# Master

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## 1 Theory - Derivation of governing equations

Differential equations describing the change in mass fractions for the different components in radial direction within the catalyst pellets are to be derived. General species mass and mole balance for a component i is given respectively as:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \nabla \cdot (\rho\omega_i v) = -\nabla \cdot (j_i) + R_i \tag{1}$$

$$\frac{\partial}{\partial t}(cx_i) + \nabla \cdot (cx_i u) = -\nabla \cdot (J_i) + R_i \tag{2}$$

Where:

| | |
|---|---|
| $\frac{\partial}{\partial t}(\rho\omega_i)\,,\ \frac{\partial}{\partial t}(cx_i)$ | Represents the change in mole or mass concentration with time |
| $\nabla \cdot (\rho\omega_i v\,,\ \nabla \cdot (cx_i u)$ | Represents the convective transport |
| $\nabla \cdot (j_i)\,,\ \nabla \cdot (J_i)$ | Represents the diffusional transport |
| $R_i$ | Represents the reaction rate |

The catalyst particle is assumed to be spherical. The divergence of a vector and a scalar in spherical coordinates can be defined respectively as:

$$\nabla \cdot \vec{v} = \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 v_\xi) + \frac{1}{\xi^2 \sin\theta}\frac{\partial}{\partial \theta}(v_\theta \sin\theta) + \frac{1}{\xi^2 \sin\theta}\frac{\partial v_\phi}{\partial \phi} \tag{3}$$

$$\nabla s = \frac{\partial s}{\partial \xi}\hat{e}_i + \frac{1}{\xi}\frac{\partial s}{\partial \theta}\hat{e}_j + \frac{1}{\xi \sin\theta}\frac{\partial s}{\partial \phi}\hat{e}_k \tag{4}$$

Since the catalyst particle is assumed to be spherical it is resonable to assume symmetry around the centre of the particle - i.e., no change when changing the inclination angle $\theta$ or the azimuth angle $\phi$. Hence the derivatives in $\theta$ and $\phi$ may be disconsidered. as a result the diffusive and the convective term may be written respectively as:

$$\nabla \cdot (J_i) = \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 J_i) \tag{5}$$

$$\nabla \cdot (\rho\omega_i \vec{u}_\xi) = \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho\omega_i u_\xi) \tag{6}$$

As a result, the radial mass and mole fraction profile for a spherical catalyst particle can be written respectively as:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho\omega_i v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{7}$$

$$\frac{\partial}{\partial t}(cx_i) + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 cx_i u_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 J_i) + R_i \tag{8}$$

## 1.1 Radial temperature profile within the catalyst particle

A stationary differential equation describing the radial temperature profile within the catalyst particles is to be derived. The contributions from the different terms in the general energy equation are explained in tabla X.

The general energy equation given on mass and mole form respectively:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + \rho\sum_{i=1}^{n}\omega_i Cp_i v\,\nabla\cdot T = -\nabla\cdot q + (-\triangle H_R)R + Q \tag{9}$$

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + c\sum_{i=1}^{n}x_i Cp_i v\,\nabla\cdot T = -\nabla\cdot q + (-\triangle H_R)R + Q \tag{10}$$

The radiation heat flux is not considered in the next parts of deriving a simplifyed energy equation. Assuming symmetry around the centre of the particles as for the composition in the particles - i.e., no change in temperature when chaning the inclination angle$\theta$ or azimuth angle$\phi$. The energy equation can then be written for the mass and mole based models respectively as:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + \rho\sum_{i=1}^{n}\omega_i Cp_i v\,\frac{\partial T}{\partial \xi} = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 q) + (-\triangle H_R)R \tag{11}$$

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + c\sum_{i=1}^{n}x_i Cp_i v\,\frac{\partial T}{\partial \xi} = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 q) + (-\triangle H_R)R \tag{12}$$

Table 1: Explanation of the terms in the general energy equation

| | |
|---|---|
| $((1-\epsilon)\rho_p Cp_p + \epsilon\rho \sum_{i=1}^{n} \omega_i Cp_i)\frac{\partial T}{\partial t}$ | Represents the change of heat content with time |
| $\rho \sum_{i=1}^{n} \omega_i Cp_i v \nabla \cdot T$ | Represents the advective transport |
| $\nabla \cdot q$ | Represents the heat transport by conduction |
| $(-\triangle H_R)R$ | Represents the heat from chemical reactions |
| $Q$ | Represents the radiation heat flux |

## 1.2 The continuity equation

A simplified stationary equation for the continuity equation is to be derived. The terms are explained in table X. The governing continuity equation on mass and mole basis can be defined respectively as:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0 \tag{13}$$

$$\frac{\partial c}{\partial t} + \nabla \cdot (cu) = \sum_{i=1}^{n} r_i \tag{14}$$

Assuming symmetry around the centre of the particles as for the other composition in the particles- i.e., no change when changing the inclination angle $\theta$ or the azimuth angle $\phi$ - the equations on mass and mole form respectively may then be written as:

$$\frac{\partial \rho}{\partial t} + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho v_\xi) = 0 \tag{15}$$

$$\frac{\partial c}{\partial t} + \frac{1}{\xi^2}\frac{\partial}{\partial \xi} \cdot (\xi^2 c u_\xi) = \sum_{i=1}^{n} r_i \tag{16}$$

Table 2: Explanation of the terms in the general continutity equation

| | |
|---|---|
| $\frac{\partial \rho}{\partial t}, \frac{\partial c}{\partial t}$ | Represents the change of denisty and concentration with time |
| $\nabla \cdot (\rho v), \nabla \cdot (cu)$ | Represents the change of mass or moles in the control volume |
| $\sum_{i=1}^{n} r_i$ | Represents the sum of the reactions(mole generation rate) |

## 1.3 The diffusional models on mass basis

### 1.3.1 Wilke

$$j_i = -\rho D'_{sm} \nabla \cdot \omega_i \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \tag{17}$$

### 1.3.2 Maxwell-Stefan

$$j_i = \frac{-\rho \omega_i \nabla ln(\overline{M}) - \rho \nabla \omega_i + \overline{M} \omega_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j}{M_j D_{ij}}}{\overline{M} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}} \tag{18}$$

### 1.3.3 Dusty gas

$$j_i = \frac{M^2 \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\omega_i j_j}{M_j \tilde{D}_{ij}} - \frac{v \rho_i M}{M_j \tilde{D}_{iK}} - \rho(\omega_i \nabla M + M \nabla \omega_i)}{M^2 \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_D ij} + \frac{M}{D_{iK}}} \tag{19}$$

## 1.4 The diffusional models on mole basis

### 1.4.1 Wilke

$$j_i = -c D_{sm} \nabla \cdot x_i \qquad D'_{sm} = \frac{1-x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{20}$$

### 1.4.2 Maxwell-Stefan

$$j_i = \frac{-cx_i + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{21}$$

### 1.4.3 Dusty gas

$$j_i = \frac{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j x_i}{D_{ij}} - \frac{c_i u}{D_{iK}} - c\nabla x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}} \tag{22}$$

## 1.5 Transforming the simplified equations to the simplified form

The simplified general equations are made dimensionless using the correlations in table X.

Table 3: Correlations used to make the equations dimensionless

| | | |
|---|---|---|
| $$\xi^* = \frac{\xi}{\xi_{ref}} \tag{23}$$ | $$u^* = \frac{u}{u_{ref}} \tag{24}$$ | $$q^* = \frac{q_\xi \xi_{ref}}{\lambda T_{ref}} \tag{25}$$ |
| $$u_{ref} = \frac{Dref}{\xi_{ref}} \tag{26}$$ | $$p^* = \frac{p}{p_{ref}} \tag{27}$$ | $$\rho^* = \frac{\rho}{\rho_{ref}} \tag{28}$$ |
| $$c^* = \frac{c}{c_{ref}} \tag{29}$$ | $$j^* = \frac{j}{\frac{D_{ref}\rho_{ref}}{\xi_{ref}}} \tag{30}$$ | $$J^* = \frac{J}{\frac{D_{ref}c_{ref}}{\xi_{ref}}} \tag{31}$$ |
| $$t^* = \frac{t}{\frac{\xi_{ref}^2}{Dref}} \tag{32}$$ | $$M_w^* = \frac{M_w}{M_{ref}} \tag{33}$$ | $$T^* = \frac{T}{T_{ref}} \tag{34}$$ |

Using these correlations in the simplified equations gives the basic dimensionless equations used in this thesis.

## 1.6 Dimensionless simplified governing equations

### 1.6.1 The basic dimensionless mass and mole balance equation

Mass:

$$\frac{\partial}{\partial t^*}(\rho^* \omega_i) + \frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} \rho^* \omega_i v_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} j_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{35}$$

Mole:

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{36}$$

#### 1.6.2 The basic dimensionless temperature equation

Mass:

$$\begin{aligned}\frac{\partial T^*}{\partial t^*} =& -\frac{\rho^* \rho_{ref} v_r^* \sum_{i=1}^n \omega_i C p_i \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p C p_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n \omega_i C p_i)} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p C p_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i C p_i) D_{ref}} \\ &+ \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p C p_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i C p_i) D_{ref} T_{ref}}\end{aligned} \tag{37}$$

Mole:

$$\begin{aligned}\frac{\partial T^*}{\partial t^*} =& -\frac{c^* c_{ref} v_r^* \sum_{i=1}^n x_i C p_i' \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p C p_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i C p_i')} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p C p_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i C p_i') D_{ref}} \\ &+ \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p C p_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i C p_i') D_{ref} T_{ref}}\end{aligned} \tag{38}$$

#### 1.6.3 The basic dimensionless continuity equation

Mass:

$$\frac{\partial \rho^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} \rho^* v^*) = 0 \tag{39}$$

Mole:

$$\frac{\partial c^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = (\frac{\xi_{ref}^2}{c_{ref} D_{ref}})\sum_{i=1}^n r_i \tag{40}$$

### 1.7 The dimensionless mass diffusion models

#### 1.7.1 Wilke

$$j_i^* = -\rho^* \frac{D'_{sm}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^n \frac{\omega_j}{M_j D_{ij}}} \tag{41}$$

#### 1.7.2 Maxwell-Stefan

$$j_i^* = \frac{\frac{-\rho^* \omega_i}{D_{ref}}\frac{1}{\overline{M}}\frac{\partial}{\partial \xi^*}(\overline{M}) - \frac{\rho^*}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} + \overline{M}\omega_i \sum_{\substack{j=1\\ j\neq i}}^n \frac{j_j^*}{M_j D_{ij}}}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^i \frac{\omega_j}{M_j D_{ij}}} \tag{42}$$

### 1.8 The diffusional models on mole basis

#### 1.8.1 Wilke

$$j_i^* = -c^* D_{sm} \nabla \cdot x_i \qquad D'_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{43}$$

#### 1.8.2 Maxwell-Stefan

$$j_i^* = \frac{-c^* \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1\\j\neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1\\j\neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{44}$$

# 2 Table of the generalised and dimensionless mased based equations

# 3 Table of the generalised and dimensionless mole based equations

# 4 Case number 1 - Maxwell-Stefan

General about the case, SMR etc

## 4.1 Derivation of the equations to use in the model.

This is a simplifyed model assuming steady state and no convective transport in the pellet, also basic boundary conditions are used, where the transfer resistances are disconsidered. A model on both mass and mole basis is to be derived. Also the method of implementation is shown to indicate how the problem is solved using orthogonal collocation.

### 4.1.1 General for the derivation of both the mass and mole based models

The temperature equation eqX is solved in combination with fouriers law eqX. The temperature equation is only modified by introducing the assumptions assumed for this case.

The Species balance for respectively the mass and mole model eqX and eqX, is used to calulate the fluxes. This is done by solving the species balance for N-1 components and the last component by the constitutive law's eqX and eqX. In the species balance the continuity equation eqX and eqX is identifiyed for the respective model and inserted giving the species balance used in the model.

The mass fractions is solved by using the Maxwell-Stefan diffusion model for N-1 components, the last component is solved by the constitutive law's eqX and eqX for respectively the mass and mole based model. This model is only simplified and reformulated to the implemented form.

A summary of the equations derivated in detail in the next sections are shown in table X for the mass based model and table X for the mole based.

## 4.2 Mass based model

### 4.2.1 The temperature balance

The general temperature balance derived earlier (37):

$$\begin{aligned}\frac{\partial T^*}{\partial t^*} =& -\frac{\rho^* \rho_{ref} v_r^* \sum_{i=1}^n \omega_i Cp_i \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n \omega_i Cp_i)} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref}} \\ &+ \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref} T_{ref}}\end{aligned} \tag{45}$$

Steady state is assumed:

$$\begin{aligned}0 =& -\frac{\rho^* \rho_{ref} v_r^* \sum_{i=1}^n \omega_i Cp_i \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n \omega_i Cp_i)} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref}} \\ &+ \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref} T_{ref}}\end{aligned} \tag{46}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^n x_i Cp_i) D_{ref} T_{ref}} \tag{47}$$

The equation is rearranged and the used equation is given as:

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{48}$$

### 4.2.2 Species mass balance

The mass based fluxes are obtained from the species mass balance. The general dimensionless equation is given as derived earlier (35):

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{49}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{50}$$

The first term is written out to identify the continuity equation.

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) + \omega_i\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{51}$$

The second term is identified as the LHS of the mass based continuity equation (39) when steady state is assumed, swapped for the RHS of the mass based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{52}$$

No convective transport is assumed, and the equation is rearranged:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{53}$$

The first term is expanded to reflect the implemented equation:

$$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{54}$$

### 4.2.3 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model as given in (42):

$$j_i^* = \frac{\frac{-\rho^*\omega_i}{D_{ref}}\frac{1}{\overline{M}}\frac{\partial}{\partial \xi^*}(\overline{M}) - \frac{\rho^*}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} + \overline{M}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_j D_{ij}}}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_j D_{ij}}} \tag{55}$$

Rearranged to the implemented form:

$$j_i^*\frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M}D_{ref}}{\rho^*}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_j D_{ij}} \tag{56}$$

#### 4.2.4 Density equation

The density is obtained from ideal gas law multiplied with average molecular weight.

$$pV = NRT| \cdot \overline{M} \tag{57}$$

$$\frac{p\overline{M}}{RT} = \rho \tag{58}$$

#### 4.2.5 Summary of the mass based model, including boundary conditions

The derived equations are gathered in table 8. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

Table 4: Mass based equations, constitutive laws and boundary conditions

| Equations: | Constitutive Laws: |
|---|---|
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{59}$$ | Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \tag{60}$$ |
| Mass balance: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{61}$$ | Definition: $$\sum_{i=1}^{n} j_i = 0 \tag{62}$$ |
| Diffusion, Maxwell-Stefan: $$j_i^* \frac{\overline{M}D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M}D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}} \tag{63}$$ | Definition: $$\sum_{i=1}^{n} \omega_i = 1 \tag{64}$$ |
| Ideal gas law modified for density: $$\frac{p\overline{M}}{RT} = \rho \tag{65}$$ | |
| Boundary conditions in the symmetry point $\xi^* = 0$ $$j_i = 0 \tag{66}$$ $$q = 0 \tag{67}$$ | Boundary conditions at the surface $\xi^* = \xi_p^*$ $$T = T^b \tag{68}$$ $$\omega_i = \omega_i^b \tag{69}$$ |

## 4.3 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 9. In the table the used equations combined with boundary conditions are shown. The solution strategy is also visualised in the form on how it would be implemeted by the use of orthogonal collocation, shown in figure 7.

### 4.3.1 Temperature equtation

The temperature equation combined with the fouriers law is solved separately to obtain the temperature. The method of implementation is shown in figure 7.

### 4.3.2 Species Mass balance and Maxwell-Stefan diffusion

The species mass balance is solved to obtain the mass based fluxes. The mass based fluxes are then used to obtain the mass fractions throughout the catalyst particle using the maxwell stefan diffusion model.

### 4.3.3 Density

The density equation is solved outside the numerical problem and is solved using the previous iterative values.

Table 5: Summary of the solution strategy

| Equations, LHS represents terms in the problem matrix and the RHS represents the terms in the source vector: | Boundary conditions: |
|---|---|
| Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \qquad (70)$$ | Boundary condtion at $\xi = \xi^p$ $$T = T^b \qquad (71)$$ |
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \qquad (72)$$ | Boundary condtition at $\xi = 0$ $$q = 0 \qquad (73)$$ |
| Species mass balance, used for N-1 components: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \qquad (74)$$ | Boundary condition at $\xi = 0$ $$j_i = 0 \qquad (75)$$ |
| Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} j_i = 0 \qquad (76)$$ | No boundary condtion $$-$$ |
| Maxwell-Stefan diffusion model for N-1 components: $$j_i^* \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^*}{M_j D_{ij}} \qquad (77)$$ | Boundary condtition at $\xi = \xi^p$ : $$\omega_i = \omega_i^b \qquad (78)$$ |
| Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} \omega_i = 1 \qquad (79)$$ | No boundary condtion $$-$$ |
| Ideal gas law modified for density*: $$\frac{p\overline{M}}{RT} = \rho \qquad (80)$$ | No boundary condtion $$-$$ |

*Solved outside of the numerical collocation system and calculated from previous iteration values

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix}
q \\ T \\ j_{CH_4} \\ j_{CO} \\ j_{CO_2} \\ j_{H_2} \\ j_{N_2} \\ j_{H_2O} \\ \omega_{CH_4} \\ \omega_{CO} \\ \omega_{CO_2} \\ \omega_{H_2} \\ \omega_{N_2} \\ \omega_{H_2O}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1
\end{bmatrix}
$$

Figure 1: default

$$MS_1 = \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}$$

$$MS_2 = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}}$$

$$SB_1 = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}}$$

## 4.4 Mole based model

### 4.4.1 The temperature balance

The general temperature balance derived earlier (38):

$$\frac{\partial T^*}{\partial t^*} = -\frac{c^*\ c_{ref} v_r^* \sum_{i=1}^n x_i Cp_i' \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i')} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_r) R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \quad (81)$$

Steady state is assumed:

$$0 = -\frac{c^*\ c_{ref} v_r^* \sum_{i=1}^n x_i Cp_i' \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i')} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \quad (82)$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_r) R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \quad (83)$$

The equation is rearranged and the used equation is given as:

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2 (-\triangle H_r) R}{T_{ref} \lambda} \quad (84)$$

### 4.4.2 Species mole balance

The mole based fluxes are obtained from the species mole balance. The general dimensionless equation is given as derived earlier (36):

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (85)$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (86)$$

The first term is written out to identify the continuity equation.

$$\frac{1}{\xi^{*2}} \frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i \frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (87)$$

The second term is identified as the LHS of the mole based continuity equation (40) when steady state is assumed, swapped for the RHS of the mole based continuity equation gives:

$$\frac{1}{\xi^{*2}} \frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i (\frac{\xi_{ref}^2}{c_{ref} D_{ref}}) \sum_{i=1}^n r_i = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (88)$$

No convective transport is assumed and the equation is rearranged:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}J_i^*) = (R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{89}$$

Expanding the first terms to reflect the equation used in the model:

$$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{90}$$

### 4.4.3 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model on mole basis as given in 44:

$$j_i^* = \frac{-c^*\frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j\neq i}}^{i}\frac{x_j}{D_{ij}}} \tag{91}$$

Rearranged to the implemented form:

$$\frac{j_i^*}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{i}\frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{1}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}} \tag{92}$$

### 4.4.4 Density equation

The concentration is obtained from the ideal gas law rearraged.

$$pV = NRT \tag{93}$$

$$\frac{p}{RT} = c \tag{94}$$

### 4.4.5 Summary of the mole based model, including boundary conditions

The derived equations are gathered in table 10. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

## 4.5 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 11. In the table the used equations combined with boundary conditions are shown. The solution strategy is also visualised in the form on how it would be implemeted by the use of orthogonal collocation, shown in figure **??**.

### 4.5.1 Temperature equtation

The temperature equation combined with the fouriers law is solved separately to obtain the temperature. The method of implementation is shown in figure **??**.

Table 6: Mole based equations, constitutive laws and boundary conditions

| Equations: | Constitutive Laws: |
|---|---|
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (95)$$ | Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (96)$$ |
| Species mole balance: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (97)$$ | Definition: $$\sum_{i=1}^{n} J_i = 0 \quad (98)$$ |
| Diffusion, Maxwell-Stefan: $$\frac{j_i^*}{c^*}\sum_{\substack{j=1\\j\neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{1}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \quad (99)$$ | Definition: $$\sum_{i=1}^{n} x_i = 1 \quad (100)$$ |
| Ideal gas law rearranged for concentration: $$\frac{p}{RT} = c \quad (101)$$ | |

| Boundary conditions in the symmetry point $\xi^* = 0$ | Boundary conditions at the surface $\xi^* = \xi_p^*$ |
|---|---|
| $$J_i = 0 \quad (102)$$ $$q = 0 \quad (103)$$ | $$T = T^b \quad (104)$$ $$x_i = x_i^b \quad (105)$$ |

### 4.5.2 Species Mole balance and Maxwell-Stefan diffusion

The species mass balance is solved to obtain the mole based fluxes. The mole based fluxes are then used to obtain the mole fractions throughout the catalyst particle using the maxwell stefan diffusion model.

### 4.5.3 Concentration

The concentration equation is solved outside the numerical problem and is solved using the previous iterative values.

Table 7: Summary of the solution strategy

| Equations, LHS represents terms in the problem matrix and the RHS represents the terms in the source vector: | Boundary conditions: |
|---|---|
| Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (106)$$ | Boundary condtion at $\xi = \xi^p$ $$T = T^b \quad (107)$$ |
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (108)$$ | Boundary condtition at $\xi = 0$ $$q = 0 \quad (109)$$ |
| Species mole balance, used for N-1 components: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (110)$$ | Boundary condition at $\xi = 0$ $$J_i = 0 \quad (111)$$ |
| Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} J_i = 0 \quad (112)$$ | No boundary condtion – |
| Maxwell-Stefan diffusion model for N-1 components: $$\frac{j_i^*}{c^*}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{1}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}} \quad (113)$$ | Boundary condtition at $\xi = \xi^p$ : $$x_i = x_i^b \quad (114)$$ |
| Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} x_i = 1 \quad (115)$$ | No boundary condtion – |
| Ideal gas law modified for concentration*: $$\frac{p}{RT} = c \quad (116)$$ | No boundary condtion – |

*Solved outside of the numerical collocation system and calculated from previous iteration values

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix} q \\ T \\ J_{CH_4} \\ J_{CO} \\ J_{CO_2} \\ J_{H_2} \\ J_{N_2} \\ J_{H_2O} \\ x_{CH_4} \\ x_{CO} \\ x_{CO_2} \\ x_{H_2} \\ x_{N_2} \\ x_{H_2O} \end{bmatrix}
=
\begin{bmatrix} 0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1 \end{bmatrix}
$$

Figure 2: default

$$MS_1 = \frac{1}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{x_j}{D_{ij}}$$

$$MS_2 = \frac{1}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}$$

$$SB_1 = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}}$$

## 4.6 Results and discussion

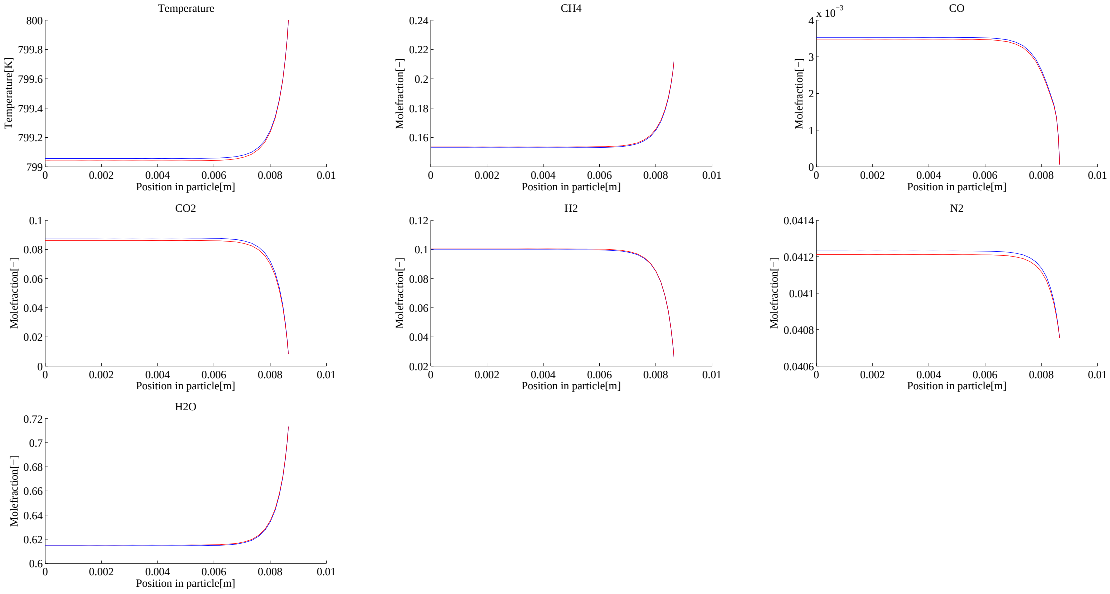


Figure 3: Comparison

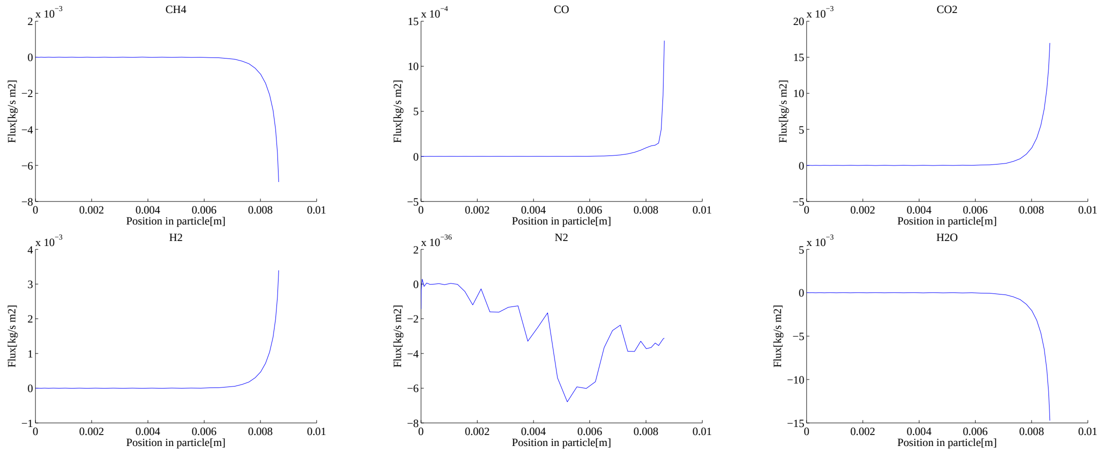


Figure 4: Mass based fluxes

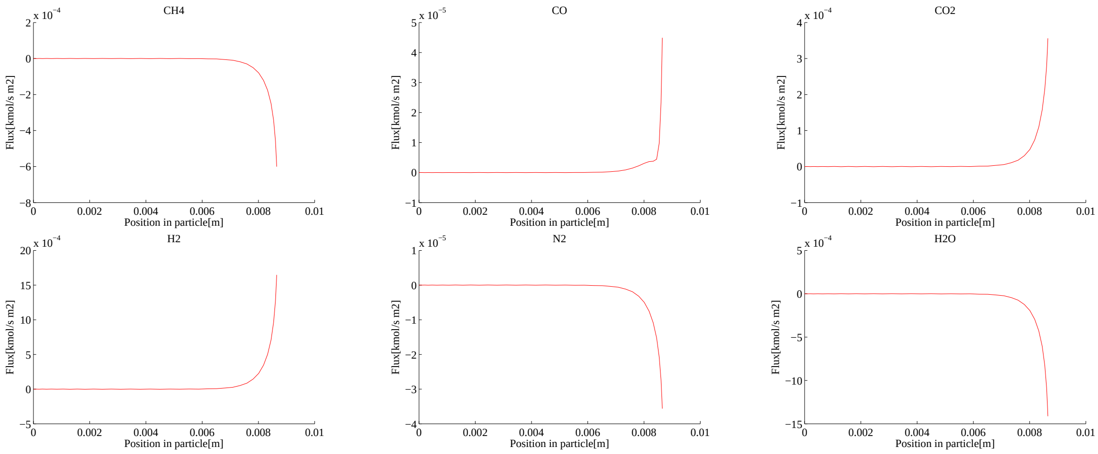


Figure 5: Mole based fluxes

# 5 Case number 2 - Wilke diffusion

General about the case, SMR etc

## 5.1 Derivation of the equations to use in the model.

This is a simplifyed model assuming steady state and no convective transport in the pellet, also basic boundary conditions are used, where the transfer resistances are disconsidered. A model on both mass and mole basis is to be derived. Also the method of implementation is shown to indicate how the problem is solved using orthogonal collocation.

### 5.1.1 General for the derivation of both the mass and mole based models

The temperature equation eqX is solved in combination with fouriers law eqX. The temperature equation is only modified by introducing the assumptions assumed for this case.

The Species balance for respectively the mass and mole model eqX and eqX, is used to calulate the fluxes. This is done by solving the species balance for N-1 components and the last component by the constitutive law's eqX and eqX. In the species balance the continuity equation eqX and eqX is identifiyed for the respective model and inserted giving the species balance used in the model.

The mass fractions is solved by using the Maxwell-Stefan diffusion model for N-1 components, the last component is solved by the constitutive law's eqX and eqX for respectively the mass and mole based model. This model is only simplified and reformulated to the implemented form.

A summary of the equations derivated in detail in the next sections are shown in table X for the mass based model and table X for the mole based.

## 5.2 Mass based model

### 5.2.1 The temperature balance

The general temperature balance derived earlier (37):

$$\frac{\partial T^*}{\partial t^*} = -\frac{\rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i Cp_i \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} \omega_i Cp_i)} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref} T_{ref}} \tag{117}$$

Steady state is assumed:

$$0 = -\frac{\rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i Cp_i \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} \omega_i Cp_i)} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref} T_{ref}} \tag{118}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref}} + \frac{\xi_{ref}^2 (-\triangle H_R) R}{((1-\epsilon)\rho_p Cp_p + \epsilon \rho^* \rho_{ref} \sum_{i=1}^{n} x_i Cp_i) D_{ref} T_{ref}} \tag{119}$$

The equation is rearranged and the used equation is given as:

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{120}$$

### 5.2.2 Species mass balance

The mass based fluxes are obtained from the species mass balance. The general dimensionless equation is given as derived earlier (35):

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{121}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{122}$$

The first term is written out to identify the continuity equation.

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) + \omega_i\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{123}$$

The second term is identified as the LHS of the mass based continuity equation (39) when steady state is assumed, swapped for the RHS of the mass based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{124}$$

No convective transport is assumed, and the equation is rearranged:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{125}$$

The first term is expanded to reflect the implemented equation:

$$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{126}$$

### 5.2.3 Wilke diffusion model

The general Wilke diffusion model as given in (41):

$$j_i^* = -\rho^*\frac{D'_{sm}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{127}$$

Rearranged to the implemented form:

$$j_i^*\frac{D_{ref}}{D'_{sm}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{128}$$

### 5.2.4 Density equation

The density is obtained from ideal gas law multiplied with average molecular weight.

$$pV = NRT| \cdot \overline{M} \tag{129}$$

$$\frac{p\overline{M}}{RT} = \rho \tag{130}$$

### 5.2.5 Summary of the mass based model, including boundary conditions

The derived equations are gathered in table 8. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

Table 8: Mass based equations, constitutive laws and boundary conditions

| Equations: | Constitutive Laws: |
|---|---|
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{131}$$ | Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \tag{132}$$ |
| Mass balance: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{133}$$ | Definition: $$\sum_{i=1}^{n} j_i = 0 \tag{134}$$ |
| Diffusion, Wilke: $$j_i^* \frac{D_{ref}}{D'_{sm}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \tag{135}$$ | Definition: $$\sum_{i=1}^{n} \omega_i = 1 \tag{136}$$ |
| Ideal gas law modified for density: $$\frac{p\overline{M}}{RT} = \rho \tag{137}$$ | |

| Boundary conditions in the symmetry point $\xi^* = 0$ | Boundary conditions at the surface $\xi^* = \xi_p^*$ |
|---|---|
| $$j_i = 0 \tag{138}$$ $$q = 0 \tag{139}$$ | $$T = T^b \tag{140}$$ $$\omega_i = \omega_i^b \tag{141}$$ |

## 5.3 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 9. In the table the used equations combined with boundary conditions are shown. The solution strategy is also visualised in the form on how it would be implemeted by the use of orthogonal collocation, shown in figure 7.

### 5.3.1 Temperature equtation

The temperature equation combined with the fouriers law is solved separately to obtain the temperature. The method of implementation is shown in figure 7.

### 5.3.2 Species Mass balance and Wilke diffusion

The species mass balance is solved to obtain the mass based fluxes. The mass based fluxes are then used to obtain the mass fractions throughout the catalyst particle using the Wilke diffusion model.

### 5.3.3 Density

The density equation is solved outside the numerical problem and is solved using the previous iterative values.

Table 9: Summary of the solution strategy

| Equations, LHS represents terms in the problem matrix and the RHS represents the terms in the source vector: | Boundary conditions: |
|---|---|
| Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \qquad (142)$$ | Boundary condtion at $\xi = \xi^p$ $$T = T^b \qquad (143)$$ |
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \qquad (144)$$ | Boundary condtition at $\xi = 0$ $$q = 0 \qquad (145)$$ |
| Species mass balance, used for N-1 components: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \qquad (146)$$ | Boundary condition at $\xi = 0$ $$j_i = 0 \qquad (147)$$ |
| Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} j_i = 0 \qquad (148)$$ | No boundary condtion – |
| Wilke diffusion model for N-1 components: $$j_i^* \frac{D_{ref}}{D'_{sm}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \qquad (149)$$ | Boundary condtition at $\xi = \xi^p$ : $$\omega_i = \omega_i^b \qquad (150)$$ |
| Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} \omega_i = 1 \qquad (151)$$ | No boundary condtion – |
| Ideal gas law modified for density*: $$\frac{p\overline{M}}{RT} = \rho \qquad (152)$$ | No boundary condtion – |

*Solved outside of the numerical collocation system and calculated from previous iteration values

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix}
q \\ T \\ j_{CH_4} \\ j_{CO} \\ j_{CO_2} \\ j_{H_2} \\ j_{N_2} \\ j_{H_2O} \\ \omega_{CH_4} \\ \omega_{CO} \\ \omega_{CO_2} \\ \omega_{H_2} \\ \omega_{N_2} \\ \omega_{H_2O}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1
\end{bmatrix}
$$

Figure 6: default

$$MS_1 = \frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\ j\neq i}}^{i}\frac{\omega_j}{M_j D_{ij}}$$

$$MS_2 = \frac{-\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*} + \frac{\overline{M}D_{ref}}{\rho^*}\omega_i\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{j_j^*}{M_j D_{ij}}$$

$$SB_1 = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}}$$

## 5.4 Mole based model

### 5.4.1 The temperature balance

The general temperature balance derived earlier (38):

$$\frac{\partial T^*}{\partial t^*} = -\frac{c^*\ c_{ref} v_r^* \sum_{i=1}^n x_i Cp_i' \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i')} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_r)R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \tag{153}$$

Steady state is assumed:

$$0 = -\frac{c^*\ c_{ref} v_r^* \sum_{i=1}^n x_i Cp_i' \frac{\partial T^*}{\partial \xi^*}}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i')} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \tag{154}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_r)R}{((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^n x_i Cp_i') D_{ref} T_{ref}} \tag{155}$$

The equation is rearranged and the used equation is given as:

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_r)R}{T_{ref}\lambda} \tag{156}$$

### 5.4.2 Species mole balance

The mole based fluxes are obtained from the species mole balance. The general dimensionless equation is given as derived earlier (36):

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{157}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{158}$$

The first term is written out to identify the continuity equation.

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{159}$$

The second term is identified as the LHS of the mole based continuity equation (40) when steady state is assumed, swapped for the RHS of the mole based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i (\frac{\xi_{ref}^2}{c_{ref} D_{ref}}) \sum_{i=1}^n r_i = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{160}$$

No convective transport is assumed and the equation is rearranged:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial\xi^*}(\xi^{*2}J_i^*) = (R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{161}$$

Expanding the first terms to reflect the equation used in the model:

$$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial\xi^*} = (R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{162}$$

### 5.4.3 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model on mole basis as given in 44:

$$j_i^* = \frac{-c^*\frac{\partial x_i}{\partial\xi^*} + \sum_{\substack{j=1\\ j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1\\ j\neq i}}^{i}\frac{x_j}{D_{ij}}} \tag{163}$$

Rearranged to the implemented form:

$$\frac{j_i^*}{c^*}\sum_{\substack{j=1\\ j\neq i}}^{i}\frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial\xi^*} = \frac{1}{c^*}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}} \tag{164}$$

### 5.4.4 Density equation

The concentration is obtained from the ideal gas law rearraged.

$$pV = NRT \tag{165}$$

$$\frac{p}{RT} = c \tag{166}$$

### 5.4.5 Summary of the mole based model, including boundary conditions

The derived equations are gathered in table 10. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

## 5.5 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 11. In the table the used equations combined with boundary conditions are shown. The solution strategy is also visualised in the form on how it would be implemeted by the use of orthogonal collocation, shown in figure **??**.

### 5.5.1 Temperature equtation

The temperature equation combined with the fouriers law is solved separately to obtain the temperature. The method of implementation is shown in figure **??**.

Table 10: Mole based equations, constitutive laws and boundary conditions

<table>
<tr><td>Equations:</td><td>Constitutive Laws:</td></tr>
<tr><td>Temperature equation:<br>$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (167)$$<br>Species mole balance:<br>$$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (169)$$<br>Diffusion, Maxwell-Stefan:<br>$$\frac{j_i^*}{c^*}\sum_{\substack{j=1\\ j\neq i}}^{i}\frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{1}{c^*}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}} \quad (171)$$<br>Ideal gas law rearranged for concentration:<br>$$\frac{p}{RT} = c \quad (173)$$</td><td>Fourier's law<br>$$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (168)$$<br>Definition:<br>$$\sum_{i=1}^{n} J_i = 0 \quad (170)$$<br>Definition:<br>$$\sum_{i=1}^{n} x_i = 1 \quad (172)$$</td></tr>
<tr><td>Boundary conditions in the symmetry point $\xi^* = 0$<br>$$J_i = 0 \quad (174)$$<br>$$q = 0 \quad (175)$$</td><td>Boundary conditions at the surface $\xi^* = \xi_p^*$<br>$$T = T^b \quad (176)$$<br>$$x_i = x_i^b \quad (177)$$</td></tr>
</table>

### 5.5.2 Species Mole balance and Maxwell-Stefan diffusion

The species mass balance is solved to obtain the mole based fluxes. The mole based fluxes are then used to obtain the mole fractions throughout the catalyst particle using the maxwell stefan diffusion model.

### 5.5.3 Concentration

The concentration equation is solved outside the numerical problem and is solved using the previous iterative values.

Table 11: Summary of the solution strategy

| Equations, LHS represents terms in the problem matrix and the RHS represents the terms in the source vector: | Boundary conditions: |
|---|---|
| Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \qquad (178)$$ | Boundary condtion at $\xi = \xi^p$ $$T = T^b \qquad (179)$$ |
| Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \qquad (180)$$ | Boundary condtition at $\xi = 0$ $$q = 0 \qquad (181)$$ |
| Species mole balance, used for N-1 components: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \qquad (182)$$ | Boundary condition at $\xi = 0$ $$J_i = 0 \qquad (183)$$ |
| Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} J_i = 0 \qquad (184)$$ | No boundary condtion – |
| Maxwell-Stefan diffusion model for N-1 components: $$\frac{j_i^*}{c^*}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{1}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^* x_i}{D_{ij}} \qquad (185)$$ | Boundary condtition at $\xi = \xi^p$ : $$x_i = x_i^b \qquad (186)$$ |
| Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} x_i = 1 \qquad (187)$$ | No boundary condtion – |
| Ideal gas law modified for concentration*: $$\frac{p}{RT} = c \qquad (188)$$ | No boundary condtion – |

*Solved outside of the numerical collocation system and calculated from previous iteration values

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & MS_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix}
q \\ T \\ J_{CH_4} \\ J_{CO} \\ J_{CO_2} \\ J_{H_2} \\ J_{N_2} \\ J_{H_2O} \\ x_{CH_4} \\ x_{CO} \\ x_{CO_2} \\ x_{H_2} \\ x_{N_2} \\ x_{H_2O}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ MS_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1
\end{bmatrix}
$$

Figure 7: default

$$MS_1 = \frac{1}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{x_j}{D_{ij}}$$

$$MS_2 = \frac{1}{c^*}\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}$$

$$SB_1 = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}}$$

## 5.6 Results and discussion

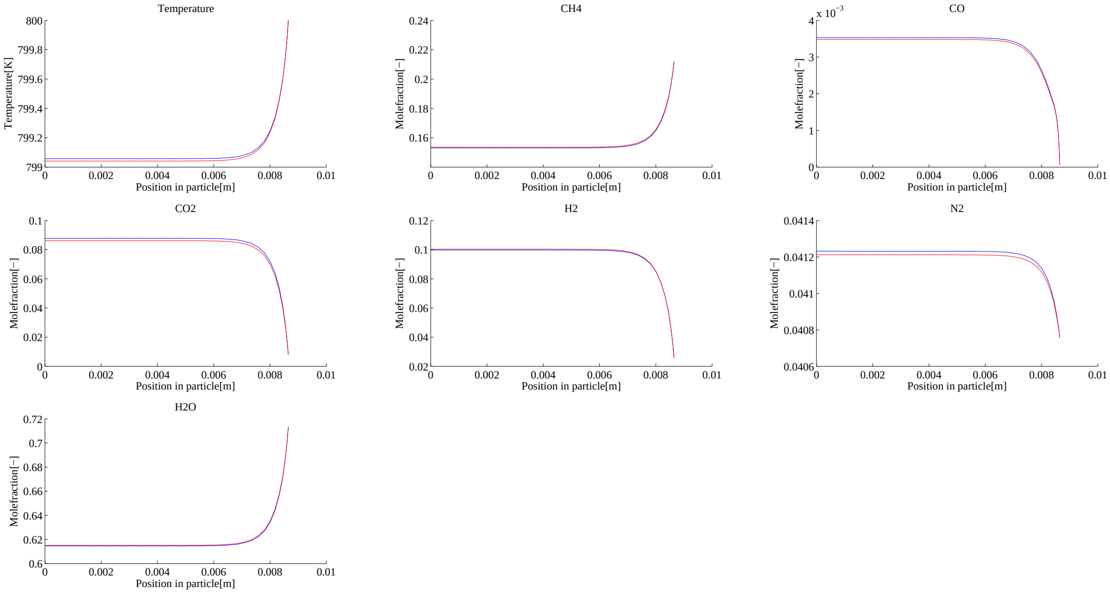


Figure 8: Comparison

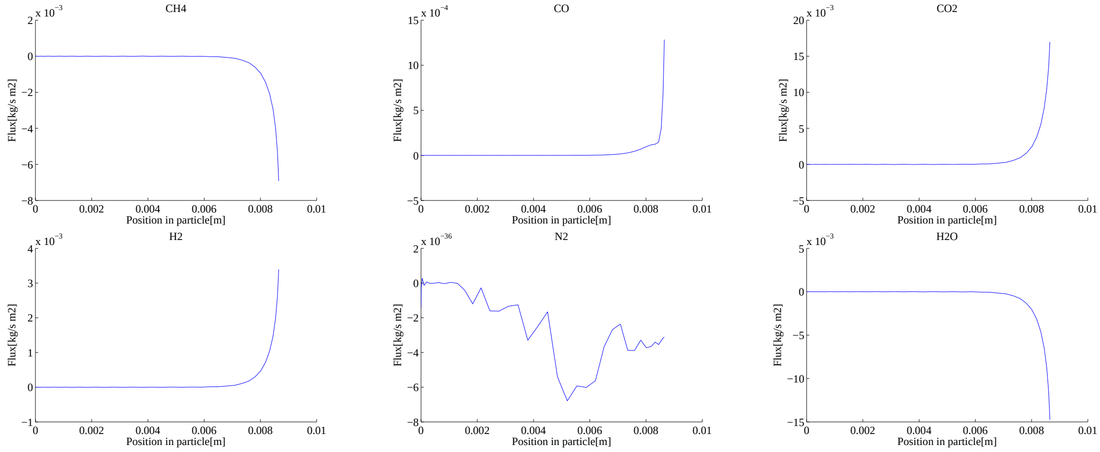


Figure 9: Mass based fluxes

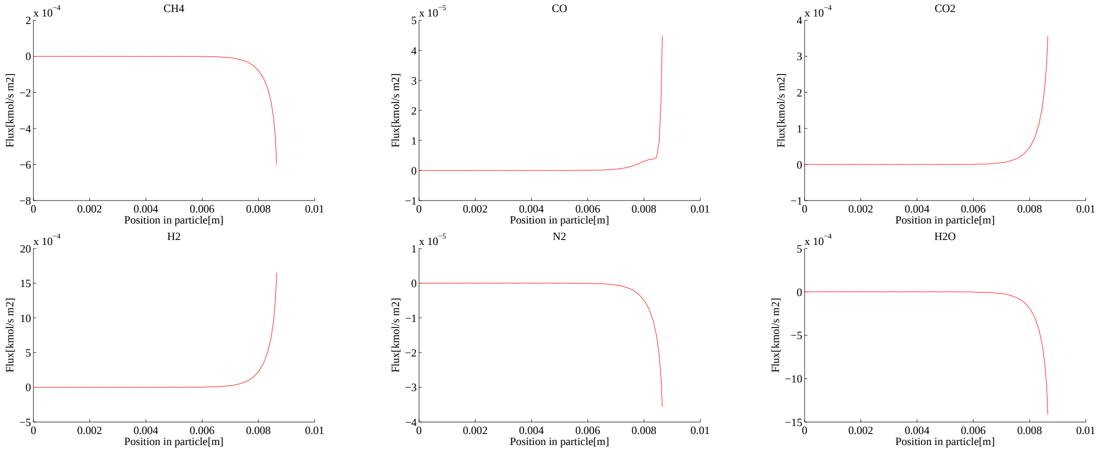


Figure 10: Mole based fluxes