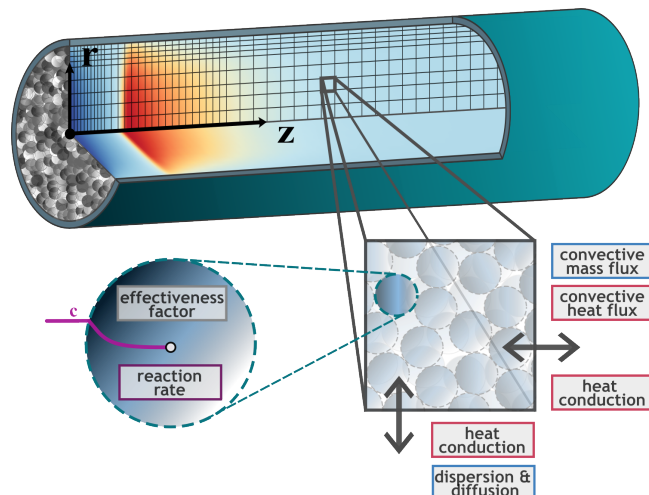# CARD Reactor Equations Overview
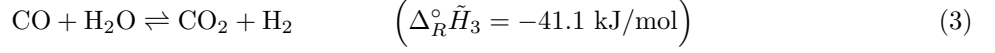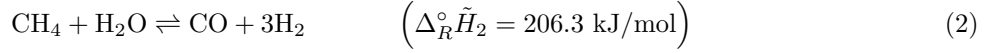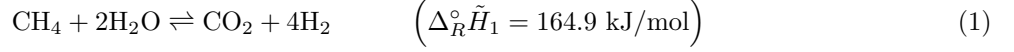
Contents

1 Reaction scheme

The reaction scheme for carbon dioxide methanation is given by [1, p. 1022]:

$$CH_4 + 2H_2O \rightleftharpoons CO_2 + 4H_2 \qquad \left(\Delta_R^\circ \tilde{H}_1 = 164.9 \text{ kJ/mol}\right) \tag{1}$$

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \qquad \left(\Delta_R^\circ \tilde{H}_2 = 206.3 \text{ kJ/mol}\right) \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad \left(\Delta_R^\circ \tilde{H}_3 = -41.1 \text{ kJ/mol}\right) \tag{3}$$

The reactions are described in the following equations with the index ζ. The index α describes the existing components of the fluid (gas) mixture: CH_4, H_2O, CO, H_2, CO_2.
In this simulation only the first reaction equation with the kinetic according to Koschany et.al. is taken into account.

2 Fixed bed porosity

For Spheres with the diameter d_p and the reactor tube diameter d_t the bed void fraction ϵ can be calculated with [2, p. 708]:

$$\epsilon = \begin{cases} 0.4 + 0.05\,(d_p/d_t) + 0.412\,(d_p/d_t)^2 & d_p/d_t \leq 0.5 \\ 0.528 + 2.464\,(d_p/d_t - 0.5) & 0.5 \leq d_p/d_t \leq 0.536 \\ 1 - 0.667\,(d_p/d_t)^3\,(2d_p/d_t - 1)^{-0.5} & d_p/d_t \geq 0.536 \end{cases} \tag{4}$$

3 Species conservation (ODE):

$$\epsilon \cdot \bar{\rho}_{\text{fl.}} \cdot \frac{\partial w_\alpha}{\partial t} = - \underbrace{\frac{\partial j_{\alpha,z}}{\partial z}}_{\substack{\text{axial} \\ \text{mass flow}}} - \underbrace{\frac{1}{r} \cdot \frac{\partial (j_{\alpha,r} \cdot r)}{\partial r}}_{\substack{\text{radial} \\ \text{mass flow}}} + \underbrace{(1 - \epsilon) \cdot M_\alpha \cdot \sum_\zeta (\eta_\zeta \cdot \nu_{\alpha,\zeta} \cdot \tilde{r}_\zeta)}_{\substack{\text{change by} \\ \text{reaction}}} \tag{5}$$

3.1 Mean mass density of the liquid phase

With the ideal gas law

$$c_\alpha = \frac{p_\alpha}{\tilde{R} \cdot T} \Leftrightarrow \bar{c}_{\text{fl.}} = \frac{p}{\tilde{R} \cdot T} \tag{6}$$

the mean mass density of the liquid phase $\bar{\rho}_{\text{fl.}}$ can be calculated with the mean molar mass of the liquid phase $\bar{M}_{\text{fl.}}$:

$$\bar{M}_{\text{fl.}} = \left(\sum_\alpha \frac{w_\alpha}{M_\alpha}\right)^{-1} \tag{7}$$

$$\bar{\rho}_{\text{fl.}} = \bar{c}_{\text{fl.}} \cdot \bar{M}_{\text{fl.}} \tag{8}$$

3.2 Axial mass flow

Source: [1, p. 1024]:
The mass flow j_α of the component α consists of convection and dispersion. The latter takes diffusion as well as flow induced transportation effects (e.g. back mixing) into account.

$$j_{\alpha,z} = -(\underbrace{\mathscr{D}_{\alpha,z}^{\text{eff}} \cdot \frac{\partial (w_\alpha \cdot \bar{\rho}_{\text{fl.}})}{\partial z}}_{\text{dispersion}} + \underbrace{v_z \cdot w_\alpha \cdot \bar{\rho}_{\text{fl.}}}_{\text{convection}}) \tag{9}$$

The ratio of the mass transport by convection to that by diffusion is described by the Bodenstein number Bo:

$$Bo = \frac{v_z \cdot L}{\mathscr{D}_z} = \frac{Pe_{z,\text{ fl.}} \cdot L}{d_{\text{p}}} \qquad \text{with} \quad Pe_{z,\text{ fl.}}(Re_{\text{p}} > 10) \to 2 \tag{10}$$

For $Bo > 100$ axial convective mass transport dominates significantly and mass dispersion (i.e. axial back-mixing) becomes negligible:

$$j_{\alpha,z} = -v_z \cdot \bar{\rho}_{\text{fl.}} \cdot \partial w_\alpha \tag{11}$$

3.3 Radial mass flow

Equation (9) can also be used to describe the radial mass flow:

$$j_{\alpha,r} = -(\underbrace{\mathscr{D}_{\alpha,r}^{\text{eff}} \cdot \frac{\partial \beta_\alpha}{\partial r}}_{\text{dispersion}} + \underbrace{v_r \cdot \beta_\alpha \frac{\partial \beta_\alpha}{\partial z}}_{\text{convection}}) \tag{12}$$

with

$$\beta_\alpha = \rho \cdot w_\alpha \tag{13}$$

Since no radial fluid flow is assumed (plug flow) the convection term equals zero and the mass flow can be described as:

$$j_{\alpha,r} = -\mathscr{D}_{\alpha,r}^{\text{eff}} \cdot \frac{\partial \beta_\alpha}{\partial r} \tag{14}$$

The effective radial species dispersion for a packed-bed with spherical particles can be calculated using the model of Winterberg et al. shown in the VDI heat atlas [7, chap. M7.6]:

$$\mathscr{D}_{\alpha,r}^{\text{eff}} = \delta_{\text{bed}} + K_1 \cdot \text{Pe}_0 \frac{v_{z,\ r=0}}{v_z} f(R_{\text{Reactor}} - r) \cdot \delta_{\alpha,\text{fl.}} \tag{15}$$

with

$$K_1 = \frac{1}{8} \cdot \left(1 + \frac{3}{\text{Pe}_{0,\ c}^{0.5}}\right)^{-1} \tag{16}$$

$$\text{Pe}_0 = v_z \cdot \epsilon \cdot \frac{d_{\text{cat}}}{\delta_{\alpha,\text{fl.}}} \ ; \qquad \text{Pe}_{0,\ c} = v_{z,\ r=0} \cdot \epsilon \cdot \frac{d_{\text{cat}}}{\delta_{\alpha,\text{fl.}}} \tag{17}$$

$$f(R_{\text{reactor}} - r) = \begin{cases} \left(\dfrac{R_{\text{Reactor}} - r}{K_2 d}\right)^2 & \text{for } 0 < R_{\text{Reactor}} - r \leq K_2 d \\ 1 & \text{for } K_2 d < R_{\text{Reactor}} - r \leq R \end{cases} \tag{18}$$

$$K_2 = 0.44 \tag{19}$$

δ_{bed} is the diffusion coefficient of the fixed bed with no fluid flow. It can be calculated via [7, chap. D6.3]:

$$\delta_{\text{bed}} = (1 - \sqrt{1 - \epsilon}) \cdot \delta_{\alpha,\text{fl.}} \tag{20}$$

The diffusion coefficient $\delta_{\alpha,\text{fl.}}$ can be calculated as an mixture averaged diffusion coefficient of the species α diffusing into a mixture of other gases (binary diffusion coefficients):

$$\delta_{\alpha,r} = \frac{\dfrac{\bar{\rho}_{\text{fl.}}}{\bar{M}_{\text{fl.}}} - \dfrac{\rho_\alpha}{M_\alpha}}{\sum\limits_{\substack{j \\ j \neq \alpha}} \dfrac{\rho_j}{M_j \cdot \delta_{\alpha,j}}} \tag{21}$$

The binary diffusion coefficients for the Stefan regime ($Kn \ll 1$) can be calculated with the Fuller equation:

$$\frac{\delta_{i,j\ \text{Stefan}}}{\frac{\text{m}^2}{\text{s}}} = \frac{1.013 \cdot 10^{-7} \left(\frac{T}{\text{K}}\right)^{1.75} \cdot \left[\left(\dfrac{M_i}{\frac{\text{g}}{\text{mol}}}\right)^{-1} + \left(\dfrac{M_j}{\frac{\text{g}}{\text{mol}}}\right)^{-1}\right]^{-\frac{1}{2}}}{\dfrac{p}{\text{bar}} \cdot \left[(\sum v_i)^{\frac{1}{3}} + (\sum v_j)^{\frac{1}{3}}\right]^2} \tag{22}$$

3.4 Reaction rate

Koschany et al. exclusively considered CO_2 methanation (1) to describe they experimental kinetic data. The corresponding Langmuir-Hinshelwood-Hougen-Watson (LHHW) rate equation is [4, p. 511]:

$$r_1 = \frac{k \cdot p_{\text{CO}_2}^{0.5} \cdot p_{\text{H}_2}^{0.5} \cdot \left(1 - \dfrac{p_{\text{CH}_4} \cdot p_{\text{H}_2\text{O}}^2}{K_{\text{eq}} \cdot p_{\text{CO}_2} \cdot p_{\text{H}_2}^4}\right)}{\left(1 + K_{\text{OH}} \cdot \dfrac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}^{0.5}} + K_{\text{H}_2} \cdot p_{\text{H}_2}^{0.5} + K_{\text{mix}} \cdot p_{\text{CO}_2}^{0.5}\right)^2} \tag{23}$$

which is determined by the following correlations for rate coefficient k, adsorption constant K_x and equilibrium constant K_{eq} (Arrhenius/Van't Hoff type) [4, p. 507]:

$$k \quad = k_{0,\ \text{ref}} \cdot \exp\left\{ \frac{E_A}{\tilde{R}} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right\} \tag{24}$$

$$K_x \quad = K_{x,0,\text{ref}} \cdot \exp\left\{ \frac{\Delta H_x}{\tilde{R}} \left(\frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right\} \tag{25}$$

$$K_{eq} \quad = 137 \cdot T^{-3.998} \cdot \exp\left\{ \frac{158.7 \ \text{kJ/mol}}{\tilde{R} \cdot T} \right\} \tag{26}$$

A unit conversion is required to adequately implement this rate equation:

$$\tilde{r}_1 = r_1 \cdot \rho_{\text{cat}} \cdot 1000 \qquad \text{with} \ [\tilde{r}] = \frac{mol}{m_{\text{cat}}^3 \cdot s}.$$

The parameter set for the NiAl(O)$_x$ catalysts is given as [4, p. 512]:

T_{ref}	550	K
$k_{0,\ \text{ref}}$	3.46e−4	mol/(bar s g$_{\text{cat}}$)
E_A	77.5	kJ/mol
$K_{\text{OH},0,\ \text{ref}}$	0.5	bar$^{-0.5}$
ΔH_{OH}	22.4	kJ/mol^2
$K_{\text{H2},0,\ \text{ref}}$	0.44	bar$^{-0.5}$
ΔH_{H2}	-6.2	kJ/mol
$K_{\text{mix},0,\ \text{ref}}$	0.88	bar$^{-0.5}$
ΔH_{mix}	-10	kJ/mol

3.5 Effectiveness factor

Source: [1, p. 1025]
The most relevant resistance is inside the catalyst (intra-particle transport limitation). In contrast, interfacial transport limitations between solid and gas phase are found to be negligible for similar reactor configurations. In order to account for temperature dependent intraparticle mass transport limitations in combination with the pseudo-homogeneous phase assumption, Kiewidt and Thöming proposed to use an effectiveness factor based on the Thiele modulus for spherical particles:

$$\eta_1 = \frac{3}{\Phi_1} \left[\frac{1}{\tanh\left(\Phi_1\right)} - \frac{1}{\Phi_1} \right] \tag{27}$$

where the Thiele modulus considers the key reaction for methanation (1) as a first order reaction with respect to carbon dioxide as key component, such that

$$\Phi_1 = \frac{d_{\text{cat}}}{2} \cdot \sqrt{\frac{\nu_{\text{CO}_2} \cdot \tilde{r}_1}{\delta_{\text{CO}_2,\ p}^{\text{eff}} \cdot c_{\text{CO}_2}}} \tag{28}$$

Therefore, the effective diffusivity inside the particle $\delta_{\text{CO}_2,\ p}^{\text{eff}}$ accounts for Stefan and Knudsen diffusion with

$$\delta_{\text{CO}_2,\ p} = \left[\frac{\tau_p^2}{\epsilon_p} \cdot \left(\frac{1}{\delta_{\text{CO}_2,\ p}^{\text{Stefan}}} + \frac{1}{\delta_{\text{CO}_2,\ p}^{\text{Knudsen}}} \right) \right]^{-1} \tag{29}$$

According to the kinetic gas theory the diffusion coefficient in the Knudsen regime can be calculated with

$$\delta_{\text{CO}_2,\ p}^{\text{Knudsen}} = \frac{d_p}{3} \sqrt{\frac{8 \cdot \tilde{R} \cdot T}{\pi \cdot M_{\text{CO}_2}}} \tag{30}$$

The molecular diffusion coefficient is calculated via the Fuller equation (22) and the mixture averaged diffusion coefficients for CO2 with equation (21).

4

4 Energy conservation (ODE):

$$\left(\rho \cdot c_{\mathrm{p}}\right)^{\mathrm{eff}} \cdot \frac{\partial T}{\partial t} = \underbrace{-v_{\mathrm{z}} \cdot \sum_{\alpha}\left(\rho_{\alpha} \cdot c_{\mathrm{p},\alpha}\right) \cdot \frac{\partial T}{\partial z}}_{\textbf{convective heat flux}} - \underbrace{\left(\frac{\partial \dot{q}_{\mathrm{z}}}{\partial z} + \frac{1}{r}\frac{\partial\left(\dot{q}_{\mathrm{r}} \cdot r\right)}{\partial r}\right)}_{\textbf{heat conduction}} - \underbrace{(1-\epsilon) \cdot \sum_{\zeta}\left(\eta_{\zeta} \cdot \Delta_R^{\circ}\tilde{H}_{\zeta} \cdot \tilde{r}_{\zeta}\right)}_{\textbf{reaction heat}} \tag{31}$$

with $\left(\rho \cdot c_p\right)^{\mathrm{eff}}$ being the effective product of the density and specific heat capacity for the fixed bed which contains both fluid and catalyst:

$$\left(\rho \cdot c_p\right)^{\mathrm{eff}} = (1-\epsilon) \cdot \rho_{\mathrm{cat}} \cdot c_{p,\mathrm{cat}} + \epsilon \cdot \bar{\rho}_{\mathrm{fl.}} \cdot c_{p,\mathrm{fl.}} \quad \text{with } c_{p,\mathrm{fl.}} = \sum_{\alpha}\left(w_{\alpha} \cdot c_{p,\alpha}\right) \tag{32}$$

4.1 Heat conduction

The axial and radial heat flux density $\dot{q}$ is given by:

$$\dot{q}_z = -\lambda_z^{\mathrm{eff}} \cdot \frac{\partial T}{\partial z} \quad \text{and} \quad \dot{q}_r = -\lambda_r^{\mathrm{eff}} \cdot \frac{\partial T}{\partial r} \tag{33}$$

At the radial boundary condition *reactor wall*, the term changes to:

$$\dot{q}_r = -\alpha_{\mathrm{w}}\left(T_{\mathrm{wall,i}} - T\right) \tag{34}$$

4.1.1 Effective axial thermal conductivity

Source: [1, p. 1024-1025]
With the axial thermal Péclet number Pe_z^{eff} follows:

$$\lambda_z^{\mathrm{eff}} = \frac{v_z \cdot \bar{\rho}_{\mathrm{fl.}} \cdot c_{p,\mathrm{fl.}} \cdot d_p}{Pe_z^{\mathrm{eff}}} \tag{35}$$

According to Dixon and Cresswell for large $\dfrac{D_{\mathrm{Reactor}}}{d_p}$ ratios one can rely on:

$$Pe_z^{\mathrm{eff}} = \left(\frac{1}{Pe_{z,\,\mathrm{fl.}}} + \frac{\dfrac{\lambda_{\mathrm{bed}}}{\lambda_{\mathrm{fl.}}}}{Re_p \cdot Pr}\right)^{-1} \quad \text{with} \quad Pe_{z,\,\mathrm{fl.}}(Re_{\mathrm{p}} > 10) \to 2 \tag{36}$$

with the particle Reynolds number

$$Re_p = \frac{|v_z - v_p| \cdot d_p}{\nu_{\mathrm{fl.}}} = \frac{|v_z - v_p| \cdot d_p \cdot \bar{\rho}_{\mathrm{fl.}}}{\eta_{\mathrm{fl.}}} \quad \text{with} \quad v_p = 0\frac{m}{s} \tag{37}$$

and the Prandtl number [7, chap. A2]

$$Pr = \frac{\nu}{a} = \frac{\eta \cdot c_p}{\lambda} \quad \text{with} \quad a = \frac{\lambda}{\rho \cdot c_p} \tag{38}$$

4.1.2 Effective radial thermal conductivity

The effective radial thermal conductivity for a packed-bed with spherical particles can be calculated using the model of Winterberg et al. shown in the VDI heat atlas [7, chap. M7.6]:

$$\lambda_{\mathrm{r}}^{\mathrm{eff}} = \lambda_{\mathrm{bed}} + \frac{1}{8}\mathrm{Pe}_0\frac{v_{\mathrm{z,\,r=0}}}{v_{\mathrm{z}}}f(R_{\mathrm{Reactor}} - r) \cdot \lambda_{\mathrm{fl.}} \tag{39}$$

with

$$\mathrm{Pe}_0 = v_{\mathrm{z}} \cdot \epsilon \cdot \bar{\rho}_{\mathrm{fl.}} \cdot c_{\mathrm{p,\,fl.}}\frac{d_{\mathrm{cat}}}{\lambda_{\mathrm{fl.}}} \tag{40}$$

$$f(R_{\mathrm{reactor}} - r) = \begin{cases} \left(\dfrac{R_{\mathrm{Reactor}} - r}{K_2 d}\right)^2 & \text{for } 0 < R_{\mathrm{Reactor}} - r \leq K_2 d \\ 1 & \text{for } K_2 d < R_{\mathrm{Reactor}} - r \leq R \end{cases} \tag{41}$$

5

$$K_2 = 0.44 + 4 \cdot \exp\left(-\frac{\text{Re}_0}{70}\right) \tag{42}$$

$$\text{Re}_0 = \frac{v_\text{z} \cdot \epsilon \cdot d_\text{cat} \cdot \bar{\rho}_\text{fl.}}{\eta_\text{fl.}} \tag{43}$$

The thermal conductivity of the bed λ_bed can be calculated with the model of Zehner and Schlünder [7, chap. M7.6]:

$$k_\text{bed} = \frac{\lambda_\text{bed}}{\lambda_\text{fl.}} = k_{\text{bed, }0} + \left(1 - \sqrt{1-\epsilon}\right) \cdot k_\text{rad} + \sqrt{1-\epsilon}\left(\frac{1}{k_\text{rad}} + \frac{1}{k_\text{p}}\right)^{-1} \tag{44}$$

The parameter $k_{\text{bed, }0}$ is the quotient of the thermal conductivity of the bed and fluid if the fluid is stationary and not flowing. It can be calculated with the model of Zehner, Bauer and Schlünder from [7, chap. 6.3-4]:

$$k_{\text{bed, }0} = 1 - \sqrt{1-\epsilon} + \sqrt{1-\epsilon} \cdot k_\text{c} \tag{45}$$

with the relative thermal conductivity of the core of the unit cell k_c:

$$k_\text{c} = \frac{2}{N}\left(\frac{B}{N^2}\frac{k_\text{p}-1}{k_\text{p}}\ln\left(\frac{k_\text{p}}{B}\right) - \frac{B+1}{2} - \frac{B-1}{N}\right) \tag{46}$$

containing the parameters:

$$N = 1 - \frac{B}{k_\text{p}} \tag{47}$$

The deformation parameter B is calculated via:

$$B = 1.25\left(\frac{1-\epsilon}{\epsilon}\right)^{10/9} \tag{48}$$

The parameters k_p and k_rad are calculated via [7, chap. 6.3-4]:

$$k_\text{p} = \frac{\lambda_\text{cat}}{\lambda_\text{fl.}} \tag{49}$$

$$k_\text{rad} = \frac{4 \cdot \sigma}{\left(\frac{2}{\varepsilon} - 1\right)} \cdot T^3 \cdot \frac{d_\text{cat}}{\lambda_\text{fl.}} \tag{50}$$

with the emission coefficient of the particle surface ε and the radiation coefficient of the black body

$$\sigma = 5.67 \cdot 10^{-8} \frac{W}{m^2 \cdot K^4} \tag{51}$$

The thermal gas conductivity $\lambda_\text{fl.}$ is taken from Poling et al. [6]:

$$\lambda_\text{fl.} = \sum_{\alpha_1}\left(\frac{x_{\alpha_1} \cdot \lambda_{\alpha_1}}{\sum_{\alpha_2}\left(x_{\alpha_2} \cdot \phi_{\alpha_1,\alpha_2}\right)}\right) \tag{52}$$

which is determined by thermal component conductivities λ_α and a dynamic viscosity mixing rule

$$\phi_{\alpha_1,\alpha_2} = \frac{\left[1 + \left(\frac{\eta_{\alpha_1}}{\eta_{\alpha_2}}\right)^{\frac{1}{2}} \cdot \left(\frac{M_{\alpha_2}}{M_{\alpha_1}}\right)^{\frac{1}{4}}\right]^2}{\sqrt{8 \cdot \left(1 + \frac{M_{\alpha_1}}{M_{\alpha_2}}\right)}} \tag{53}$$

4.1.3 Heat transfer coefficient at the reactor wall

The heat transfer coefficient between the inner reactor wall and the bed can be described with a Nusselt-correlation [7, chap. M7.7]:

$$\alpha_\text{W} = \text{Nu}_\text{W} \cdot \frac{\lambda_\text{fl.}}{d_\text{cat}} \tag{54}$$

The Nusselt number at the wall can be calculated via:

$$\text{Nu}_\text{W} = \left(1.3 + \frac{5 \cdot d_\text{cat}}{D_\text{Reactor}}\right)\frac{\lambda_\text{bed}}{\lambda_\text{fl.}} + 0.19 \cdot \text{Re}_0^{0.75} \cdot \text{Pr}^{1/3} \tag{55}$$

With the Prandtl number:

$$\text{Pr} = \frac{\eta \cdot c_p}{\lambda_\text{fl.}} \tag{56}$$

Inner - outer reactor wall

The thermal resistance of the cooling jacket $\dfrac{1}{k_{\text{jac}}}$ is obtained via [1]:

$$k_{\text{jac}} = \left(\frac{1}{\lambda_{\text{jac}}} \cdot \ln\left(\frac{R + s_{\text{jac}}}{R} \right) \right)^{-1} \tag{57}$$

The inner wall temperatur is calculated via:

$$T_{\text{wall,i}} = \frac{\alpha_{\text{bed}}^{\text{total}} \cdot T_{\text{bed}} + \dfrac{k_{\text{jac}}}{s_{\text{jac}}} \cdot T_{\text{wall}}}{\alpha_{\text{bed}}^{\text{total}} + \dfrac{k_{\text{jac}}}{s_{\text{jac}}}} \tag{58}$$

Outer reactor wall - coolant

The heat transfer coefficient between the outer reactor wall and the coolant can be obtained by Nusselt correlations for the coolant flow. In this case a constant wall temperature T_{wall} is assumed (project task), which leads to $\alpha_{\text{wall, fluid}} \to \infty$.

5 Mass conservation (AE):

Source: [1, p. 1023]
With the assumption of gas velocity changes happening exclusively due to mass conservation and an overall constant axial mass flow, the following equation holds:

$$v = v_{z=0} \cdot \frac{\rho_{z=0}}{\rho} \tag{59}$$

6 Pressure drop (AE):

With the assumption that the dynamic momentum balance of a fixed-bed is typically dominated by friction the Ergun equation is used to compute the pressure drop over the fixed bed [3]:

$$\frac{\partial p}{\partial z} = v_z \cdot \frac{(1 - \epsilon)}{\epsilon^3} \cdot \left(\underbrace{\frac{150 \cdot (1 - \epsilon) \cdot \mu_{\text{fl.}}}{d_{\text{p}}^2}}_{\textbf{viscous term}} + \underbrace{\frac{1.75 \cdot \bar{\rho}_{\text{fl.}}}{d_{\text{p}}} \cdot v_z}_{\textbf{turbulent term}} \right) \tag{60}$$

The Ergun equation has an application range for spherical pellets with $\dfrac{d_{\text{reactor}}}{d_p} > 7$.

7 Discretization:

For a numerical solution of the ODE's, the spatial derivatives $\frac{\partial \theta}{\partial (z,r)}$ with $\theta = j_\alpha, w_\alpha, \dot{q}, T, p$ are approximated with $\frac{\Delta \theta}{\Delta (z,r)}$. In this chapter, the physical parameters are not shown for simplicity.

The discretization scheme for the finite-volume-approach is shown in Figure 1 with the centroids C, the faces F and the respective differences.
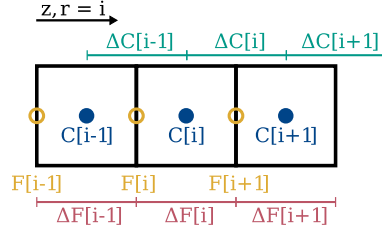

Figure 1: Finite-volume discretization scheme

7.1 Species and Energy Conservation Discretization

Since the species and energy conservation are calculated in analogue models, the discretization is also analogue. In the following, $\phi = T, w_i$ and $\Phi = \dot{q}, j_i$ are used as general derived parameters.

7.1.1 Axial

With first order upwind scheme:

$$\frac{\Delta \phi}{\Delta z} = \frac{\phi_{\mathrm{F[i+1]}} - \phi_{\mathrm{F[i]}}}{\Delta \mathrm{F[i]}} = \frac{\phi_{\mathrm{C[i]}} - \phi_{\mathrm{C[i-1]}}}{\Delta \mathrm{F[i]}} \tag{61}$$

7.1.2 Radial

In radial direction, two central difference schemes are combined to approximate the second derivative:

$$\frac{\Delta \Phi}{\Delta r} = \frac{\Delta \left(\frac{\Delta \phi}{\Delta r} \right)}{\Delta r} = \frac{\frac{\Delta \phi_{\mathrm{in}}}{\Delta r_{\mathrm{in}}} - \frac{\Delta \phi_{\mathrm{out}}}{\Delta r_{\mathrm{out}}}}{\Delta F[i]} \tag{62}$$

The inner derivative is approximated with a center difference scheme:

$$\frac{\Delta \phi_{\mathrm{in}}}{\Delta r} = \frac{\phi_{\mathrm{C[i-1]}} - \phi_{\mathrm{C[i]}}}{\Delta C[i-1]} \tag{63}$$

$$\frac{\Delta \phi_{\mathrm{out}}}{\Delta r} = \frac{\phi_{\mathrm{C[i]}} - \phi_{\mathrm{C[i+1]}}}{\Delta C[i]} \tag{64}$$

7.2 Pressure Drop Discretization

With first order upwind scheme:

$$\frac{\Delta p}{\Delta z} = \frac{p_{\mathrm{F[i+1]}} - p_{\mathrm{F[i]}}}{\Delta \mathrm{F[i]}} = \frac{p_{\mathrm{C[i]}} - p_{\mathrm{C[i-1]}}}{\Delta \mathrm{F[i]}} \tag{65}$$

8 Substance Properties:

8.1 Species Properties

Table 1: General species properties for CH_4, H_2, CO_2 and H_2.

Property		Unit	CH_4	H_2	CO_2	H_2	Source
Diffusion Volume	v_i	–	25.14	13.1	26.9	6.12	[7, chap. D1.10]
Molecular Weight	M_i	$kg\,mol^{-1}$	0.01604	0.01802	0.04401	0.002016	[5]

8.2 Temperature Dependent Species Properties

The properties heat capacity, thermal conductivity and dynamic viscosity of the chemical species can be calculated with a heat dependency. A second degree polynomial fit, shown below, was performed with data taken from the NIST-Database at isobaric conditions of p = 5 bar and the temperature ranges shown in the table captions [5]. If temperature dependent material properties in the model is set to true, the properties are calculated with the and temperature as input variable, otherwise constant values are used. The constant values are calculated with the same polynomial coefficients at T = 500 K.

$$y = k_1 + k_2 \cdot x + k_3 \cdot x^2 \tag{66}$$

Table 2: Polynomial coefficients for CH_4. Fitted data in temperature range: T = 300-600 K

Property	Property Unit	k_1	k_2	k_3
c_p	$J\,kg^{-1}\,K^{-1}$	1587.0057	1.5893	0.00207
η	$Pa\,s$	5.223333e-07	3.968143e-08	-1.364762e-11
λ	$W\,m^{-1}\,K^{-1}$	2.054738e-03	7.050143e-05	1.239619e-07

Table 3: Polynomial coefficients for H_2O. Fitted data in temperature range: T = 500-1000 K

Property	Property Unit	k_1	k_2	k_3
c_p	$J\,kg^{-1}\,K^{-1}$	2389.797	-1.129	0.001044
η	$Pa\,s$	-4.954286e-06	4.593789e-08	-3.341071e-12
λ	$W\,m^{-1}\,K^{-1}$	-2.047571e-03	5.770379e-05	4.061786e-08

Table 4: Polynomial coefficients for CO_2. Fitted data in temperature range: T = 300-1000 K

Property	Property Unit	k_1	k_2	k_3
c_p	$J\,kg^{-1}\,K^{-1}$	613.504	1.005	-0.000384
η	$Pa\,s$	-6.721429e-08	5.467619e-08	-1.347381e-11
λ	$W\,m^{-1}\,K^{-1}$	-9.104310e-03	8.906750e-05	-8.951190e-09

Table 5: Polynomial coefficients for H_2. Fitted data in temperature range: T = 300-1000 K

Property	Property Unit	k_1	k_2	k_3
c_p	$J\,kg^{-1}\,K^{-1}$	14304.773	0.05288	0.000608
η	$Pa\,s$	2.801093e-06	2.172896e-08	-3.832798e-12
λ	$W\,m^{-1}\,K^{-1}$	6.286452e-02	4.312905e-04	-3.483333e-08

8.3 Reactor

Table 6: Reactor specific properties. All values are taken from Bremer [1].

Property		Unit	Value
Diameter	D_{Reactor}	0.02	m
Length	L_{Reactor}	2.5	m
Wall Thickness	s_{jac}	0.002	m
Wall Thermal Conductivity	λ_{jac}	20	$\text{W m}^{-1}\,\text{K}^{-1}$

8.4 Catalyst

Table 7: Catalyst specific properties. All values are taken from Bremer [1].

Property		Value	Unit
Diameter	d_{cat}	0.002	m
Tortuosity	τ_{p}	2	—
Porosity	ϵ_{p}	0.6	—
Pore Diameter	d_{p}	$1 \cdot 10^{-8}$	m
Emission Coefficient	ε	0.9	—
Density (porous)	ρ_{cat}	2355.2	kg m^{-3}
Heat Capacity	$c_{\text{p, cat}}$	1107	$\text{J kg}^{-1}\,\text{K}^{-1}$
Thermal Conductivity	λ_{cat}	3.6	$\text{W m}^{-1}\,\text{K}^{-1}$

References

[1] Jens Bremer and Kai Sundmacher. "Operation range extension via hot-spot control for catalytic CO2 methanation reactors". In: *Reaction Chemistry & Engineering* 4.6 (May 28, 2019), pp. 1019–1037. ISSN: 2058-9883. DOI: 10.1039/C9RE00147F. URL: https://pubs.rsc.org/en/content/articlelanding/2019/re/c9re00147f (visited on 12/30/2024).

[2] Anthony G. Dixon. "Correlations for wall and particle shape effects on fixed bed bulk voidage". In: *The Canadian Journal of Chemical Engineering* 66.5 (1988), pp. 705–708. ISSN: 1939-019X. DOI: 10.1002/cjce.5450660501. URL: https://onlinelibrary.wiley.com/doi/abs/10.1002/cjce.5450660501 (visited on 12/30/2024).

[3] Sabri Ergun. "Fluid Flow through Packed Columns". In: *Chemical engineering progress,48(2)* (1952).

[4] Franz Koschany, David Schlereth, and Olaf Hinrichsen. "On the kinetics of the methanation of carbon dioxide on coprecipitated NiAl(O)x". In: *Applied Catalysis B: Environmental* 181 (Feb. 1, 2016), pp. 504–516. ISSN: 0926-3373. DOI: 10.1016/j.apcatb.2015.07.026. URL: https://www.sciencedirect.com/science/article/pii/S092633731530045X (visited on 12/30/2024).

[5] Peter Linstrom. *NIST Chemistry WebBook, NIST Standard Reference Database 69*. 1997. DOI: 10.18434/T4D303. URL: http://webbook.nist.gov/chemistry/ (visited on 01/15/2025).

[6] Bruce E. Poling, John M. Prausnitz, and John P. O'Connell. *Properties of Gases and Liquids*. Fifth edition. McGraw-Hill's AccessEngineering. New York, N.Y: McGraw-Hill Education, 2001. ISBN: 9780070116825 9780071499996.

[7] VDI e. V., ed. *VDI-Wärmeatlas*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2013. ISBN: 978-3-642-19980-6 978-3-642-19981-3. DOI: 10.1007/978-3-642-19981-3. URL: https://link.springer.com/10.1007/978-3-642-19981-3 (visited on 11/14/2024).