling et al. [Pol01].

Finally, a unit conversion is required to adequately implement these rate equations to eqn (4) and (5):

$$\tilde{r}_\beta = r_\beta\, \rho_{\text{cat}}\, 1000/3600.$$

Koschany et al.

Koschany et al. [Kos16] exclusively considered CO_2 methanation to describe they experimental kinetic data. The corresponding rate equation is:

$$r_{\text{meth}} = k\, p_{CO_2}^{0.5}\, p_{H_2}^{0.5} \left(1 - \frac{p_{CH_4}\, p_{H_2O}^2}{K_{\text{eq}}\, p_{CO_2}\, p_{H_2}^4}\right) \bigg/ \text{DEN}^2, \tag{A.4}$$

$$\text{DEN} = 1 + K_{\text{OH}}\, \frac{p_{H_2O}}{p_{H_2}^{0.5}} + K_{H_2}\, p_{H_2}^{0.5} + K_{\text{mix}}\, p_{CO_2}^{0.5}, \tag{A.5}$$

which is determined by the following correlations for rate coefficient k, adsorption constant K_x and equilibrium constant K_{eq}:

$$k = k_{0,\text{ref}}\, \exp\left(\frac{E_A}{\mathcal{R}}\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right), \tag{A.6}$$

$$K_x = K_{x,0,\text{ref}}\, \exp\left(\frac{\Delta H_x}{\mathcal{R}}\left(\frac{1}{T_{\text{ref}}} - \frac{1}{T}\right)\right), \tag{A.7}$$

$$K_{\text{eq}} = 137\, T^{-3.998}\, \exp\left(\frac{158.7\,\text{kJ/mol}}{\mathcal{R}\, T}\right). \tag{A.8}$$

Again, a unit conversion is required to adequately implement this rate equation to eqn (4) and (5):

$$\tilde{r}_{\text{meth}} = r_{\text{meth}}\, \rho_{\text{cat}}\, 1000.$$

Table A.2: Kinetic parameters for Eqs. (A.6) to (A.8); (see Koschany et al. [Kos16])

T_{ref}	550	K
$k_{0,ref}$	3.46e-4	mol/(bar s g_{cat})
E_A	77.5	kJ/mol
$K_{OH,0,ref}$	0.5	$bar^{-0.5}$
ΔH_{OH}	22.4	kJ/mol
$K_{H2,0,ref}$	0.44	$bar^{-0.5}$
ΔH_{H2}	-6.2	kJ/mol
$K_{mix,0,ref}$	0.88	$bar^{-0.5}$
ΔH_{mix}	-10	kJ/mol

A.3 Reference case details

In order to enable a simple replication of our results, we outline detailed information on the reference reactor setting in Table 1 and the corresponding steady state assuming a coolant temperature of $T_{cool} = 550$ K. Furthermore, surface plots illustrate the finite volume mesh density and provide a clearer visualization of our chosen PDE discretization.
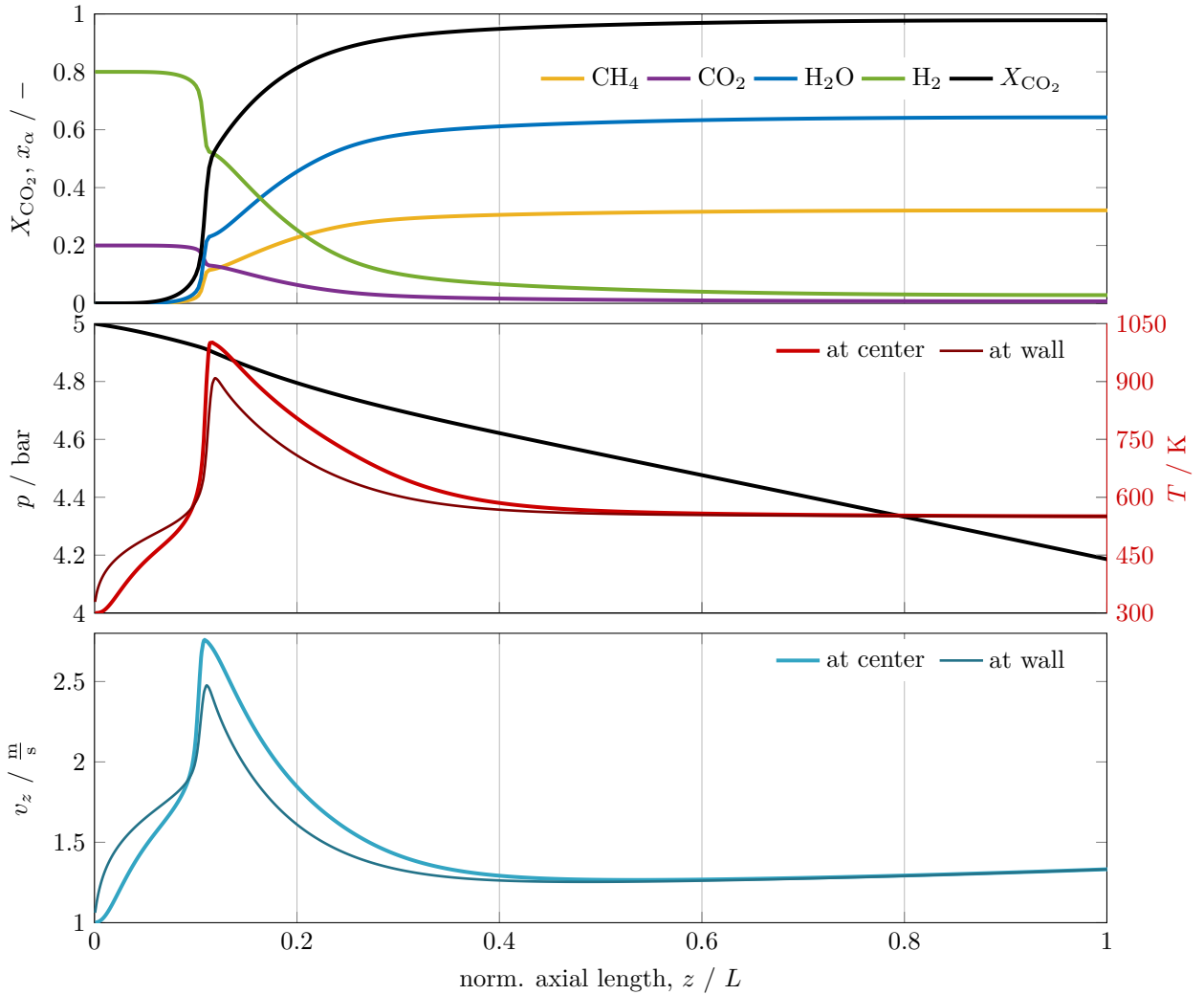

Figure A.2: Conversion, composition, temperature, pressure and velocity changes along the entire reactor length; reactor setting according to Table 1 and at $T_{cool} = 550$ K
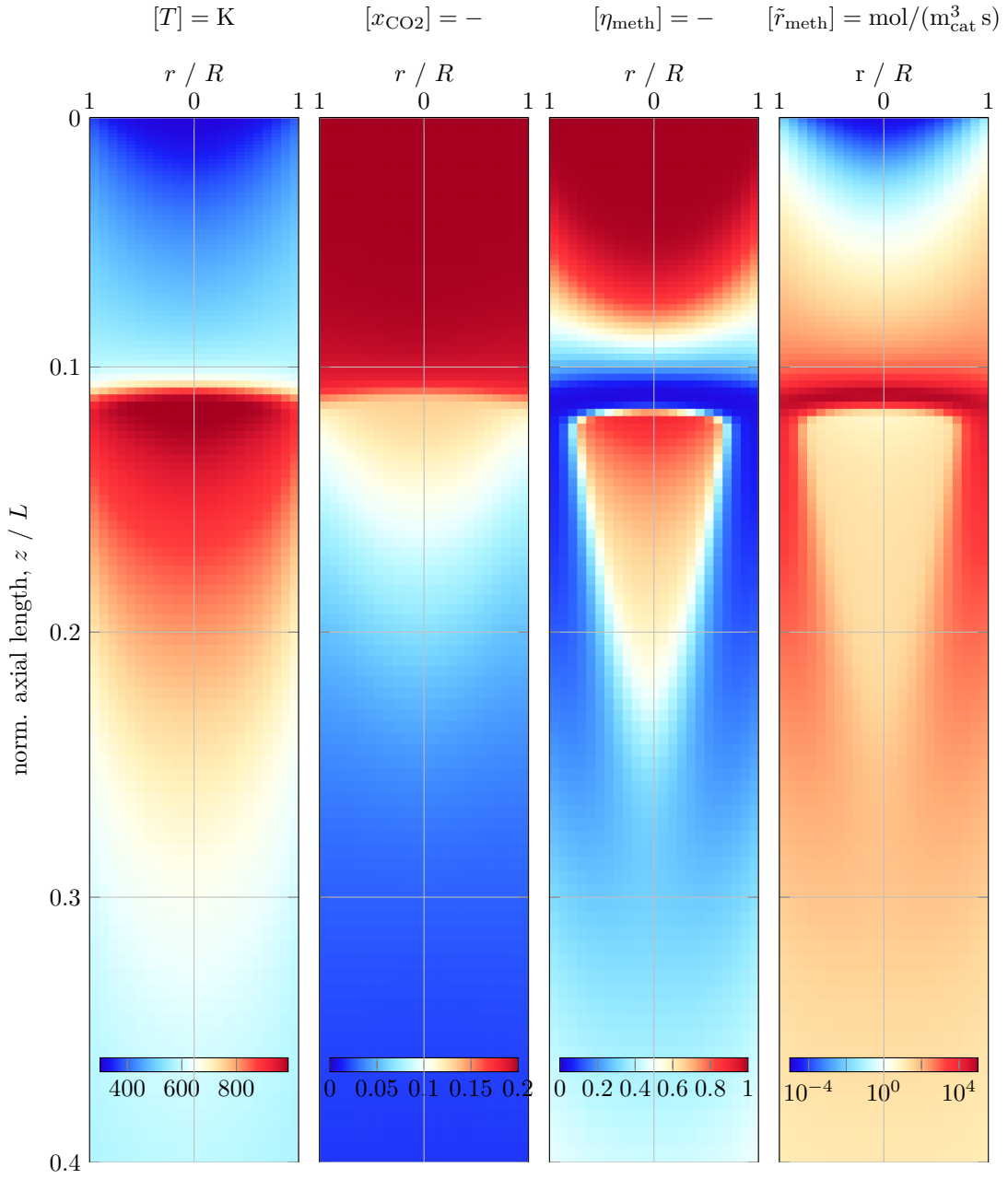
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Reaction

Figure A.3: Temperature, CO$_2$-composition, effectiveness factor and reaction rate changes around the reactive zone; reactor setting according to Table 1 and at $T_{\mathrm{cool}} = 550\,\mathrm{K}$
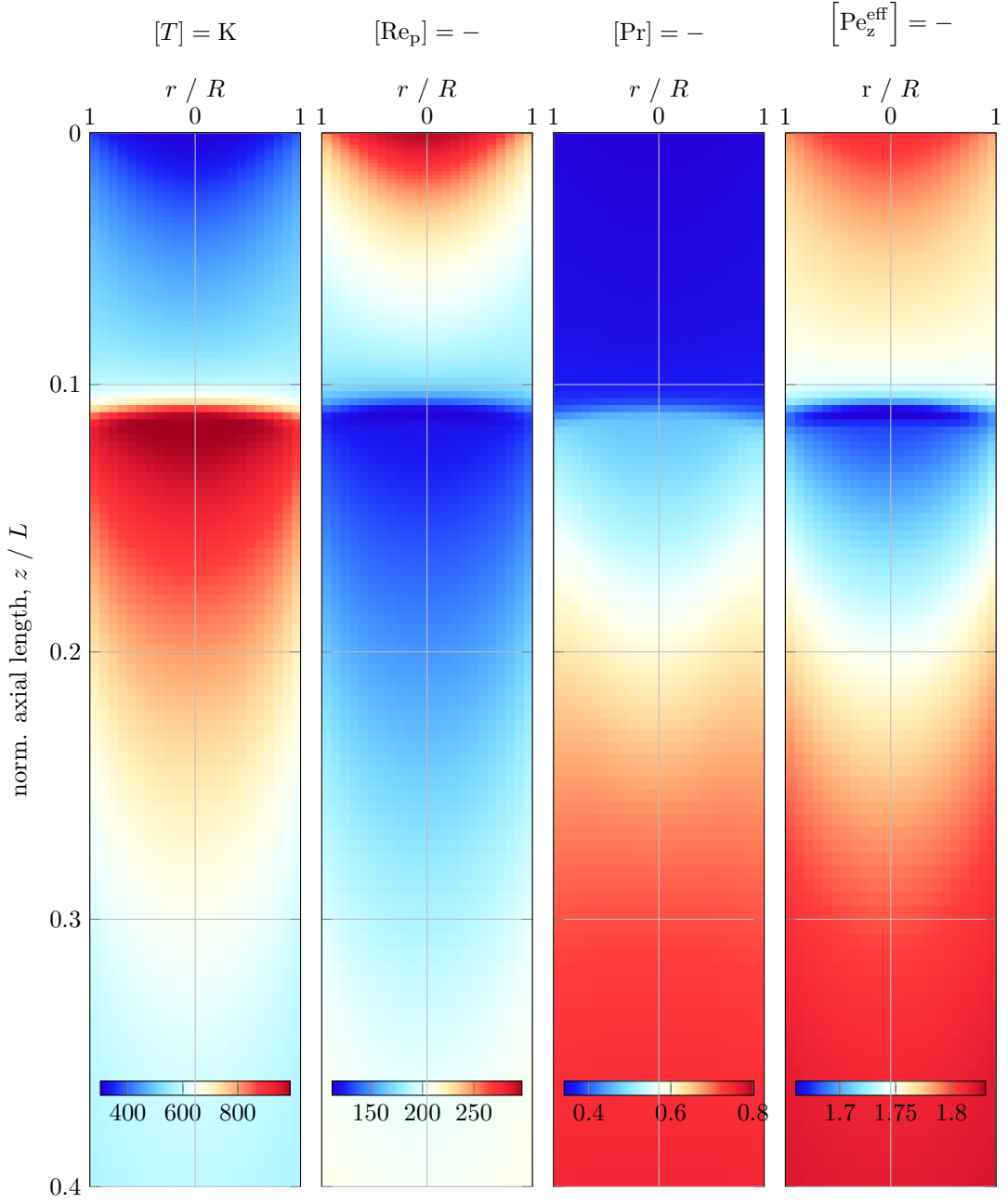
Heat and mass transport

Figure A.4: Temperature, Reynolds number, Prandtl number and effective axial Péclet number around the reactive zone; reactor setting according to Table 1 and at $T_{\text{cool}} = 550\,\text{K}$
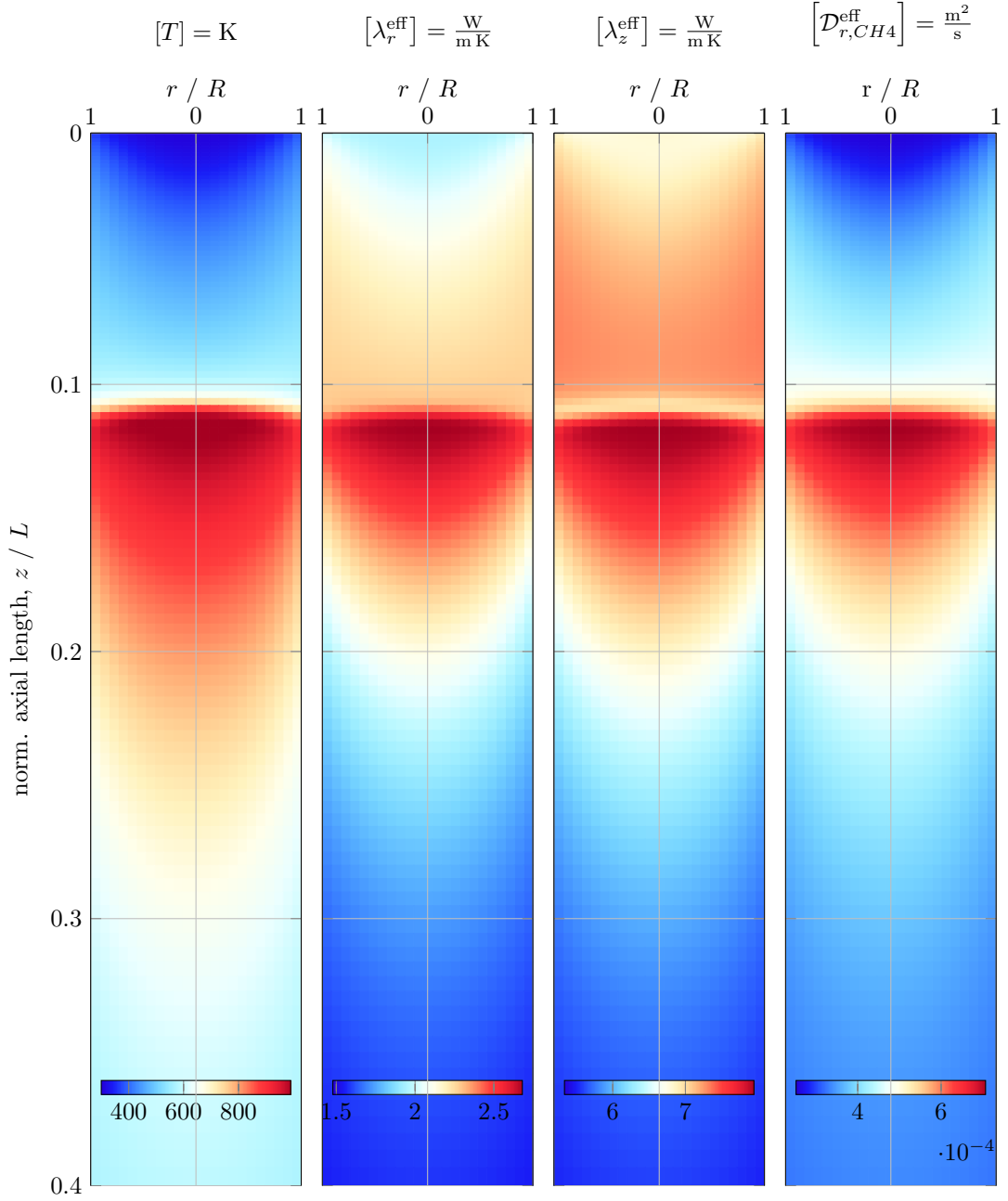
Figure A.5: Temperature, effective radial conductivity, effective axial conductivity and effective CH_4 diffusion coefficient around the reactive zone; reactor setting according to Table 1 and at $T_{\text{cool}} = 550\,\text{K}$
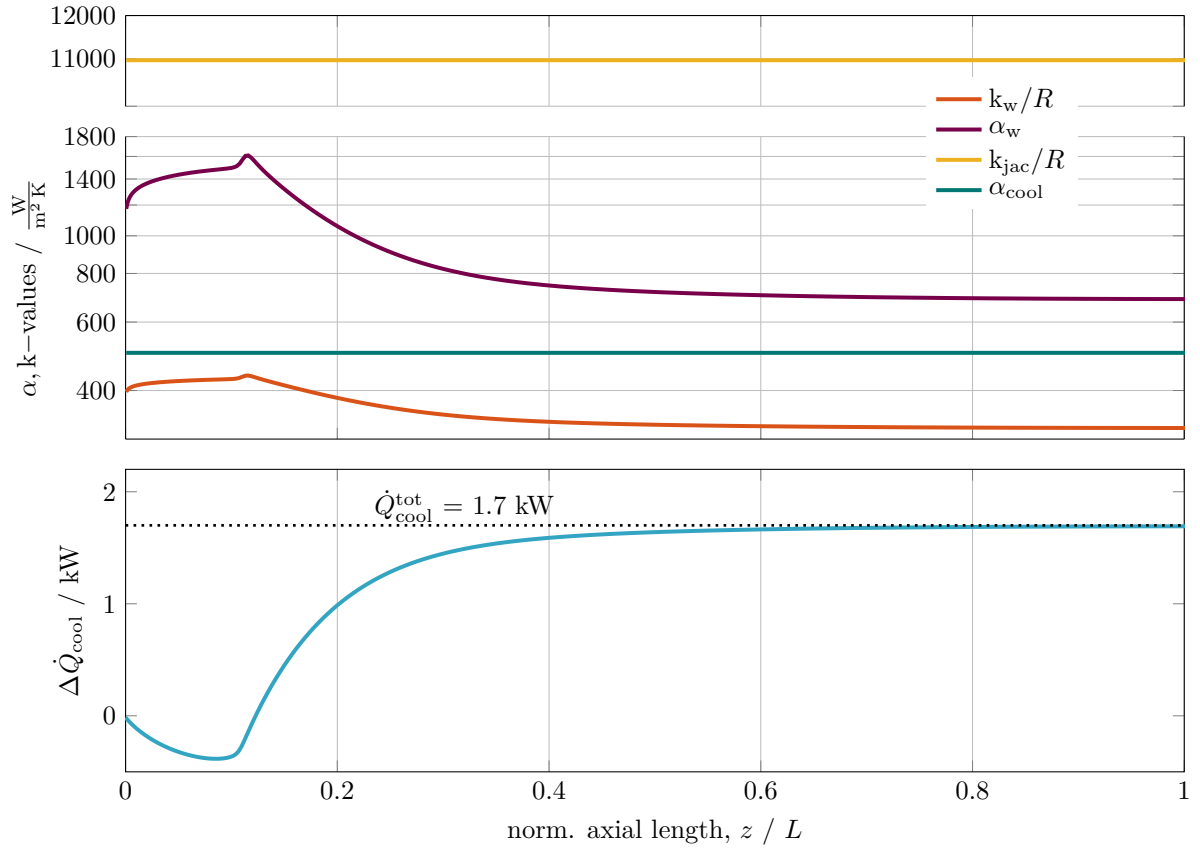
Figure A.6: Heat transport coefficients and cumulative heat transfer from reactor to coolant along the entire reactor length; reactor setting according to Table 1 and at $T_{\text{cool}} = 550\,\text{K}$
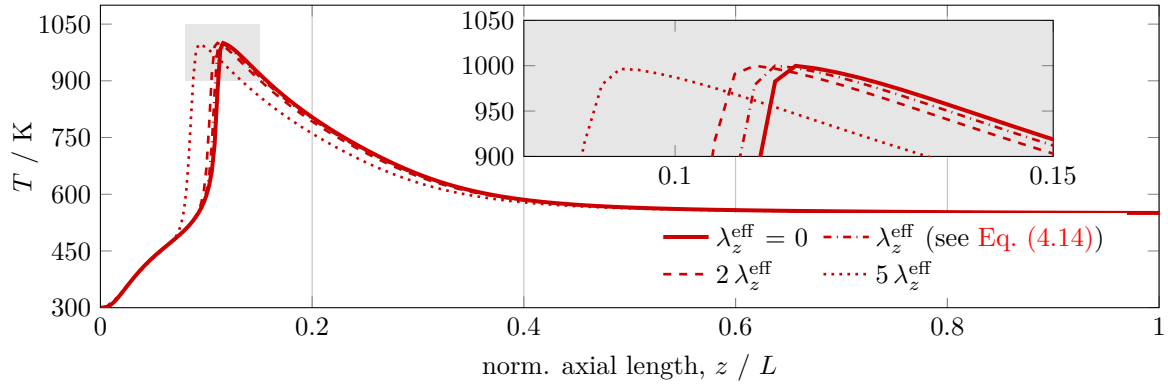
A.4 Influence of axial heat dispersion

Figure A.7: Influence of axial heat dispersion on steady-state temperature profile (at center); reactor setting according to Table 1 and at $T_{\mathrm{cool}} = 550\,\mathrm{K}$

References

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