Innhold

1 Theory - Derivation of governing equations

The basic governing equations used in this thesis are to be derived from general governing equations. This is done to make the derivation for each case shorter and more spesific. During the deduction of these basic equations the different terms are also explained. For all equations the divergence needs to be specified in spherical coordinates for both a vector and a scalar. These equations can be defined respectively as:

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

$$\nabla s = \frac{\partial s}{\partial \xi}\hat{e}_i + \frac{1}{\xi}\frac{\partial s}{\partial \theta}\hat{e}_j + \frac{1}{\xi \sin\theta}\frac{\partial s}{\partial \phi}\hat{e}_k \tag{2}$$

These equations can be further simplified for this thesis. 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 θ or the azimuth angle ϕ. Hence the derivatives in θ and ϕ may be disconsidered. As a result the divergence of a vector and scalar in this thesis will be given respectively as:

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

$$\nabla s = \frac{\partial s}{\partial \xi}\hat{e}_i \tag{4}$$

1.1 Mass based basic governing equations

1.1.1 Species mass balance

Differential equations describing the change in mass fractions for the different components in radial direction within the catalyst pellets are to be derived. The different terms are explained in table 1, and general species mass balance for a component i is given as:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \nabla \cdot (\rho\omega_i v) = -\nabla \cdot (j_i) + R_i \tag{5}$$

Tabell 1: Explanation of the different terms in the species mass balance

$\frac{\partial}{\partial t}(\rho\omega_i)$	Represents the change in density for each species i with time
$\nabla \cdot (\rho\omega_i v)$	Represents the convective transport
$\nabla \cdot (j_i)$	Represents the diffusional transport
R_i	Represents the reaction rate

Introducing the divergence of a vector (3) for both the diffusional and convective term gives the simplified species mass balance:

$$\frac{\partial}{\partial t}(\rho\omega_i) + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho\omega_i v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{6}$$

1.1.2 Temperature equation

A 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 table 2. The general governing energy equation can be given as:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + \rho\sum_{i=1}^{n}\omega_i Cp_i v\,\nabla\cdot T = -\nabla\cdot q + (-\triangle H_R)R + Q \tag{7}$$

Tabell 2: 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

The radiation heat flux is not considered in the next parts of deriving a simplifyed energy equation. Introducing the divergence of a scalar (4) for the advective term and the divergence of a vector (3) for the conduction term gives the simplified energy equation on mass form:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T}{\partial t} + \rho\sum_{i=1}^{n}\omega_i Cp_i v\,\frac{\partial T}{\partial \xi} = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 q) + (-\triangle H_R)R \tag{8}$$

1.1.3 The continuity equation

A simplified equation for the continuity equation is to be derived. The terms are explained in table 3. The governing continuity equation on mass basis can be defined as:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho v) = 0 \tag{9}$$

Tabell 3: Explanation of the terms in the general continutity equation

$\frac{\partial \rho}{\partial t}$	Represents the change of density with time
$\nabla \cdot (\rho v)$	Represents the change of mass or moles in the control volume

Introducing the divergence of a vector (3) for the second term gives the simplified mass based continuity equation:

$$\frac{\partial \rho}{\partial t} + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho v_\xi) = 0 \tag{10}$$

1.2 Mass based diffusion models

The general diffusion models are not simplifyed and are given on explecit form:

1.2.1 Wilke

$$j_i = -\rho D'_{im} \nabla \omega_i \qquad D'_{im} = \frac{1-\omega_i}{\overline{M} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \tag{11}$$

1.2.2 Wilke–Bosanquet

$$j_i = -\rho D'_{i,eff} \nabla \omega_i \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{iK}} \tag{12}$$

1.2.3 Maxwell-Stefan

$$j_i = \frac{-\rho \omega_i \nabla ln(\overline{M}) - \rho \nabla \omega_i + \overline{M} \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j}{M_j D_{ij}}}{\overline{M} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}} \tag{13}$$

1.2.4 Dusty gas

$$j_i = \frac{M^2 \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_i j_j}{M_j \tilde{D}_{ij}} - \frac{v \rho_i M}{\tilde{D}_{iK}} - \rho(\omega_i \nabla M + M \nabla \omega_i)}{M^2 \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_D ij} + \frac{M}{D_{iK}}} \tag{14}$$

1.3 Mole based basic governing equations

1.3.1 Species mole balance

Differential equations describing the change in mole fractions for the different components in radial direction within the catalyst pellets are to be derived. The different terms are explained in table 4, and general species mole balance for a component i is given as:

$$\frac{\partial}{\partial t}(cx_i) + \nabla \cdot (cx_i u) = -\nabla \cdot (J_i) + R_i \tag{15}$$

Tabell 4: Explanation of the different terms in the species mass balance

$\frac{\partial}{\partial t}(cx_i)$	Represents the change in concentration for the different species i with time
$\nabla \cdot (cx_i u)$	Represents the convective transport
$\nabla \cdot (J_i)$	Represents the diffusional transport
R_i	Represents the reaction rate

Introducing the divergence of a vector (3) for both the diffusional and convective term gives the simplified species mole balance:

$$\frac{\partial}{\partial t}(cx_i) + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 cx_i u_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 J_i) + R_i \tag{16}$$

1.3.2 Temperature equation

A 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 table 5. The general governing energy equation can be given as:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho \sum_{i=1}^{n} x_i Cp_i')\frac{\partial T}{\partial t} + c\sum_{i=1}^{n} x_i Cp_i' v \nabla T = -\nabla q + (-\triangle H_R)R + Q \tag{17}$$

Tabell 5: Explanation of the terms in the general energy equation

$((1-\epsilon)\rho_p Cp_p + \epsilon\rho \sum_{i=1}^{n} x_i Cp_i')\frac{\partial T}{\partial t}$	Represents the change of heat content with time
$c\sum_{i=1}^{n} x_i Cp_i' v \nabla T$	Represents the advective transport
∇q	Represents the heat transport by conduction
$(-\triangle H_R)R$	Represents the heat from chemical reactions
Q	Represents the radiation heat flux

The radiation heat flux is not considered further as it is not needed. Introducing the divergence of a scalar (4) for the advective term and the divergence of a vector (3) for the conduction term gives the simplified energy equation on mole basis:

$$((1-\epsilon)\rho_p Cp_p + \epsilon c \sum_{i=1}^{n} x_i Cp_i')\frac{\partial T}{\partial t} + c\sum_{i=1}^{n} x_i Cp_i' v \frac{\partial T}{\partial \xi} = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 q) + (-\triangle H_R)R \tag{18}$$

1.3.3 The continuity equation

A simplified equation for the continuity equation is to be derived. The terms are explained in table 6. The governing continuity equation on mole basis can be defined as:

$$\frac{\partial c}{\partial t} + \nabla \cdot (cu) = \sum_{i=1}^{n} r_i \tag{19}$$

Tabell 6: Explanation of the terms in the general continutity equation

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

Introducing the divergence of a vector (3) for the second term gives the simplified mole based continuity equation:

$$\frac{\partial c}{\partial t} + \frac{1}{\xi^2}\frac{\partial}{\partial \xi} \cdot (\xi^2 c u_\xi) = \sum_{i=1}^{n} r_i \tag{20}$$

1.4 Mole based diffusion models

The general diffusion models are not simplifyed and are given on explecit form:

1.4.1 Wilke

$$j_i = -cD_{sm}\nabla \cdot x_i \qquad D'_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{21}$$

1.4.2 Wilke–Bosanquet

$$j_i = -cD_{i,eff}\nabla \cdot x_i i \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{iK}} \tag{22}$$

1.4.3 Maxwell-Stefan

$$j_i = \frac{-cx_i + \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j x_i}{D_{ij}}}{\sum_{\substack{j=1\\ j\neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{23}$$

1.4.4 Dusty gas

$$j_i = \frac{\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j x_i}{D_{ij}} - \frac{c_i u}{D_{iK}} - c\nabla x_i}{\sum_{\substack{j=1\\ j\neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}} \tag{24}$$

1.5 ideal gas law, conversion of velocities etc

1.5.1 mass based flux-velocity conversion

$$j_i = \rho_i(u_i - v) \tag{25}$$

$$u - v = \sum_{i=1}^{N} x_i(u_i - v) \tag{26}$$

$$\omega_i = \frac{x_i M_i}{\overline{M}} \tag{27}$$

Inserting the first into the second:

$$u - v = \sum_{i=1}^{N} \frac{x_i j_i}{\rho_i} \tag{28}$$

writing out ρ_i as $\omega_i \rho$ and using equation 27, gives the conversion equation:

$$u - v = \sum_{i=1}^{N} \frac{j_i \overline{M}}{\rho M_i} \tag{29}$$

1.5.2 mole based flux-velocity conversion

$$J_i = c_i(u_i - u) \tag{30}$$

$$v - u = \sum_{i=1}^{N} \omega_i(u_i - u) \tag{31}$$

$$x_i = \frac{\omega_i \overline{M}}{M_i} \tag{32}$$

Inserting the first into the second:

$$v - u = \sum_{i=1}^{N} \omega_i \frac{J_i}{c_i} \tag{33}$$

$$\tag{34}$$

writing out c_i as $x_i c$ and using equation 32 gives the conversion equation:

$$v - u = \sum_{i=1}^{N} \frac{J_i M_i}{c_i \overline{M}} \tag{35}$$

1.5.3 Ideal gas law

Different versions of the ideal gas law is used for the different cases. The standard is used for concentration:

$$pV = nRT$$
$$\frac{p}{RT} = c \tag{36}$$

multiplied with moleweight gives the density equation used:

$$\frac{p\overline{M}}{RT} = \rho \tag{37}$$

The derivative of both the concentration and the density equation with respect to the radial position are given respectively as:

$$\frac{\partial c}{\partial \xi} = \frac{\partial p}{\partial \xi}\frac{1}{RT} - \frac{\partial T}{\partial \xi}\frac{p}{RT^2} \tag{38}$$

$$\frac{\partial \rho}{\partial \xi} = \frac{\partial p}{\partial \xi}\frac{\overline{M}}{RT} - \frac{\partial T}{\partial \xi}\frac{p\overline{M}}{RT^2} + \frac{\partial \overline{M}}{\partial \xi}\frac{p}{RT} \tag{39}$$

1.5.4 Darcy's law

$$v = -\frac{B}{\mu}\frac{\partial p}{\partial \xi} \qquad B = \frac{\epsilon}{\tau}\frac{d_0^2}{32} \tag{40}$$

1.5.5 Constitutive laws

for mass based models:

$$\sum_{i=1}^{n} j_i = 0 \tag{41}$$

$$\sum_{i=1}^{n} \omega_i = 1 \tag{42}$$

for mole based models:

$$\sum_{i=1}^{n} J_i = 0 \tag{43}$$

$$\sum_{i=1}^{n} x_i = 1 \tag{44}$$

1.6 Transforming the simplified equations to the dimensionless form

The simplified general equations are made dimensionless using the correlations in table 7. By using these correlations in the simplified equations we will aquire the basic dimensionless equations used in this thesis.

Tabell 7: Correlations used to make the equations dimensionless

$$\xi^* = \frac{\xi}{\xi_{ref}} \quad (45) \qquad u^* = \frac{u}{u_{ref}} \quad (46) \qquad q^* = \frac{q_\xi \xi_{ref}}{\lambda T_{ref}} \quad (47)$$

$$u_{ref} = \frac{Dref}{\xi_{ref}} \quad (48) \qquad p^* = \frac{p}{p_{ref}} \quad (49) \qquad \rho^* = \frac{\rho}{\rho_{ref}} \quad (50)$$

$$c^* = \frac{c}{c_{ref}} \quad (51) \qquad j^* = \frac{j}{\frac{D_{ref}\rho_{ref}}{\xi_{ref}}} \quad (52) \qquad J^* = \frac{J}{\frac{D_{ref}c_{ref}}{\xi_{ref}}} \quad (53)$$

$$t^* = \frac{t}{\frac{\xi_{ref}^2}{Dref}} \quad (54) \qquad M_w^* = \frac{M_w}{M_{ref}} \quad (55) \qquad T^* = \frac{T}{T_{ref}} \quad (56)$$

1.7 Summary of the dimensionless equations on mass basis

Tabell 8: Mass based model equations on dimensionless form

Species mass balance:

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{57}$$

The basic dimensionless temperature equation:

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho^*\rho_{ref}\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T^*}{\partial t^*} = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{58}$$

The basic dimensionless continuity equation:

$$\frac{\partial \rho^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v^*) = 0 \tag{59}$$

Wilke diffusion model:

$$j_i^* = -\rho^*\frac{D'_{sm}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad D'_{sm} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{60}$$

Wilke–Bosanquet diffusion model:

$$j_i^* = -\rho^*\frac{D'_{i,eff}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{iK}} \tag{61}$$

Maxwell-Stefan diffusion model:

$$j_i^* = \frac{\frac{-\rho^*\omega_i}{D_{ref}}\frac{1}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} - \frac{\rho^*}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} + \overline{M}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_j D_{ij}}}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_j D_{ij}}} \tag{62}$$

Dusty gas diffusion model:

$$j_i^* = \frac{\overline{M}^2\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{v^*\omega_i\overline{M}}{\tilde{D}_{iK}} - \frac{\omega_i\rho^*}{D_{ref}}\frac{\partial \overline{M}}{\partial \xi^*} - \frac{\rho^*\overline{M}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*}}{\overline{M}^2\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j\tilde{D}_D ij} + \frac{\overline{M}}{D_{iK}}} \tag{63}$$

1.8 Summary of the dimensionless equations on mole basis

Tabell 9: Mole based model equations on dimensionless form

Species mole balance:

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (64)$$

The basic dimensionless temperature equation:

$$((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^{n} x_i Cp'_i)\frac{\partial T^*}{\partial t^*} = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref} T_{ref}} \quad (65)$$

The basic dimensionless continuity equation:

$$\frac{\partial c^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = (\frac{\xi_{ref}^2}{c_{ref} D_{ref}})\sum_{i=1}^{n} r_i \quad (66)$$

Wilke diffusion model:

$$J_i^* = -c^* \frac{D_{sm}}{D_{ref}}\frac{\partial x_i}{\partial \xi^*} \qquad D_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{x_j}{D_{ij}}} \quad (67)$$

Wilke–Bosanquet diffusion model:

$$J_i^* = -c^* \frac{D'_{i,eff}}{D_{ref}}\frac{\partial x_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{iK}} \quad (68)$$

Maxwell-Stefan diffusion model:

$$J_i^* = \frac{-\frac{c^*}{D_{ref}}\frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{J_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{x_j}{D_{ij}}} \quad (69)$$

Dusty gas diffusion model:

$$J_i^* = \frac{-\frac{c^*}{D_{ref}}\frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{c^* x_i u^*}{D_{iK}}}{\sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}} \quad (70)$$

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all steady state models are simulated using 60 collocation points
and is run to a convergence of $1 * 10^{-}10$
More info...
Plots not shown, reason pressure concentration average molecular weight

2 Models on their simplest forms

General about the case, SMR etc

2.1 Derivation of the equations to use in the model.

This is the models on their simplest forms assuming steady state and no convective transport in the pellet, also basic boundary conditions are used. The use of basic boundary conditions elimitates the effect of transfer resistances. 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.

2.1.1 General for the derivation of both the mass and mole based models

The temperature equation (58)(65) is solved in combination with fouriers law. The temperature equation is only modified by introducing the assumptions assumed for this case.

The Species balance for respectively the mass and mole model (57) and (64), 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 (41) and (43). In the species balance the continuity equation (59) and (66) is identifiyed for the respective model and inserted giving the species balance used in the model.

The species fractions is solved by using the different diffusion models in table XXX for N-1 components, the last component is solved by the constitutive law's (42) and (44) for respectively the mass and mole based model. The diffusion models are only reformulated from their general form shown in the theory to reflect their implemented form.

A summary of the equations derivated in detail in the next sections are shown in table 10 for the mass based model and table 20 for the mole based.

2.2 Mass based model

2.2.1 The temperature balance

The general temperature balance derived earlier (58):

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho^*\rho_{ref}\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T^*}{\partial t^*} = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \quad (71)$$

Steady state is assumed:

$$0 = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \quad (72)$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \quad (73)$$

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

$$\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (74)$$

2.2.2 Species mass balance

The mass based fluxes are obtained from the species mass balance. The general dimensionless equation is given as derived earlier (57):

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{75}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{76}$$

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

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) + \omega_i\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{77}$$

The second term is identified as the LHS of the mass based continuity equation (59) when steady state is assumed, swapped for the RHS of the mass based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{78}$$

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

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{79}$$

The first term is expanded to reflect the implemented equation:

$$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{80}$$

2.2.3 Wilke diffusion model

The general Wilke diffusion model as given in (60):

$$j_i^* = -\rho^*\frac{D'_{im}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{81}$$

Rearranged to the implemented form:

$$j_i^*\frac{D_{ref}}{D'_{im}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{82}$$

2.2.4 Wilke-bosanquet diffusion model

$$j_i^* = -\rho^*\frac{D'_{i,eff}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{i,K}} \tag{83}$$

Rearranged to the implemented form:

$$j_i^*\frac{D_{ref}}{D'_{i,eff}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}}} + \frac{1}{D_{i,K}} \tag{84}$$

2.2.5 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model as given in (62):

$$j_i^* = \frac{\frac{-\rho^*\omega_i}{D_{ref}}\frac{1}{\overline{M}}\frac{\partial}{\partial\xi^*}(\overline{M}) - \frac{\rho^*}{D_{ref}}\frac{\partial\omega_i}{\partial\xi^*} + \overline{M}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_jD_{ij}}}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_jD_{ij}}} \tag{85}$$

Rearranged to the implemented form:

$$j_i^*\frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_jD_{ij}} + \frac{\partial\omega_i}{\partial\xi^*} = \frac{-\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*} + \frac{\overline{M}D_{ref}}{\rho^*}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_jD_{ij}} \tag{86}$$

2.2.6 Dusty gas diffusion model

The general Maxwell-Stefan model as given in (63):

$$j_i^* = \frac{\overline{M}^2\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_ij_j^*}{M_j\tilde{D}_{ij}} - \frac{v^*\omega_i\overline{M}}{\tilde{D}_{iK}} - \frac{\omega_i\rho^*}{D_{ref}}\frac{\partial\overline{M}}{\partial\xi^*} - \frac{\rho^*\overline{M}}{D_{ref}}\frac{\partial\omega_i}{\partial\xi^*}}{\overline{M}^2\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j\tilde{D}_Dij} + \frac{\overline{M}}{D_{iK}}} \tag{87}$$

Rearranged to the implemented form:

$$j_i^*\frac{D_{ref}}{\rho^*}(\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j\tilde{D}_{ij}} + \frac{1}{D_{iK}}) + \frac{\partial\omega_i}{\partial\xi^*} = \frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_ij_j^*}{M_j\tilde{D}_{ij}} - \frac{v^*\omega_iD_{ref}}{\tilde{D}_{iK}\rho^*} - \frac{\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*} \tag{88}$$

Assuming no convenctive transport:

$$j_i^*\frac{D_{ref}}{\rho^*}(\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j\tilde{D}_{ij}} + \frac{1}{D_{iK}}) + \frac{\partial\omega_i}{\partial\xi^*} = \frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_ij_j^*}{M_j\tilde{D}_{ij}} - \frac{\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*} \tag{89}$$

2.2.7 Density equation

The density is obtained from modified ideal gas law given earlier eqX

$$\frac{p\overline{M}}{RT} = \rho \tag{90}$$

2.2.8 Summary of the mass 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.

2.3 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 12. 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 36.

Tabell 10: Mass based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (91)$$	Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (92)$$
Mass balance: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \quad (93)$$	Definition: $$\sum_{i=1}^{n} j_i = 0 \quad (94)$$
Diffusion model: One of the four diffusionmodels in table 23 is used	Definition: $$\sum_{i=1}^{n} \omega_i = 1 \quad (95)$$
Ideal gas law modified for density: $$\frac{p\overline{M}}{RT} = \rho \quad (96)$$	

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$
$$j_i = 0 \quad (97)$$ $$q = 0 \quad (98)$$	$$T = T^b \quad (99)$$ $$\omega_i = \omega_i^b \quad (100)$$

2.3.1 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 36.

2.3.2 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.

2.3.3 Density

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

Tabell 11: Diffusion models on their implemented form

LHS is implemented in the collocation matrix, and the RHS is implemented in the source vector
Wilke: $$j_i^* \frac{D_{ref}}{D'_{im}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \quad (101)$$ Wilke-Bosanquet: $$j_i^* \frac{D_{ref}}{D'_{i,eff}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}}} + \frac{1}{D_{i,K}} \quad (102)$$ Maxwell-Stefan: $$j_i^* \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1\\j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1\\j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}} \quad (103)$$ Dusty gas: $$j_i^* \frac{D_{ref}}{\rho^*} (\overline{M} \sum_{\substack{j=1\\j\neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_{ij}} + \frac{1}{D_{iK}}) + \frac{\partial \omega_i}{\partial \xi^*} = \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1\\j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} \quad (104)$$

Tabell 12: 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 $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (105)$$	Boundary condtion at $\xi = \xi^p$ $$T = T^b \quad (106)$$
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (107)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (108)$$
Species mass balance, used for N-1 components: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \quad (109)$$	Boundary condition at $\xi = 0$ $$j_i = 0 \quad (110)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} j_i = 0 \quad (111)$$	No boundary condtion –
A diffusion model is used for N-1 components: One of the four diffusionmodels in table 23 is used	Boundary condtition at $\xi = \xi^p$: $$\omega_i = \omega_i^b \quad (112)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} \omega_i = 1 \quad (113)$$	No boundary condtion –
Ideal gas law modified for density*: $$\frac{p\overline{M}}{RT} = \rho \quad (114)$$	No boundary condtion –

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

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet+\frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix}
q \\ T \\ j_{CH_4} \\ j_{CO} \\ j_{CO_2} \\ j_{H_2} \\ j_{N_2} \\ j_{H_2O} \\ \omega_{CH_4} \\ \omega_{CO} \\ \omega_{CO_2} \\ \omega_{H_2} \\ \omega_{N_2} \\ \omega_{H_2O}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1
\end{bmatrix}
$$

Figur 1: Collocation matrix, mass based. Explanation on the labeled terms can be seen in table 35

Tabell 13: Terms in the collocation matrix and source vector

Label in matrix	Collocation matrix terms:	multiplied with:
DM_1	Wilke: $$\frac{D_{ref}}{D'_{im}\rho^*}$$	j_i^*
DM_1	Wilke-Bosanquet: $$\frac{D_{ref}}{D'_{i,eff}\rho^*}$$	j_i^*
DM_1	Maxwell-Stefan: $$\frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{i}\frac{\omega_j}{M_j D_{ij}}$$	j_i^*
DM_1	Dusty gas: $$\frac{D_{ref}}{\rho^*}(\overline{M}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_j}{M_j\tilde{D}_{ij}}+\frac{1}{D_{iK}})$$	j_i^*

Label in source vector	Source vector
DM_2	Wilke: $$0$$
DM_2	Wilke-Bosanquet: $$0$$
DM_2	Maxwell-Stefan: $$\frac{-\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*}+\frac{\overline{M}D_{ref}}{\rho^*}\omega_i\sum_{\substack{j=1\\j\neq i}}^{n}\frac{j_j^*}{M_j D_{ij}}$$
DM_2	Dusty gas: $$\frac{\overline{M}D_{ref}}{\rho^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{\omega_i j_j^*}{M_j\tilde{D}_{ij}}-\frac{\omega_i}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*}$$
SB_1	Source term species balance: $$R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}}$$

2.4 Mole based model

2.4.1 The temperature balance

The general temperature balance derived earlier (65):

$$((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref}\sum_{i=1}^{n} x_i Cp'_i)\frac{\partial T^*}{\partial t^*} = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{115}$$

Steady state is assumed:

$$0 = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{116}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{117}$$

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

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_r)R}{T_{ref}\lambda} \tag{118}$$

2.4.2 Species mole balance

The mole based fluxes are obtained from the species mole balance. The general dimensionless equation is given as derived earlier (64):

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{119}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{120}$$

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

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{121}$$

The second term is identified as the LHS of the mole based continuity equation (66) when steady state is assumed, swapped for the RHS of the mole based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i(\frac{\xi_{ref}^2}{c_{ref}D_{ref}})\sum_{i=1}^{n} r_i = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{122}$$

No convective transport is assumed and the equation is rearranged:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{123}$$

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

$$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{124}$$

2.4.3 Wilke diffusion model

The general Wilke diffusion model on mole basis as given in 67:

$$J_i^* = -c^* D_{sm} \frac{\partial x_i}{\partial \xi^*} \qquad D_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{125}$$

Rearranged to the implemented form:

$$J_i^* \frac{D_{ref}}{c^* D_{sm}} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad D_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{126}$$

2.4.4 Wilke-bosanquet diffusion model

$$j_i^* = -c^* \frac{D'_{i,eff}}{D_{ref}} \frac{\partial x_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{i,K}} \tag{127}$$

Rearranged to the implemented form:

$$j_i^* \frac{D_{ref}}{D'_{i,eff} c^*} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}} \tag{128}$$

2.4.5 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model on mole basis as given in 69:

$$j_i^* = \frac{-c^* \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{129}$$

Rearranged to the implemented form:

$$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \tag{130}$$

2.4.6 Dusty gas diffusion model

The general Maxwell-Stefan model on mole basis as given in 70:

$$J_i^* = \frac{-\frac{c^*}{D_{ref}} \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{c^* x_i u^*}{D_{iK}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}} \tag{131}$$

Rearranged to the implemented form:

$$J_i^* \frac{D_{ref}}{c^*} (\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}) = -\frac{\partial x_i}{\partial \xi^*} + \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}} \tag{132}$$

2.4.7 Concentration equation

The concentration is obtained from the ideal gas law eqX.

$$\frac{p}{RT} = c \tag{133}$$

2.4.8 Summary of the mole based model, including boundary conditions

The derived equations are gathered in table 20. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

Tabell 14: Mole based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{134}$$	Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \tag{135}$$
Species mole balance: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{136}$$	Definition: $$\sum_{i=1}^{n} J_i = 0 \tag{137}$$
Diffusion model: One of the four diffusionmodels in table 28 is used	Definition: $$\sum_{i=1}^{n} x_i = 1 \tag{138}$$
Ideal gas law rearranged for concentration: $$\frac{p}{RT} = c \tag{139}$$	

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$
$$J_i = 0 \tag{140}$$ $$q = 0 \tag{141}$$	$$T = T^b \tag{142}$$ $$x_i = x_i^b \tag{143}$$

2.5 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 21. 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 37.

Tabell 15: Diffusion models on their implemented form

LHS is implemented in the collocation matrix, and the RHS is implemented in the source vector
Wilke: $$J_i^* \frac{D_{ref}}{c^* D_{sm}} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad D_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{144}$$
Wilke-Bosanquet: $$j_i^* \frac{D_{ref}}{D'_{i,eff} c^*} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}} \tag{145}$$
Maxwell-Stefan: $$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \tag{146}$$
Dusty gas: $$J_i^* \frac{D_{ref}}{c^*} (\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}) = -\frac{\partial x_i}{\partial \xi^*} + \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}} \tag{147}$$

2.5.1 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 37.

2.5.2 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.

2.5.3 Concentration

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

Tabell 16: 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 $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (148)$$	Boundary condtion at $\xi = \xi^p$ $$T = T^b \quad (149)$$
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (150)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (151)$$
Species mole balance, used for N-1 components: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (152)$$	Boundary condition at $\xi = 0$ $$J_i = 0 \quad (153)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} J_i = 0 \quad (154)$$	No boundary condtion –
A diffusion model is used for N-1 components: One of the four diffusionmodels in table 23 is used	Boundary condtition at $\xi = \xi^p$: $$x_i = x_i^b \quad (155)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} x_i = 1 \quad (156)$$	No boundary condtion –
Ideal gas law modified for concentration*: $$\frac{p}{RT} = c \quad (157)$$	No boundary condtion –

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

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{2}{\xi^*}\bullet + \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet
\end{bmatrix}
\begin{bmatrix}
q \\ T \\ J_{CH_4} \\ J_{CO} \\ J_{CO_2} \\ J_{H_2} \\ J_{N_2} \\ J_{H_2O} \\ x_{CH_4} \\ x_{CO} \\ x_{CO_2} \\ x_{H_2} \\ x_{N_2} \\ x_{H_2O}
\end{bmatrix}
=
\begin{bmatrix}
0 \\ \frac{-\triangle H_r \xi^{*2}}{T_{ref}\lambda} \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 0 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ SB_1 \\ 1
\end{bmatrix}
$$

Figur 2: Collocation matrix - Maxwell-Stefan, mole based

Tabell 17: Terms in the collocation matrix and source vector

Label in matrix	Collocation matrix terms:	multiplied with:
DM_1	Wilke: $$\frac{D_{ref}}{D'_{im}c^*}, \qquad D_{im} = \frac{1-x_i}{\sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_j}{D_{ij}}}$$	J_i^*
DM_1	Wilke-Bosanquet: $$\frac{D_{ref}}{D'_{i,eff}c^*}, \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{\substack{j=1\\j\neq i}}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}}$$	J_i^*
DM_1	Maxwell-Stefan: $$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{i} \frac{x_j}{D_{ij}}$$	J_i^*
DM_1	Dusty gas: $$\frac{D_{ref}}{c^*}(\sum_{\substack{j=1\\j\neq i}}^{i} \frac{x_j}{D_{ij}}$$	J_i^*

Label in source vector	Source vector
DM_2	Wilke: $$0$$
DM_2	Wilke-Bosanquet: $$0$$
DM_2	Maxwell-Stefan: $$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n} \frac{J_j^* x_i}{D_{ij}}$$
DM_2	Dusty gas: $$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref}x_i u^*}{D_{iK}}$$
SB_1	Source term species balance: $$(R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}}$$

2.6 Results and discussion

2.6.1 General for all diffusion models

As stated this is the models on their simplest forms with the assumption of steady state, no convective flow and simple boundary conditions. The Steam methane reforming reaction is simulated. The mole fractions of the reactants $H_2OandCH_4$ are expected to decrease from the surface to the center of the particle, and increase for the products CO_2, CO, H_2. The mole fraction of the inert gas N_2 is expected to change some with the change in motive power for the diffusion of nitrogen, also there is some effect from the reaction due to mole generation.

The simulation of the SMR reaction requires heavy under-relaxation of the diffusion model in order to converge. The Wilke-Bosanquet diffusion model tend to be the most sensitive whereas the Maxwell-Stefan model the most robust. These simulations are underrelaxed by a factor of 1-2 in the order of 10^{-4} depending on the diffusion model. For each model the highest possible under relaxation value is used to reduce the amount of iterations and total calculation time.

2.6.2 Wilke and Wilke-Bosanquet models

Starting out with the Wilke diffusion mode on its simplest form, one can immidiately see from the result plots in figure 3 and 4 that the mole and mass based model does not yield the same results.The differences here is due to the inconsitensy in the wilke model. This can best be explained by looking at the molefraction plot for nitrogen and comparing it with the wilke equation on the different forms.

The wilke equation on mass basis is only depented on the component which it is solving for, this means that for nitrogen since it does not react will have a flat profile in massfractions, and the increase seen in molefractions is only due to the increase in molarweight. One would then expect flat mole fraction profile for nitrogen using the mole based wilke model, but in the mole based species balance it is accounted for mole generation rate which give the rather great change in the composition. this effect can easily be spotted in the comparison of the fluxes

The differences in the the temperature equation is due to the different reaction rates because of the inconsistent wilke model. The differences in the flux equations is the effect of not considering convective flow. Not considering convective flow is mainly causing the mole based model to deviate as the convective flow is neglectable on mass basis, this means that only the diffusive fluxes are compared.

Adding the effect of knudsen diffusivities in the Wilke-Bosanquet model does not give any significant change from the standard Wilke model as it can be seen from the figures 5 and 6

2.6.3 Maxwell-Stefan and Dusty gas models

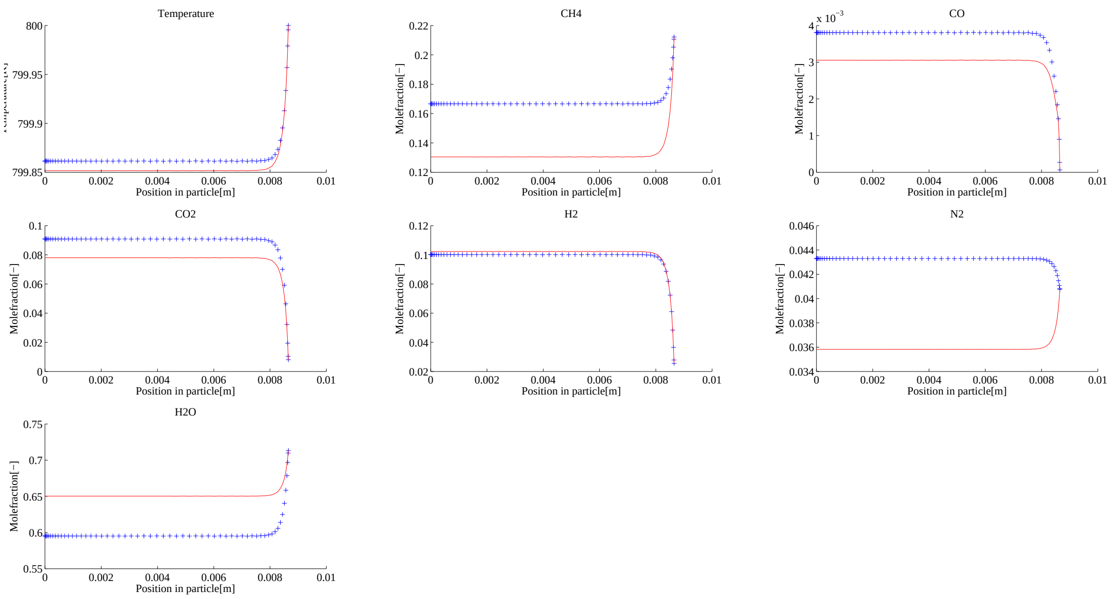
A quick look at the results for the Maxwell-Stefan model in figure 7 and 8 one can immidately see that this model gives much more comparable results between mass and mole based models compared to the Wilke diffusion models. One would also expect this since the Maxwell-Stefan model is a more rigorous diffusion model which consideres the other components not just itself. This is easily spotted comparing the diffusion equations in table XXX.

The results for simplest form considering the dusty gas diffusion model is abit different, the differences can be seen in figure 9. This is also a rigorous diffusion model along with the Maxwell-

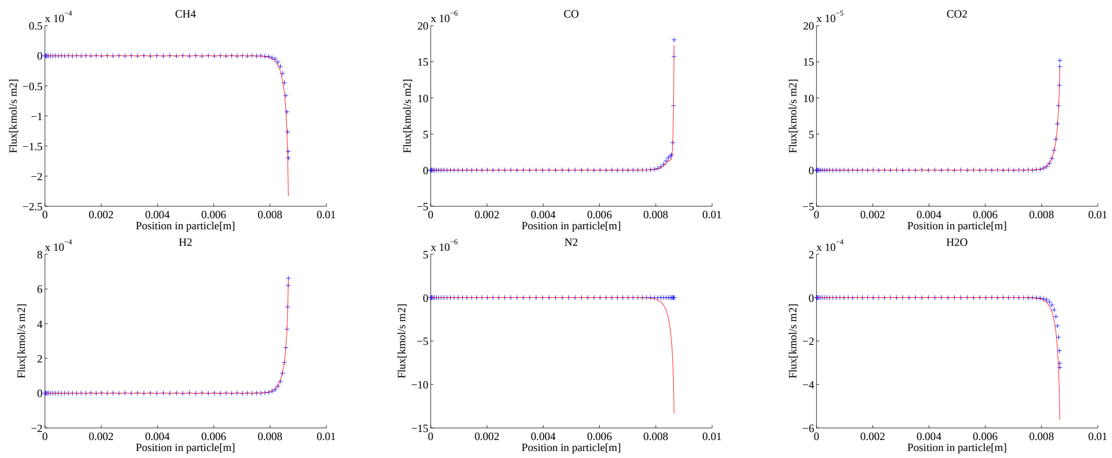
Stefan diffusion model. However with the addition of knudsen diffusivites the dusty gas diffusion model also have a convective term which is not considered on this level. When the models are compared in the chapter with convective flow one can see that the convective terms on mass basis are neglectable but on mole basis it has a significant value, This is further discussed in chapter XXX.

The temperature equation for both models are more similar than for the wilke model due to the more similar reaction rates. The flux comparisons on mole and mass basis for all models in figure 4,6,8 and 10 all show great similarity between the diffusion models because of the very rapid reaction. The reaction is so rapid that the diffusion equations will yield almost no effect back to the species balances equations which is used to calculate the fluxes.

2.6.4 Wilke plots

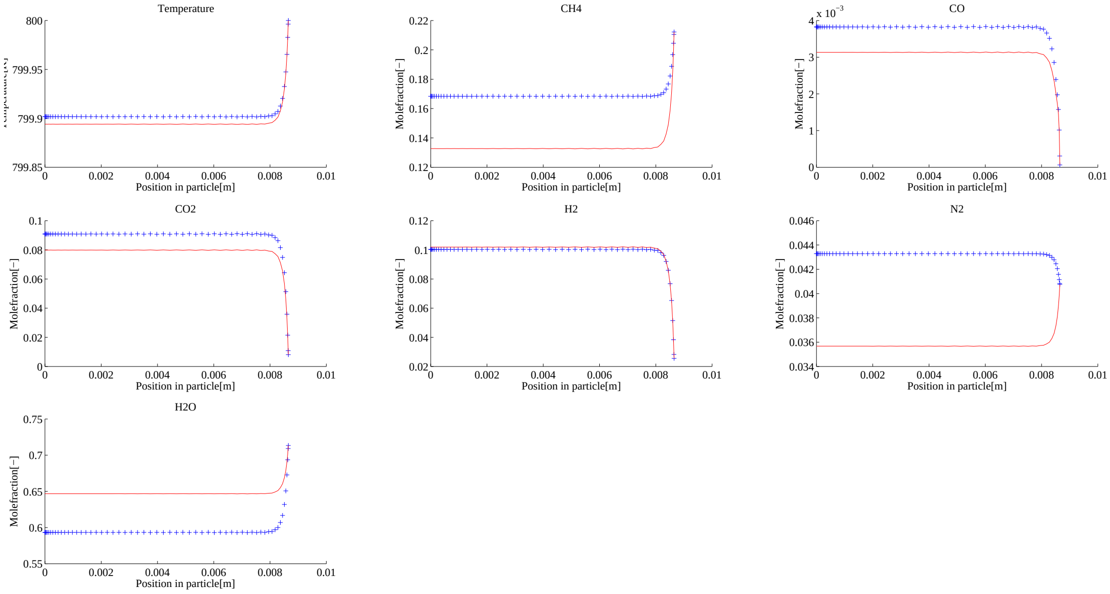


Figur 3: Mass and mole based models, the mass based is converted to mol fractions. Mass based mode isl in blue crosses and the mole based is the red line.

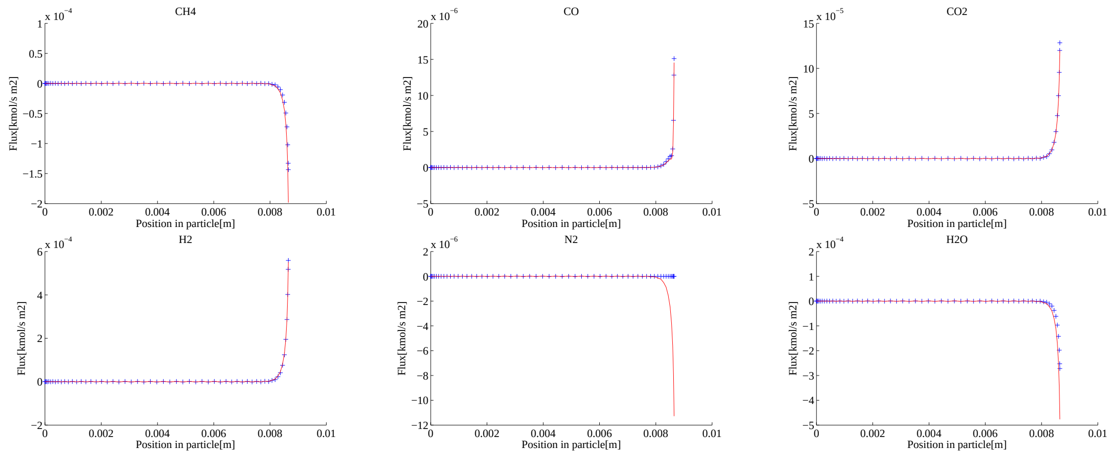


Figur 4: Mole based total fluxes, mass based model is the blue crosses and the mole based is the red line

2.6.5 Wilke-Bosanquet

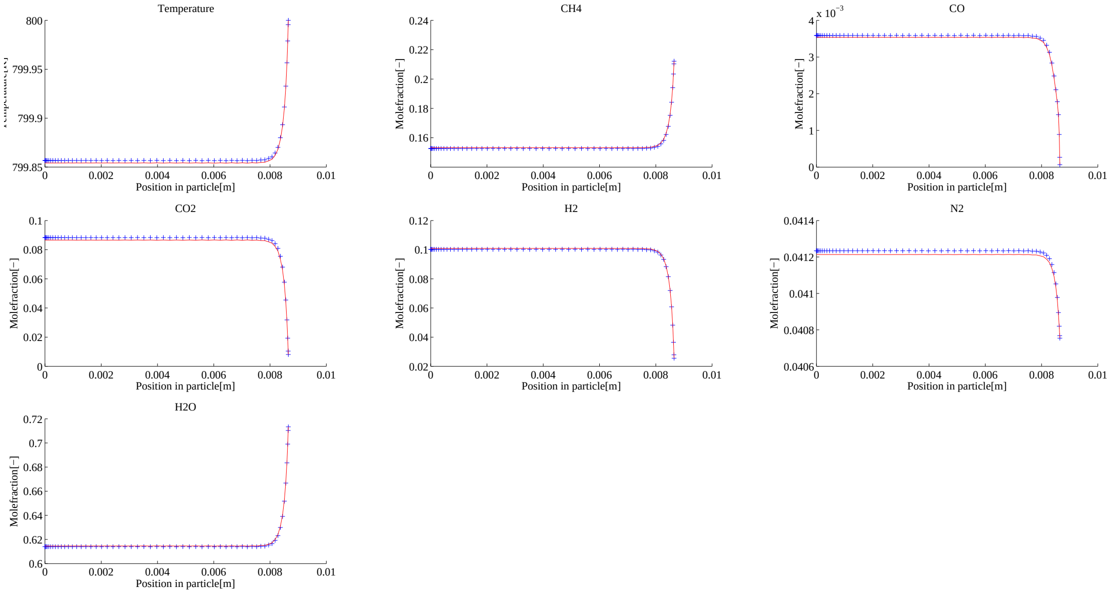


Figur 5: Comparison

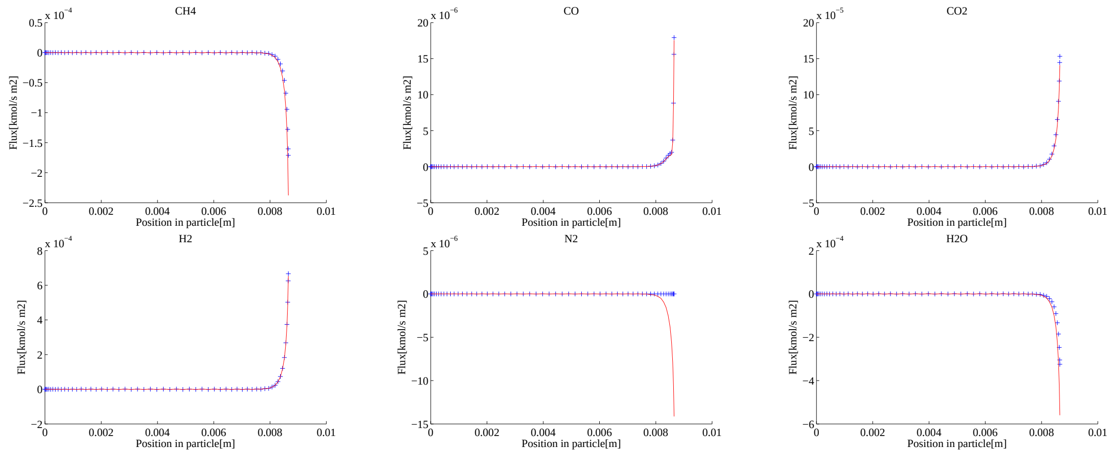


Figur 6: Mole based total fluxes

2.6.6 Maxwell-Stefan

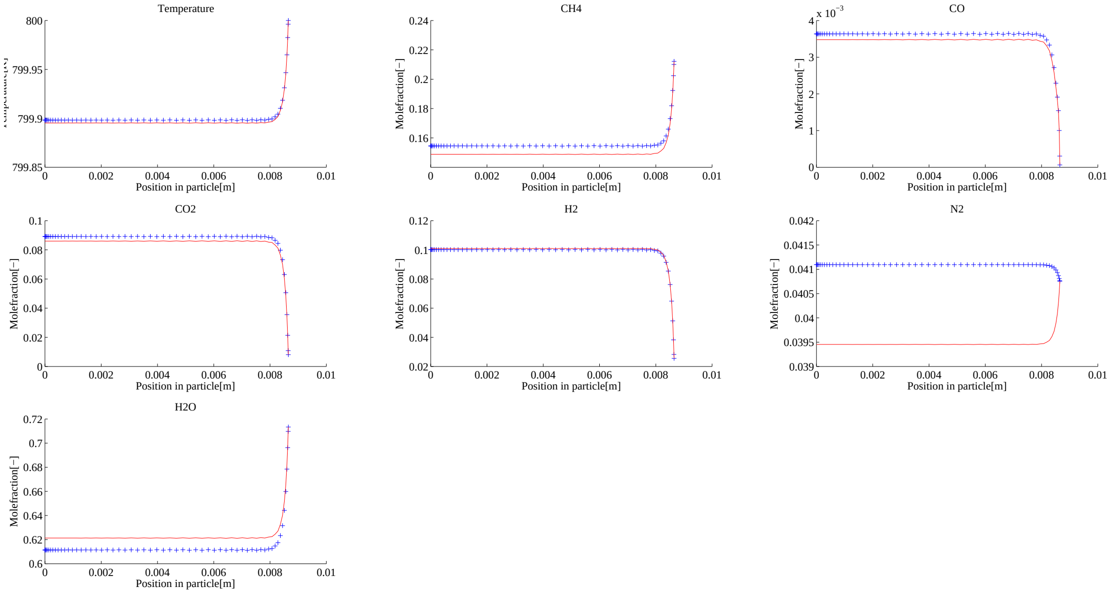


Figur 7: Comparison

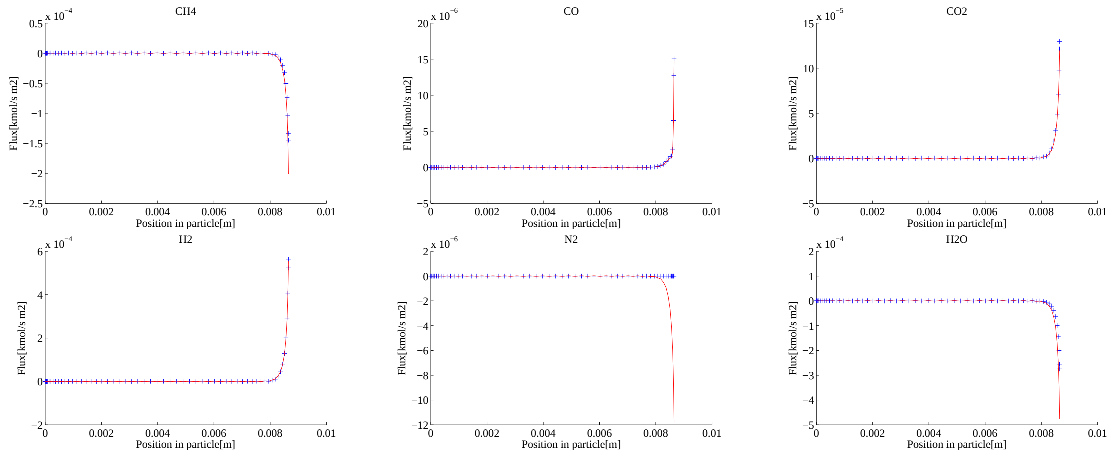


Figur 8: Mole based total fluxes

2.6.7 Dusty-gas



Figur 9: Comparison



Figur 10: Mole based total fluxes

3 Case number 1b Alternative dimensionless method

The fluxes are made dimensionless using non constant values

General about the case, SMR etc

3.1 Derivation of the equations to use in the model.

This model only differs from the case 1 by not assuming constant values when making the fluxes dimensionless. The mass based model from the previous case will be compared to an alternative method of making the mass fluxes dimensionless. This is done to validate that it is resonable to assume constant values.

3.1.1 General for the derivation of the mass based model

The temperature equation (58) is solved in combination with fouriers law. The temperature equation is only modified by introducing the assumptions assumed for this case.

The Species balance for the mass model (171), 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 (173). In the species balance the continuity equation (59) is identifiyed 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 (42).

A summary of the equations derivated in detail in the next sections are shown in table 18 for the mass based model.

3.2 Mass based model

3.2.1 The temperature balance

The general temperature balance derived earlier (58):

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho^*\rho_{ref}\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T^*}{\partial t^*} = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{158}$$

Steady state is assumed:

$$0 = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{159}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{160}$$

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

$$\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{161}$$

3.2.2 Species mass balance

The mass based fluxes are obtained from the species mass balance. To account for the alternative method of making the flux dimensionless, we will start out from the general species mass balance with dimensions. The general equation is given as noted earlier (6):

$$\frac{\partial}{\partial t}(\rho\omega_i) + \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho\omega_i v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{162}$$

Steady state is assumed.

$$\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho\omega_i v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{163}$$

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

$$\frac{\partial \omega_i}{\partial \xi}(\rho v_\xi) + \omega_i \frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 \rho v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{164}$$

The second term is identified as the LHS of the mass based continuity equation (10) when steady state is assumed, swapped for the RHS of the mass based continuity equation gives:

$$\frac{\partial \omega_i}{\partial \xi}(\rho v_\xi) = -\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) + R_i \tag{165}$$

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

$$\frac{1}{\xi^2}\frac{\partial}{\partial \xi}(\xi^2 j_i) = R_i \tag{166}$$

The first term is expanded to reflect the implemented equation:

$$\frac{2j_i}{\xi} + \frac{\partial j_i}{\partial \xi} = R_i \tag{167}$$

Alternative method for making the fluxes dimensionless:

$$j_i^* = \frac{j\xi_{ref}}{D_s \rho} \tag{168}$$

where ρ can be written out to:

$$j_i^* = \frac{j\xi_{ref}}{D_s c^* c_{ref}\overline{M}} \tag{169}$$

Introducing the last equation into the species mass balance to transform it to a dimensionless form:

$$\frac{2j_i^* D_s c^* c_{ref}\overline{M}}{\xi^* \xi_{ref}^2} + \frac{c_{ref}}{\xi ref^2}\frac{\partial}{\partial \xi^*}(j_i^* D_s c^* \overline{M}) = R_i \tag{170}$$

Rearranging and writing out the differential:

$$\frac{2j_i^* D_s c^* \overline{M}}{\xi^*} + D_s c^* \overline{M}\frac{\partial j_i^*}{\partial \xi^*} + j_i^* c^* \overline{M}\frac{\partial D_s}{\partial \xi^*} + j_i^* D_s \overline{M}\frac{\partial c^*}{\partial \xi^*} + j_i^* D_s c^* \frac{\partial \overline{M}}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{c_{ref}} \tag{171}$$

Clean up equation:

$$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} + \frac{j_i^*}{D_s}\frac{\partial D_s}{\partial \xi^*} + \frac{j_i^*}{c^*}\frac{\partial c^*}{\partial \xi^*} + \frac{j_i^*}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{\rho D_s} \tag{172}$$

3.2.3 Constitutive law for the species balance

a modified constitutive law is needed as now the dimensionless fluxes will not sum to 0.

$$\sum_{i=1}^{n} j_i^* D_s c^* = 0 \tag{173}$$

3.2.4 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model with dimension as given in (13):

$$j_i = \frac{-\rho\omega_i \nabla ln(\overline{M}) - \rho\nabla\omega_i + \overline{M}\omega_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j}{M_j D_{ij}}}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}} \tag{174}$$

Specifies that:

$$D_s^{-1} = \overline{M}\sum_{\substack{j=1\\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} \tag{175}$$

Transforming to dimensionless form:

$$j_i^* = \xi_{ref} \frac{-\rho\omega_i \frac{1}{\overline{M}} \frac{\partial\overline{M}}{\partial\xi^*\xi_{ref}} - \rho\frac{\partial\omega_i}{\partial\xi^*\xi_{ref}} + \overline{M}\omega_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j^* D_s c^* c_{ref}\overline{M}}{M_j D_{ij}\xi_{ref}}}{c^* c_{ref}\overline{M}} \tag{176}$$

Cleaning the equation:

$$j_i^* = -\omega_i \frac{1}{\overline{M}}\frac{\partial\overline{M}}{\partial\xi^*} - \frac{\partial\omega_i}{\partial\xi^*} + \omega_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j^* D_s\overline{M}}{M_j D_{ij}} \tag{177}$$

3.2.5 Concentration equation

The concentration is obtained from the ideal gas law given earlier eqX

$$\frac{p}{RT} = c \tag{178}$$

3.2.6 Summary of the mass based model, including boundary conditions

The derived equations are gathered in table 18. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

3.3 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 19. 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 11.

Tabell 18: Mass based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (179)$$	Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (180)$$
Mass balance: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} + \frac{j_i^*}{D_s}\frac{\partial D_s}{\partial \xi^*} + \frac{j_i^*}{c^*}\frac{\partial c^*}{\partial \xi^*} + \frac{j_i^*}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{\rho D_s} \quad (181)$$	Definition: $$\sum_{i=1}^{n} j_i^* D_s \rho = 0 \quad (182)$$
Diffusion, Maxwell-Stefan: $$j_i^* = -\omega_i \frac{1}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} - \frac{\partial \omega_i}{\partial \xi^*} + \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^* D_s \overline{M}}{M_j D_{ij}} \quad (183)$$	Definition: $$\sum_{i=1}^{n} \omega_i = 1 \quad (184)$$
Ideal gas law, concentration and density: $$\frac{p}{RT} = c \qquad \frac{p\overline{M}}{RT} = \rho \quad (185)$$	

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$
$$j_i = 0 \quad (186)$$ $$q = 0 \quad (187)$$	$$T = T^b \quad (188)$$ $$\omega_i = \omega_i^b \quad (189)$$

3.3.1 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 11.

3.3.2 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.

3.3.3 Concentration

The ideal gas law is solved outside the numerical problem and is solved using the previous iterative values.

Tabell 19: 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 $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (190)$$	Boundary condtion at $\xi = \xi^p$ $$T = T^b \quad (191)$$
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (192)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (193)$$
Species mass balance, used for N-1 components: $$\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{\rho D_s} - \frac{j_i^*}{D_s}\frac{\partial D_s}{\partial \xi^*} - \frac{j_i^*}{c^*}\frac{\partial c^*}{\partial \xi^*} - \frac{j_i^*}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} \quad (194)$$	Boundary condition at $\xi = 0$ $$j_i = 0 \quad (195)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} j_i^* D_s \rho = 0 \quad (196)$$	No boundary condtion –
Maxwell-Stefan diffusion model for N-1 components: $$j_i^* = -\omega_i \frac{1}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} - \frac{\partial \omega_i}{\partial \xi^*} + \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^* D_s \overline{M}}{M_j D_{ij}} \quad (197)$$	Boundary condtition at $\xi = \xi^p$: $$\omega_i = \omega_i^b \quad (198)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} \omega_i = 1 \quad (199)$$	No boundary condtion –
Ideal gas law, concentration and density*: $$\frac{p}{RT} = c \qquad \frac{p\overline{M}}{RT} = \rho \quad (200)$$	No boundary condtion –

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

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

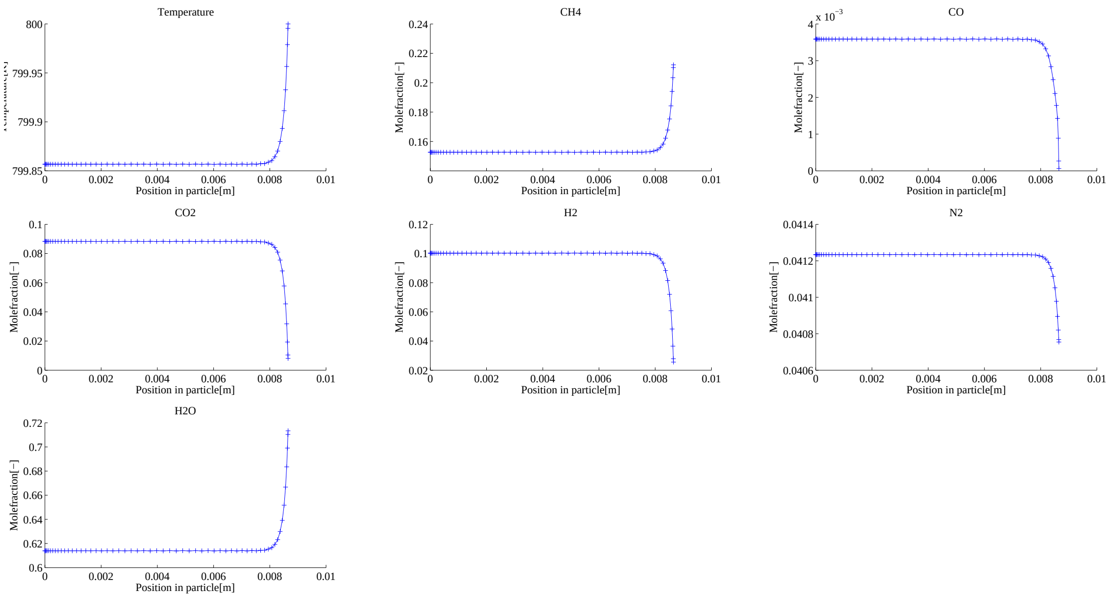
Figur 11: Collocation matrix - Maxwell-Stefan, mass based

$$MS_1 = -\omega_i \frac{1}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \omega_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* D_s \overline{M}}{M_j D_{ij}}$$

$$SB_1 = R_i \frac{\xi_{ref}^2}{\rho D_s} - \frac{j_i^*}{D_s} \frac{\partial D_s}{\partial \xi^*} - \frac{j_i^*}{c^*} \frac{\partial c^*}{\partial \xi^*} - \frac{j_i^*}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*}$$

3.4 Results and discussion

The effect of using constant vs variable values when making the diffusion fluxes dimensionless are compared for the mass based model in the figure XXX. As it can be seen from the figure this has no effect. However it is recommended to use constant values as this will yield a much simpler model, using variable values will cause a more troublesome implementation due to the fact that the fluxes will no longer be directly in scale.



Figur 12: Comparison

4 Effect of continuity equation in the species balance

For the simple models not considering convective flow the inclusion of the continuity equation only has an effect on the mole based model.This is because the continuity equation on mass basis equals to zero and does not contribute with any new terms. For the more rigorous models icluding the convective terms the use of the continuity equation should not have any effect.

A model for the most crucial case mole based case is to be derived.

4.1 Mole based model not including the continuity equation

4.1.1 The temperature balance

The general temperature balance derived earlier (65):

$$((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^{n} x_i Cp_i') \frac{\partial T^*}{\partial t^*} = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp_i' \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{201}$$

Steady state is assumed:

$$0 = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp_i' \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{202}$$

no convective transport is assumed:

$$0 = -\frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{203}$$

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

$$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_r)R}{T_{ref}\lambda} \tag{204}$$

4.1.2 Species mole balance

The mole based fluxes are obtained from the species mole balance. The general dimensionless equation is given as derived earlier (64):

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{205}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{206}$$

No convective transport is assumed and the equation is rearranged:

$$0 = -\frac{1}{\xi^{*2}} \frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{207}$$

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

$$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{208}$$

4.1.3 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model on mole basis as given in 69:

$$j_i^* = \frac{-c^* \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{209}$$

Rearranged to the implemented form:

$$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \tag{210}$$

4.1.4 Concentration equation

The concentration is obtained from the ideal gas law eqX.

$$\frac{p}{RT} = c \tag{211}$$

4.1.5 Summary of the mole based model, including boundary conditions

The derived equations are gathered in table 20. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

4.2 Solution strategy

The different equations are first discussed in short with text and the main summary of the solution strategy is given in table 21. 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 37.

4.2.1 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 37.

4.2.2 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.

4.2.3 Concentration

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

Tabell 20: Mole based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (212)$$	Fourier's law $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (213)$$
Species mole balance: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (214)$$	Definition: $$\sum_{i=1}^{n} J_i = 0 \quad (215)$$
Diffusion, Maxwell-Stefan: $$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \quad (216)$$	Definition: $$\sum_{i=1}^{n} x_i = 1 \quad (217)$$
Ideal gas law rearranged for concentration: $$\frac{p}{RT} = c \quad (218)$$	

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$
$$J_i = 0 \quad (219)$$ $$q = 0 \quad (220)$$	$$T = T^b \quad (221)$$ $$x_i = x_i^b \quad (222)$$

Tabell 21: 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 $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (223)$$	Boundary condtion at $\xi = \xi^p$ $$T = T^b \quad (224)$$
Temperature equation: $$\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*} = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (225)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (226)$$
Species mole balance, used for N-1 components: $$\frac{2J_i^*}{\xi^{*2}} + \frac{\partial J_i^*}{\partial \xi^*} = R_i \frac{\xi_{ref}^2}{D_{ref}c_{ref}} \quad (227)$$	Boundary condition at $\xi = 0$ $$J_i = 0 \quad (228)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} J_i = 0 \quad (229)$$	No boundary condtion –
Maxwell-Stefan diffusion model for N-1 components: $$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \quad (230)$$	Boundary condtition at $\xi = \xi^p$: $$x_i = x_i^b \quad (231)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} x_i = 1 \quad (232)$$	No boundary condtion –
Ideal gas law modified for concentration*: $$\frac{p}{RT} = c \quad (233)$$	No boundary condtion –

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

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

Figur 13: Collocation matrix - Maxwell-Stefan, mole based

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

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

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

4.2.4 Effect of continuity, rigorous models

Due to the small changes in the models and the results given by including the continuity equation in the more rigorous models the alternative species balance equations are only derived. These equations can be replaced in the semi rigorous model derived in chapter XXX.

4.2.5 Species mass balance

The mass based fluxes are obtained from the species mass balance. The general dimensionless equation is given as derived earlier (57):

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{234}$$

Steady state is assumed and the equation is rearranged.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{235}$$

The first and second term is written out:

$$\frac{2\rho^*\omega_i v_\xi^*}{\xi^*} + \frac{\partial \rho^*}{\partial \xi^*}\omega_i v_\xi^* + \frac{\partial \omega_i}{\partial \xi^*}\rho^* v_\xi^* + \frac{\partial v_\xi^*}{\partial \xi^*}\omega_i\rho^* + \frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{236}$$

The equation is rearranged to show how it is implemented. The LHS is implemented in the collocation matrix and the RHS in the source vector:

$$\frac{2\rho^*\omega_i v_\xi^*}{\xi^*} + \frac{\partial \omega_i}{\partial \xi^*}\rho^* v_\xi^* + \frac{\partial v_\xi^*}{\partial \xi^*}\omega_i\rho^* + \frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} - \frac{\partial \rho^*}{\partial \xi^*}\omega_i v_\xi^* \tag{237}$$

This equation can be swapped out for eq X in chapter XXX for a complete solution strategy.

4.2.6 Species mole balance

The mole based fluxes are obtained from the species mole balance. The general dimensionless equation is given as derived earlier (64):

$$\frac{\partial}{\partial t^*}(c^*x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}c^*x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}J_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{238}$$

Steady state is assumed and the equation is rearranged.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}c^*x_i u_\xi^*) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}J_i^*) = R_i\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{239}$$

The first and second term is written out:

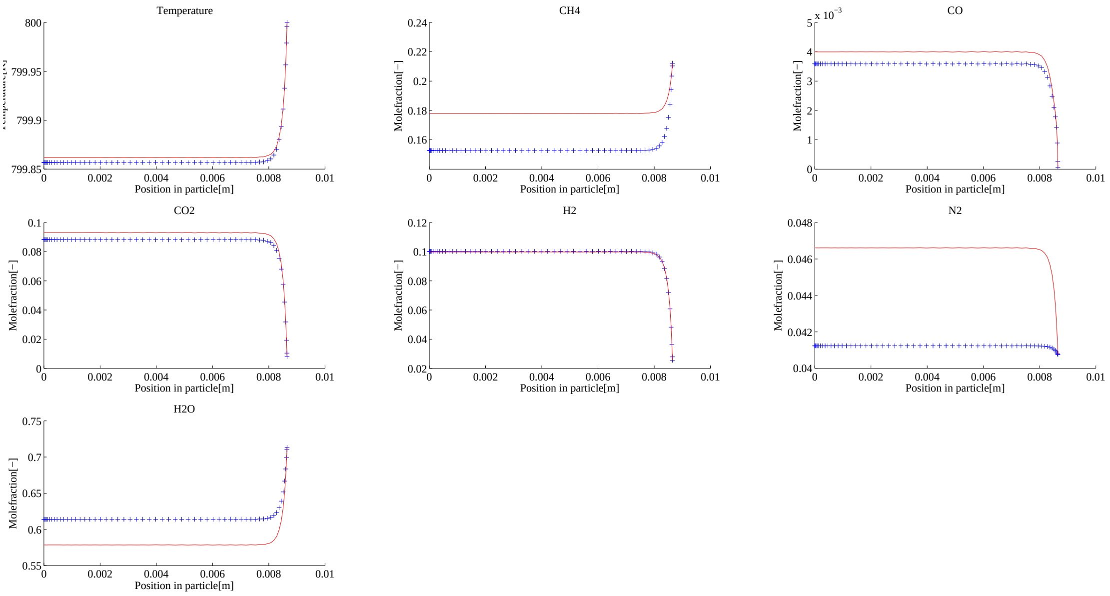
$$\frac{2c^*x_i u_\xi^*}{\xi^*} + \frac{\partial x_i}{\partial \xi^*}c^* u_\xi^* + \frac{\partial c^*}{\partial \xi^*}x_i u_\xi^* + \frac{\partial u_\xi^*}{\partial \xi^*}x_i c^* + \frac{2J_i^*}{\xi^*} + \frac{\partial J_i^*}{\partial \xi^*} = R_i\frac{\xi_{ref}^2}{D_{ref}c_{ref}} \tag{240}$$

This equation can be swapped out for eq X in chapter XXX for a complete solution strategy.

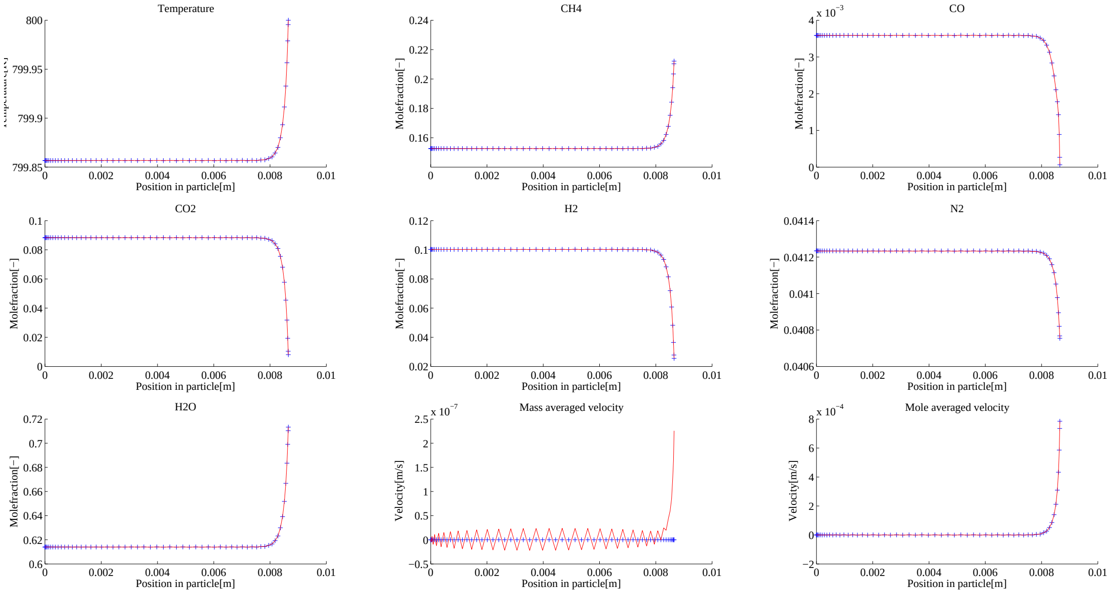
4.3 Results and discussion

The big difference by not including the sum of reactions(LHS of the continuity equation) can be seen in figure XXX. Comparing these results with figure XXX from chapter XXX one can see how great effect this has. The inclusion of the LHS of the continuity equation in the models not considering convective flow will compensate for much of the loss where the convective terms have a significant value. The inclusion of the convective is especially imporant for the mole base SMR simulation as they have a significant value which easily can be spottet from the figures by the effect the given by the LHS of the continuity equation. However if the convective terms where to be included it does not make any difference wheter the convective terms are used or if they are replaced with the LHS of the continuity equation.

, including this will give a much grater similarity with the mass based model. however this will be as expected as the models including convective flow are identical, and including the non convective term in the continuity equation makes up for much of the lossfrom not considering convectiveflow.



Figur 14: No transferlimitations and no convective flow assumed



Figur 15: No Transfer limitations

5 Rigorous steady state models

General about the case, SMR etc

5.1 Derivation of the equations to use in the model.

This is the rigorous steady state models where only steady state is assumed. The results are also considering the rigorous steady state models assuming no transfer limitations. Models on both mass and mole basis is to be derived. The method of implementation is presented using orthogonal collocation.

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

The temperature equation (58)(65) is solved in combination with fouriers law. The temperature equation is only modified by introducing the assumptions assumed for this case.

The Species balance for respectively the mass and mole model (57) and (64), 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 (41) and (43). In the species balance the continuity equation (59) and (66) is identifiyed for the respective model and inserted giving the species balance used in the model.

The species fractions is solved by using the different diffusion models in table XXX for N-1 components, the last component is solved by the constitutive law's (42) and (44) for respectively the mass and mole based model. The diffusion models are only reformulated from their general form shown in the theory to reflect their implemented form.

A summary of the equations derivated in detail in the next sections are shown in table 10 for the mass based model and table 20 for the mole based.

5.2 Mass based model

5.2.1 The temperature balance

The general temperature balance derived earlier (58):

$$((1-\epsilon)\rho_p Cp_p + \epsilon\rho^*\rho_{ref}\sum_{i=1}^{n}\omega_i Cp_i)\frac{\partial T^*}{\partial t^*} = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{241}$$

Steady state is assumed:

$$0 = -\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{242}$$

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

$$\frac{D_{ref}}{\lambda}\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} = -(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*}) + \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{243}$$

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 (57):

$$\frac{\partial}{\partial t^*}(\rho^*\omega_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{244}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^*\omega_i v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{245}$$

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

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) + \omega_i\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{246}$$

The second term is identified as the LHS of the mass based continuity equation (59) when steady state is assumed, swapped for the RHS of the mass based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial \omega_i}{\partial \xi^*}(\xi^{*2}\rho^* v_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}j_i^*) + R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{247}$$

The second term is expanded and the equation is rearranged to reflect the implemented equation:

$$\frac{\partial \omega_i}{\partial \xi^*}(\rho^* v_\xi^*) + (\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*}) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \tag{248}$$

5.2.3 Mass based continuity equation

Velocity is obtained from the mass based continuty equation, starting out from the general equation (59)

$$\frac{\partial \rho^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v^*) = 0 \tag{249}$$

Steady state is assumed:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}\rho^* v^*) = 0 \tag{250}$$

The derivative term is expanded to reflect the used equation:

$$\frac{2}{\xi^*}v^*\rho^* + \frac{\partial \rho^*}{\partial \xi^*}v^* + \frac{\partial v^*}{\partial \xi^*}\rho^* = 0 \tag{251}$$

5.2.4 Wilke diffusion model

The general Wilke diffusion model as given in (60):

$$j_i^* = -\rho^*\frac{D'_{im}}{D_{ref}}\frac{\partial \omega_i}{\partial \xi^*} \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{252}$$

Rearranged to the implemented form:

$$j_i^*\frac{D_{ref}}{D'_{im}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{\omega_j}{M_j D_{ij}}} \tag{253}$$

5.2.5 Wilke-bosanquet diffusion model

$$j_i^* = -\rho^* \frac{D'_{i,eff}}{D_{ref}} \frac{\partial \omega_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{i,K}} \tag{254}$$

Rearranged to the implemented form:

$$j_i^* \frac{D_{ref}}{D'_{i,eff} \rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-\omega_i}{\overline{M} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}}} + \frac{1}{D_{i,K}} \tag{255}$$

5.2.6 Darcy's law

Darcy's law is used to obtain the pressure(40).

$$\frac{v^* \mu D_{ref}}{B p_{ref}} + \frac{\partial p^*}{\partial \xi^*} = 0 \tag{256}$$

5.2.7 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model as given in (62):

$$j_i^* = \frac{\frac{-\rho^* \omega_i}{D_{ref}} \frac{1}{\overline{M}} \frac{\partial}{\partial \xi^*}(\overline{M}) - \frac{\rho^*}{D_{ref}} \frac{\partial \omega_i}{\partial \xi^*} + \overline{M} \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}}}{\overline{M} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}} \tag{257}$$

Rearranged to the implemented form:

$$j_i^* \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}} \tag{258}$$

5.2.8 Dusty gas diffusion model

The general Maxwell-Stefan model as given in (63):

$$j_i^* = \frac{\overline{M}^2 \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{v^* \omega_i \overline{M}}{\tilde{D}_{iK}} - \frac{\omega_i \rho^*}{D_{ref}} \frac{\partial \overline{M}}{\partial \xi^*} - \frac{\rho^* \overline{M}}{D_{ref}} \frac{\partial \omega_i}{\partial \xi^*}}{\overline{M}^2 \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_D ij} + \frac{\overline{M}}{D_{iK}}} \tag{259}$$

Rearranged to the implemented form:

$$j_i^* \frac{D_{ref}}{\rho^*} (\overline{M} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_{ij}} + \frac{1}{D_{iK}}) + \frac{\partial \omega_i}{\partial \xi^*} = \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{v^* \omega_i D_{ref}}{\tilde{D}_{iK} \rho^*} - \frac{\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} \tag{260}$$

5.2.9 Density equation

The density is obtained from modified ideal gas law given earlier eqX

$$\frac{p\overline{M}}{RT} = \rho \tag{261}$$

5.2.10 Summary of the mass based model, including boundary conditions

The derived equations are gathered in table 22. In the table the consitutive laws, initial and boundary conditions used for solving the model are given.

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 12. 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 36.

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 36.

5.3.2 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.

5.3.3 Density

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

Tabell 22: Mass based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $$\frac{D_{ref}}{\lambda}\rho^*\rho_{ref}v_r^*\sum_{i=1}^{n}\omega_i Cp_i\frac{\partial T^*}{\partial \xi^*} = -(\frac{2q^*}{\xi^*}+\frac{\partial q^*}{\partial \xi^*}) + \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \quad (262)$$	Fourier's law $$q+\frac{\partial T}{\partial \xi^*}=0 \quad (263)$$
Mass balance: $$\frac{\partial \omega_i}{\partial \xi^*}(\rho^* v_\xi^*) + (\frac{2j_i^*}{\xi^*}+\frac{\partial j_i^*}{\partial \xi^*}) = R_i\frac{\xi_{ref}^2}{D_{ref}\rho_{ref}} \quad (264)$$	Definition: $$\sum_{i=1}^{n} j_i = 0 \quad (265)$$
Diffusion model: One of the four diffusionmodels in table 23 is used	Definition: $$\sum_{i=1}^{n}\omega_i = 1 \quad (266)$$
Mass based continuity equation: $$\frac{2}{\xi^*}v^*\rho^* + \frac{\partial \rho^*}{\partial \xi^*}v^* + \frac{\partial v^*}{\partial \xi^*}\rho^* = 0 \quad (267)$$	Darcy's law: $$\frac{v^*\mu D_{ref}}{Bp_{ref}} + \frac{\partial p^*}{\partial \xi^*} = 0 \quad (268)$$
Ideal gas law modified for density: $$\frac{p\overline{M}}{RT} = \rho \quad (269)$$	

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$ with transfer limitations:
$$j_i = 0 \quad (270)$$ $$q = 0 \quad (271)$$ $$v = 0 \quad (272)$$	$$q_r + \rho Cp_g T v = -h(T^b - T) \quad (273)$$ $$-k_i(\rho_i^b - \omega_i\rho) = j_i + v\rho\omega_i \quad (274)$$ $$p = p^b \quad (275)$$ Boundary conditions at the surface $\xi^* = \xi_p^*$ without transfer limitations: $$T = T^b \quad (276)$$ $$\omega_i = \omega_i^b \quad (277)$$ $$p = p^b \quad (278)$$

Tabell 23: Diffusion models on their implemented form

LHS is implemented in the collocation matrix, and the RHS is implemented in the source vector
Wilke: $$j_i^* \frac{D_{ref}}{D'_{im}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad D'_{im} = \frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}} \tag{279}$$ Wilke-Bosanquet: $$j_i^* \frac{D_{ref}}{D'_{i,eff}\rho^*} + \frac{\partial \omega_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-\omega_i}{\overline{M}\sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\omega_j}{M_j D_{ij}}}} + \frac{1}{D_{i,K}} \tag{280}$$ Maxwell-Stefan: $$j_i^* \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1\\ j\neq i}}^{i} \frac{\omega_j}{M_j D_{ij}} + \frac{\partial \omega_i}{\partial \xi^*} = \frac{-\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*} \omega_i \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}} \tag{281}$$ Dusty gas: $$j_i^* \frac{D_{ref}}{\rho^*} (\overline{M} \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_{ij}} + \frac{1}{D_{iK}}) + \frac{\partial \omega_i}{\partial \xi^*} = \frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1\\ j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{\omega_i}{\overline{M}} \frac{\partial \overline{M}}{\partial \xi^*} \tag{282}$$

Tabell 24: 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 $$q^* + \frac{\partial T^*}{\partial \xi^*} = 0 \quad (283)$$	Boundary condtion at $\xi = \xi^p$ $$hT^* = \frac{q^*\lambda}{\xi_{ref}} + \rho C p_g T^* v^* \frac{D_{ref}}{\xi_r ef} + h \quad (284)$$
Temperature equation: $$\frac{D_{ref}}{\lambda} \rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i C p_i \frac{\partial T^*}{\partial \xi^*} + (\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*}) = \frac{\xi_{ref}^2 (-\triangle H_R) R}{T_{ref} \lambda} \quad (285)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (286)$$
Species mass balance, used for N-1 components: $$\frac{\partial \omega_i}{\partial \xi^*} (\rho^* v_\xi^*) + (\frac{2j_i^*}{\xi^*} + \frac{\partial j_i^*}{\partial \xi^*}) = R_i \frac{\xi_{ref}^2}{D_{ref} \rho_{ref}} \quad (287)$$	Boundary condition at $\xi = 0$ $$j_i = 0 \quad (288)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} j_i = 0 \quad (289)$$	No boundary condtion –
Diffusion model: One of the four diffusionmodels in table 23 is used	Boundary condtition at $\xi = \xi^p$: $$\omega_i = \frac{(j_i^* \frac{D_{ref}}{\xi_{ref}} + v^* \frac{D_{ref}}{\xi_{ref}} \rho^* \omega_i)}{k_i \rho^*} + \frac{\omega_i}{\rho^*} \quad (290)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} \omega_i = 1 \quad (291)$$	No boundary condtion –
Mass based continuity equation: $$\frac{2}{\xi^*} v^* + \frac{\partial v^*}{\partial \xi^*} = -\frac{\partial \rho^*}{\partial \xi^*} \frac{v^*}{\rho^*} \quad (292)$$	Boundary condition at $\xi = 0$ $$v^* = 0 \quad (293)$$
Darcy's law: $$\frac{v^* \mu}{B p_{ref}} + \frac{\partial p^*}{\partial \xi^*} = 0 \quad (294)$$	Boundary condition at $\xi = \xi^p$ $$p = p^b \quad (295)$$
Ideal gas law modified for density*: $$\frac{p\overline{M}}{RT} = \rho \quad (296)$$	No boundary condtion –
Mole averaged velocity * ** $$u - v = \sum_{i=1}^{N} \frac{j_i \overline{M}}{\rho M_i} \quad (297)$$	No boundary condtion –

*sovled outside of the collocation matrix, i.e. purely based on previous iterative values ** Solved for comparison with the mole based model.

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
X_1 & T_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & X_1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Dl_1\bullet & \frac{\partial}{\partial \xi^*}
\end{bmatrix}
\begin{bmatrix}
q^* \\ T^* \\ j_{CH_4} \\ j_{CO} \\ j_{CO_2} \\ j_{H_2} \\ j_{N_2} \\ j_{H_2O} \\ \omega_{CH_4} \\ \omega_{CO} \\ \omega_{CO_2} \\ \omega_{H_2} \\ \omega_{N_2} \\ \omega_{H_2O} \\ v^* \\ p^*
\end{bmatrix}
=
\begin{bmatrix}
0 \\ T_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 0 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ 1 \\ MC_1 \\ 0
\end{bmatrix}
$$

Figur 16: Collocation matrix, mass based. Explanation on the labeled terms can be seen in table 35

Tabell 25: Terms in the collocation matrix

Label in matrix	Collocation matrix terms:	multiplied with:
X_1	$\frac{2}{\xi^*} + \frac{\partial}{\partial \xi^*}$	q^*, ω_i, v^*
T_1	$\frac{D_{ref}}{\lambda} \rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i Cp_i \frac{\partial}{\partial \xi^*}$	T^*
DM_1	Wilke: $\frac{D_{ref}}{D'_{im} \rho^*}$	j_i^*
DM_1	Wilke-Bosanquet: $\frac{D_{ref}}{D'_{i,eff} \rho^*}$	j_i^*
DM_1	Maxwell-Stefan: $\frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}$	j_i^*
DM_1	Dusty gas: $\frac{D_{ref}}{\rho^*} (\overline{M} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_{ij}} + \frac{1}{D_{iK}})$	j_i^*
SB_1	$\rho^* v_\xi^* \frac{\partial}{\partial \xi^*}$	ω_i
Dl_1	$\frac{\mu}{B p_{ref}}$	v^*

Tabell 26: Terms in the source vector

Label in source vector	Source vector
T_2	Source term temperature equation: $$\frac{-\triangle H_r \xi_{ref}^2}{T_{ref}\lambda}$$
DM_2	Wilke: $$0$$
DM_2	Wilke-Bosanquet: $$0$$
DM_2	Maxwell-Stefan: $$\frac{-\omega_i}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*}\omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}}$$
DM_2	Dusty gas: $$\frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{\omega_i}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*}$$
SB_2	Source term species balance: $$R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}}$$
MC_1	Source term continuity equation: $$-\frac{\partial \rho^*}{\partial \xi^*}\frac{v^*}{\rho^*}$$

5.4 Mole based model

5.4.1 The temperature balance

The general temperature balance derived earlier (65):

$$((1-\epsilon)\rho_p Cp_p + \epsilon c^* c_{ref} \sum_{i=1}^{n} x_i Cp'_i)\frac{\partial T^*}{\partial t^*} = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{298}$$

Steady state is assumed:

$$0 = -c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} - \frac{(\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*})\lambda}{D_{ref}} + \frac{\xi_{ref}^2(-\triangle H_R)R}{D_{ref}T_{ref}} \tag{299}$$

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

$$\frac{D_{ref}}{\lambda} c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} + (\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*}) = \frac{\xi_{ref}^2(-\triangle H_R)R}{T_{ref}\lambda} \tag{300}$$

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 (64):

$$\frac{\partial}{\partial t^*}(c^* x_i) + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{301}$$

Steady state is assumed.

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* x_i u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{302}$$

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

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{303}$$

The second term is identified as the LHS of the mole based continuity equation (66) when steady state is assumed, swapped for the RHS of the mole based continuity equation gives:

$$\frac{1}{\xi^{*2}}\frac{\partial x_i}{\partial \xi^*}(\xi^{*2} c^* u_\xi^*) + x_i (\frac{\xi_{ref}^2}{c_{ref} D_{ref}}) \sum_{i=1}^{n} r_i = -\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2} J_i^*) + R_i \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{304}$$

Expanding the third term and rearranging the equation to reflect the equation used in the model:

$$\frac{\partial x_i}{\partial \xi^*}(c^* u_\xi^*) + (\frac{2J_i^*}{\xi^*} + \frac{\partial J_i^*}{\partial \xi^*}) = (R_i - x_i \sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref} c_{ref}} \tag{305}$$

5.4.3 Continuity equation - Mole based

$$\frac{\partial c^*}{\partial t^*} + \frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}c^*u^*_\xi) = (\frac{\xi^2_{ref}}{c_{ref}D_{ref}})\sum_{i=1}^{n} r_i \tag{306}$$

Steady state is assumed:

$$\frac{1}{\xi^{*2}}\frac{\partial}{\partial \xi^*}(\xi^{*2}c^*u^*_\xi) = (\frac{\xi^2_{ref}}{c_{ref}D_{ref}})\sum_{i=1}^{n} r_i \tag{307}$$

The derivative is expaned wich gives the used equation:

$$\frac{2}{\xi^*}c^*u^* + \frac{\partial c^*}{\partial \xi^*}u^* + \frac{\partial u^*}{\partial \xi^*}c^* = (\frac{\xi^2_{ref}}{c_{ref}D_{ref}})\sum_{i=1}^{n} r_i \tag{308}$$

5.4.4 Darcy's law

Darcy's law is used to obtain the pressure(40).

$$\frac{v^*\mu D_{ref}}{Bp_{ref}} + \frac{\partial p^*}{\partial \xi^*} = 0 \tag{309}$$

5.4.5 Wilke diffusion model

The general Wilke diffusion model on mole basis as given in 67:

$$J^*_i = -c^*D_{sm}\frac{\partial x_i}{\partial \xi^*} \qquad D_{sm} = \frac{1-x_i}{\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j}{D_{ij}}} \tag{310}$$

Rearranged to the implemented form:

$$J^*_i\frac{D_{ref}}{c^*D_{sm}} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad D_{sm} = \frac{1-x_i}{\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j}{D_{ij}}} \tag{311}$$

5.4.6 Wilke-bosanquet diffusion model

$$j^*_i = -c^*\frac{D'_{i,eff}}{D_{ref}}\frac{\partial x_i}{\partial \xi^*} \qquad \frac{1}{D'_{i,eff}} = \frac{1}{D'_{im}} + \frac{1}{D_{i,K}} \tag{312}$$

Rearranged to the implemented form:

$$j^*_i\frac{D_{ref}}{D'_{i,eff}c^*} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{\substack{j=1\\ j\neq i}}^{n}\frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}} \tag{313}$$

5.4.7 Maxwell-Stefan diffusion model

The general Maxwell-Stefan model on mole basis as given in 69:

$$j_i^* = \frac{-c^* \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}} \tag{314}$$

Rearranged to the implemented form:

$$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \tag{315}$$

5.4.8 Dusty gas diffusion model

The general Maxwell-Stefan model on mole basis as given in 70:

$$J_i^* = \frac{-\frac{c^*}{D_{ref}} \frac{\partial x_i}{\partial \xi^*} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{c^* x_i u^*}{D_{iK}}}{\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}} \tag{316}$$

Rearranged to the implemented form SJEKKKONVETIVE!:

$$J_i^* \frac{D_{ref}}{c^*} (\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}) = -\frac{\partial x_i}{\partial \xi^*} + \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}} \tag{317}$$

5.4.9 Concentration equation

The concentration is obtained from the ideal gas law eqX.

$$\frac{p}{RT} = c \tag{318}$$

5.4.10 Summary of the mole based model, including boundary conditions

The derived equations are gathered in table 27. 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 21. 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 37.

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 37.

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.

Tabell 27: Mole based equations, constitutive laws and boundary conditions

Equations:	Constitutive Laws:
Temperature equation: $\frac{D_{ref}}{\lambda} c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp_i' \frac{\partial T^*}{\partial \xi^*} + (\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*}) = + \frac{\xi_{ref}^2 (-\triangle H_R) R}{T_{ref} \lambda}$ (319)	Fourier's law $q + \frac{\partial T}{\partial \xi^*} = 0$ (320)
Species mole balance: $\frac{\partial x_i}{\partial \xi^*}(c^* u_\xi^*) + (\frac{2J_i^*}{\xi^*} + \frac{\partial J_i^*}{\partial \xi^*}) = (R_i - x_i \sum_{i=1}^{n} r_i) \frac{\xi_{ref}^2}{D_{ref} c_{ref}}$ (321)	Definition: $\sum_{i=1}^{n} J_i = 0$ (322)
Diffusion model: One of the four diffusionmodels in table 28 is used	Definition: $\sum_{i=1}^{n} x_i = 1$ (323)
Continuity equation mole based: $\frac{2}{\xi^*} c^* u^* + \frac{\partial c^*}{\partial \xi^*} u^* + \frac{\partial u^*}{\partial \xi^*} c^* = (\frac{\xi_{ref}^2}{c_{ref} D_{ref}}) \sum_{i=1}^{n} r_i$ (324)	Mass averaged velocity(35): $v^* - u^* = \sum_{i=1}^{N} \frac{J_i^* M_i}{c_i^* \overline{M}}$ (325)
Concentration FIXDIMLØS: $c = \frac{p}{RT}$ (326)	Darcy's law: $\frac{v^* \mu D_{ref}}{B p_{ref}} + \frac{\partial p^*}{\partial \xi^*} = 0$ (327)

Boundary conditions in the symmetry point $\xi^* = 0$	Boundary conditions at the surface $\xi^* = \xi_p^*$ with transfer limitations
$J_i = 0$ (328) $q = 0$ (329) $u = 0$ (330)	$q_r + cCp_g' T v = -h(T^b - T)$ (331) $-k_i(c_i^b - x_i c) = J_i + ucx_i$ (332) $p = p^b$ (333) Boundary conditions at the surface $\xi^* = \xi_p^*$ without transfer limitations $T = T^b$ (334) $x_i = x_i^b$ (335) $p = p^b$ (336)

Tabell 28: Diffusion models on their implemented form

LHS is implemented in the collocation matrix, and the RHS is implemented in the source vector

Wilke:

$$J_i^* \frac{D_{ref}}{c^* D_{sm}} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad D_{sm} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}} \tag{337}$$

Wilke-Bosanquet:

$$j_i^* \frac{D_{ref}}{D'_{i,eff} c^*} + \frac{\partial x_i}{\partial \xi^*} = 0 \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}} \tag{338}$$

Maxwell-Stefan:

$$\frac{j_i^* D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{\partial x_i}{\partial \xi^*} = \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{j_j^* x_i}{D_{ij}} \tag{339}$$

Dusty gas:

$$J_i^* \frac{D_{ref}}{c^*} (\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}} + \frac{1}{D_{iK}}) = -\frac{\partial x_i}{\partial \xi^*} + \frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}} \tag{340}$$

Tabell 29: 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 $$q + \frac{\partial T}{\partial \xi^*} = 0 \quad (341)$$	Boundary condtion at $\xi = \xi^p$ $$hT^* = \frac{q^* \lambda}{\xi_{ref}} + cCp'_g T^* v^* \frac{D_{ref}}{\xi_{ref}} + h \quad (342)$$
Temperature equation: $$\frac{D_{ref}}{\lambda} c^* c_{ref} v_r^* \sum_{i=1}^{n} x_i Cp'_i \frac{\partial T^*}{\partial \xi^*} + (\frac{2q^*}{\xi^*} + \frac{\partial q^*}{\partial \xi^*}) = + \frac{\xi_{ref}^2 (-\triangle H_R) R}{T_{ref} \lambda} \quad (343)$$	Boundary condtition at $\xi = 0$ $$q = 0 \quad (344)$$
Species mole balance, used for N-1 components: $$\frac{\partial x_i}{\partial \xi^*}(c^* u_\xi^*) + (\frac{2J_i^*}{\xi^*} + \frac{\partial J_i^*}{\partial \xi^*}) = (R_i - x_i \sum_{i=1}^{n} r_i) \frac{\xi_{ref}^2}{D_{ref} c_{ref}} \quad (345)$$	Boundary condition at $\xi = 0$ $$J_i = 0 \quad (346)$$
Last flux(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} J_i = 0 \quad (347)$$	No boundary condtion –
Diffusion model: One of the four diffusionmodels in table 28 is used	Boundary condtition at $\xi = \xi^p$: $$x_i = \frac{(J_i^* \frac{D_{ref}}{\xi_{ref}} + u^* \frac{D_{ref}}{\xi_{ref}} c^* x_i)}{k_i c^*} + \frac{\omega_i}{c^*} \quad (348)$$
Last massfraction(H2O) in the species balance is solved by: $$\sum_{i=1}^{n} x_i = 1 \quad (349)$$	No boundary condtion –
Continuity equation mole based: $$\frac{2}{\xi^*} c^* u^* + \frac{\partial c^*}{\partial \xi^*} u^* + \frac{\partial u^*}{\partial \xi^*} c^* = (\frac{\xi_{ref}^2}{c_{ref} D_{ref}}) \sum_{i=1}^{n} r_i \quad (350)$$	Boundary condtition at $\xi = 0$ $$u = 0 \quad (351)$$
Mass averaged velocity*: $$v^* = \sum_{i=1}^{N} \frac{J_i^* M_i}{c_i^* \overline{M}} + u^* \quad (352)$$	No boundary condition –
Ideal gas law , algebraic: $$c = \frac{p}{RT} \quad (353)$$	No boundary condition –
Pressure, Darcy's law $$\frac{\partial p^*}{\partial \xi^*} = - \frac{v^* \mu D_{ref}}{B p_{ref}} \quad (354)$$	Boundary condtition at $\xi = \xi^p$: $$p = p^b \quad (355)$$

*Solved outside of the collocation matrix

$$
\begin{bmatrix}
1\bullet & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
X_1 & T_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 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 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & X_1 & 0 & 0 & 0 & 0 & 0 & SB_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 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 & 0 & 0 & 0 & 1\bullet & 0 & -\frac{p_{ref}}{RT} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & MC_1 & X_1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*}
\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} \\ c^* \\ u^* \\ p^*
\end{bmatrix}
=
\begin{bmatrix}
0 \\ T_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 0 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ 1 \\ 0 \\ MC_2 \\ Dl_1
\end{bmatrix}
$$

Figur 17: Collocation matrix - Maxwell-Stefan, mole based

Tabell 30: Terms in the collocation matrix

Label in matrix	Collocation matrix terms:	multiplied with:
X_1	$$\frac{2}{\xi^*} + \frac{\partial}{\partial \xi^*}$$	q^*, x_i, u^*
T_1	$$\frac{D_{ref}}{\lambda} \rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i C p_i \frac{\partial}{\partial \xi^*}$$	T^*
DM_1	Wilke: $$\frac{D_{ref}}{D'_{im} c^*}, \qquad D_{im} = \frac{1 - x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}}$$	J_i^*
DM_1	Wilke-Bosanquet: $$\frac{D_{ref}}{D'_{i,eff} c^*}, \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}}$$	J_i^*
DM_1	Maxwell-Stefan: $$\frac{D_{ref}}{c^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}$$	J_i^*
DM_1	Dusty gas: $$\frac{D_{ref}}{c^*} (\sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{x_j}{D_{ij}}$$	J_i^*
SB_1	$$c^* u_\xi^* \frac{\partial}{\partial \xi^*}$$	x_i
MC_1	$$u^* \frac{\partial}{\partial \xi^*}$$	c^*

Tabell 31: Terms in the source vector

Label in source vector	Source vector
T_2	Source term temperature equation: $$\frac{-\triangle H_r \xi_{ref}^2}{T_{ref}\lambda}$$
DM_2	Wilke: $$0$$
DM_2	Wilke-Bosanquet: $$0$$
DM_2	Maxwell-Stefan: $$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{J_j^* x_i}{D_{ij}}$$
DM_2	Dusty gas: $$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}}$$
SB_2	Source term species balance: $$(R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref} c_{ref}}$$
MC_2	Source term continuity equation: $$(\frac{\xi_{ref}^2}{c_{ref} D_{ref}})\sum_{i=1}^{n} r_i$$
Dl_1	Source term Darcy's law: $$-\frac{v^* \mu D_{ref}}{B p_{ref}}$$

5.6 Results and discussion no transfer limitations

Moving on towards a fully rigorous steady state model gives us the model where all terms are included expect the transfer limitations in the boundary conditions. Without the transfer limitations the simple versions is used where $T = T^b$ and $\omega_i = \omega_i^b$ at the surface. The difference from the previous models is then the addition of the convective terms. This does have a positive effect for all the mole based models, but does not yield any change for the mass based models since the mass averaged velocity is supposed to be zero.

However since most of the convective terms in the species balance is replaced by the LHS of the continuity equation, the change of adding the remaining convective terms is very small. The addition of these terms does not improve the differences from the mole and mass based models for the wilke and wilke-bosanquet models figure XXX and XXX enough to make this change noticeable. However the mole based Maxwell-Stefan and dusty gas models profits greatly by the addition of these terms as we can see from the figures XXX and XXX that these models are now completely similar. Specifically for the dusty gas model the convective terms are imporant as the diffusion model also relies on a convective term, with this term included it now corresponds well with the mass based model.

In general for all the models there are som problems with numerical error for the mole based models calculating the flux of nitrogen and some small oscillations are seen. These ocsillations transfer to the mass averaged velocity. The numerical error here are however so small that it does not affect the other components. It gives for example an icrease in pressure by $3 \times 10^{-3}\%$. The pressure plots for the models are by that reason not shown as the pressure does not change significantly from the bulk pressure.

Concentration and average molecular weight plots are also not shown as the molecular weight is directly linked with the molefraction. And the concentration plot will only be a function of the temperature since the pressure is constant.

Looking at the effect of which component that is solved with the equation XXX we can see that this has no effect when using the simple boundary conditions, this is shown for three of the components in figure XXX. However it is worth mentioning that it will be easier to get the model to converge using a component that has some precense. There wasnt seen any major differences when simulating with the different components as the last in convergeability, but the more sensitive wilke and wilke-bosanquet models did not converge when hydrogen was solved as a sum of the rest.

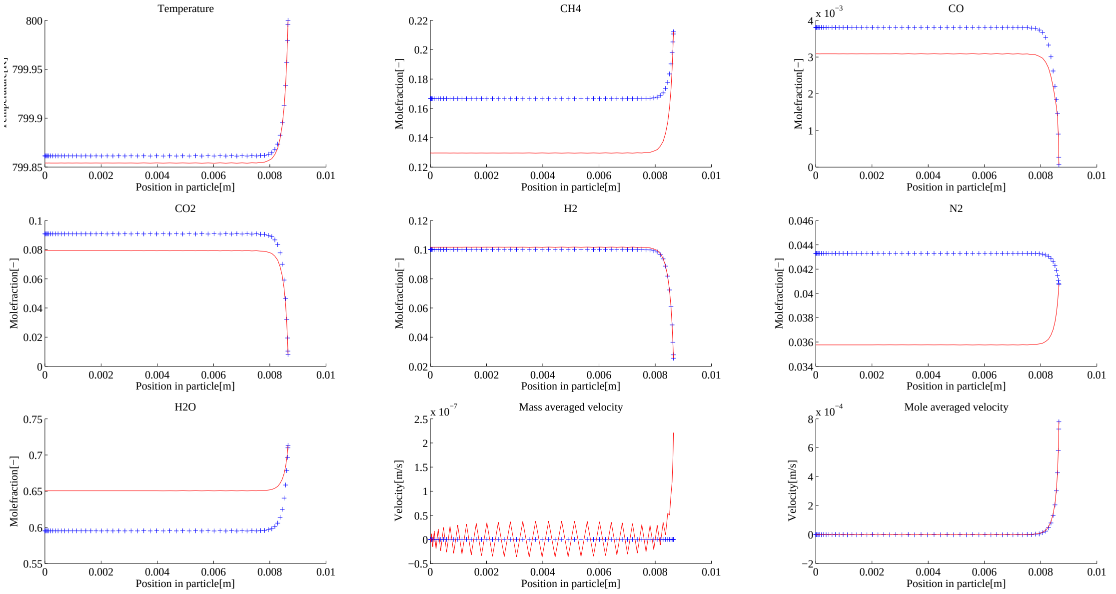
5.7 Results and discussion rigorous steady state model

Adding the transfer limitations in the boundary conditions for the temperature and the diffusion models now gives a fully rigorous steady state model where all terms are considered. This addition does have an effect on the temperature and the molefractions as we can see from the figures XXX for the different diffusion models, the changes are significant and can be easily spotted in the temperature plots.

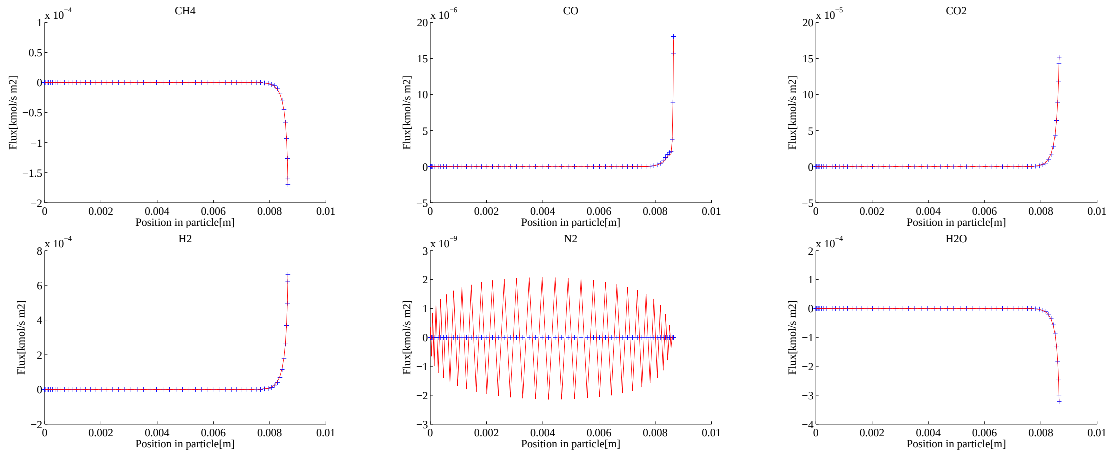
These models does not have any great differences from the models using the simple boundary conditions, and the same discussion applies here.The main difference are however when we look at the last component that is solved by the equation XXX. Here the models will not give the same results changing the last component. They are however still similar on mass and mole basis, but this is not shown in a figure.

The difference introduced is caused by the transfer limitations for the components since they are calculated from binary transfer coefficients. This gives non coherent mass transfer coefficients for the six components in this case. The effect of this non coherence is easy to spot when the last component is solved as the sum of the rest are changed as we can see from the figure XXX. REF fra bok +++XXX.

5.7.1 Wilke - No transfer limitations

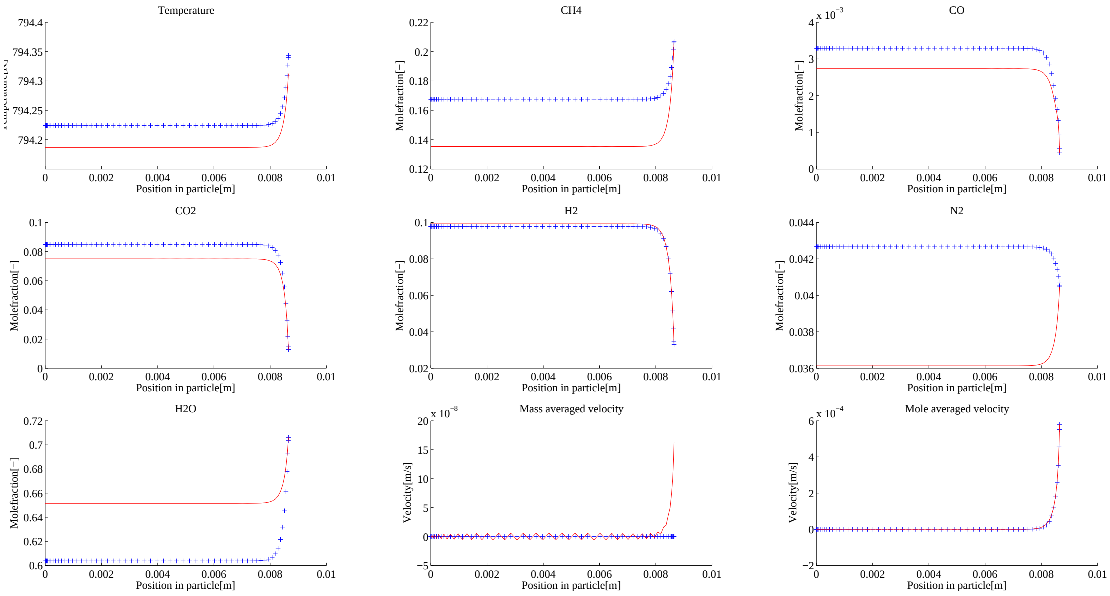


Figur 18: Comparison

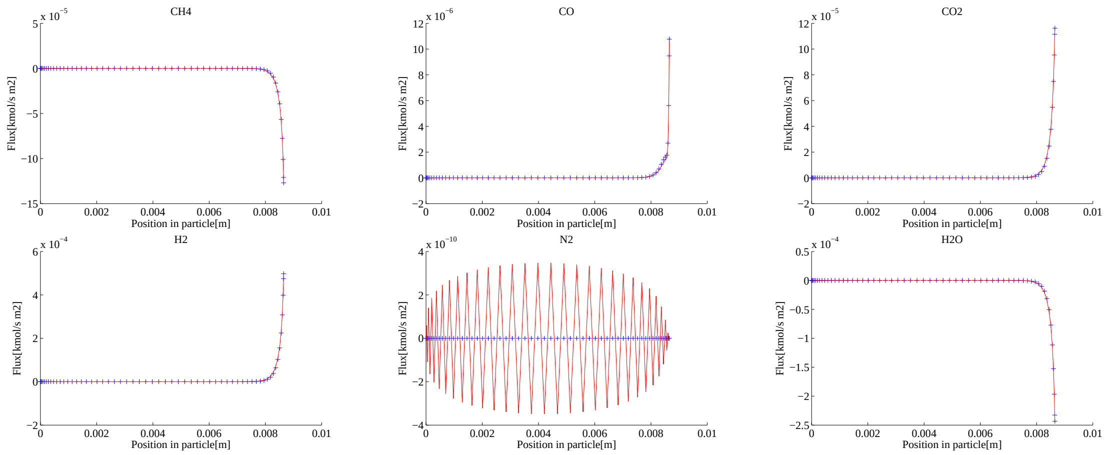


Figur 19: Mole based total fluxes

5.7.2 Wilke - Rigorous

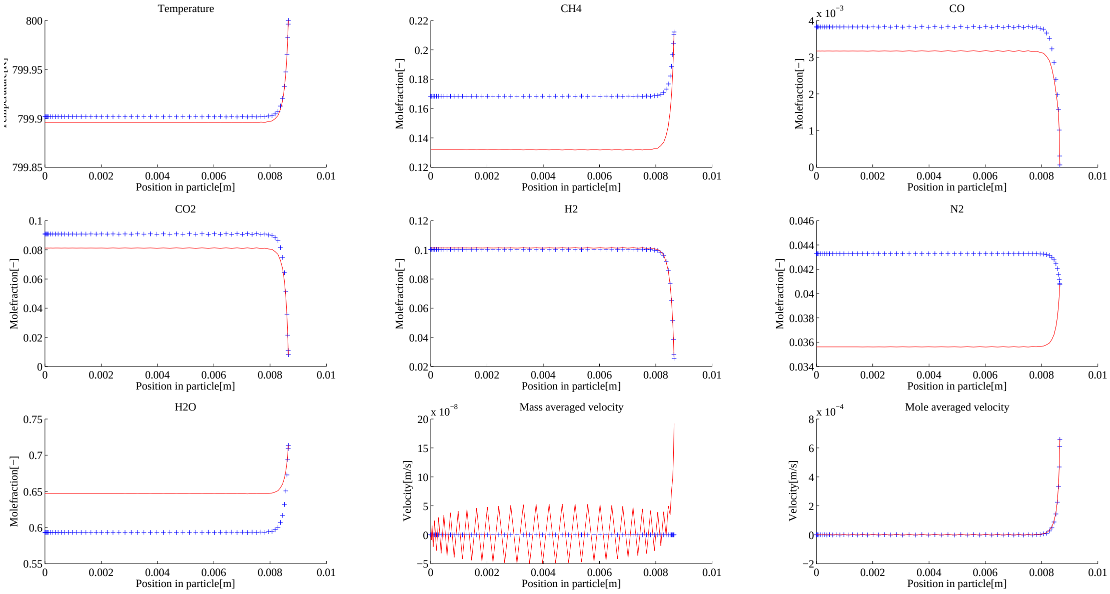


Figur 20: Comparison

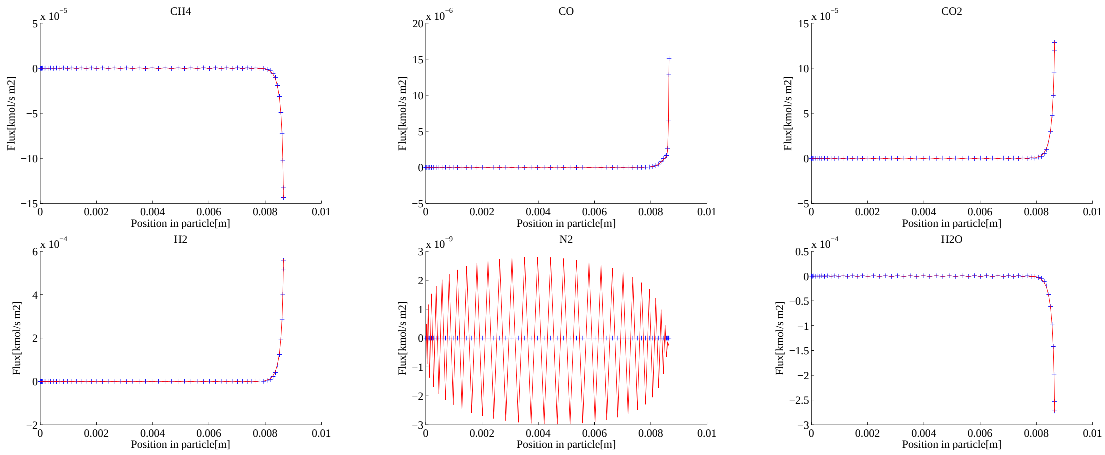


Figur 21: Mole based total fluxes

5.7.3 Wilke-Bosanquet - No transfer limitations

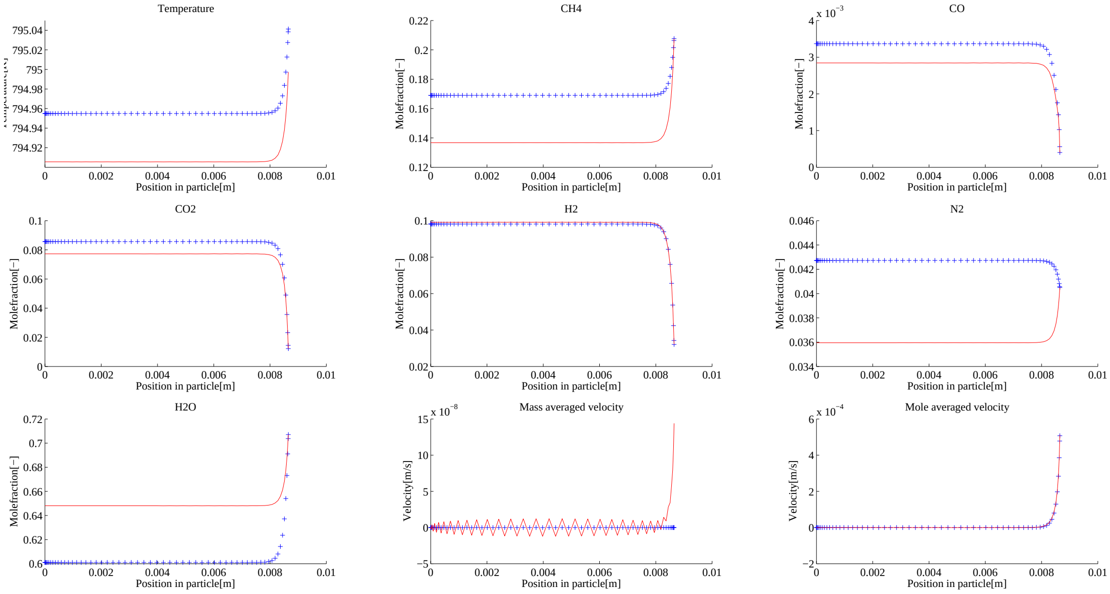


Figur 22: Comparison

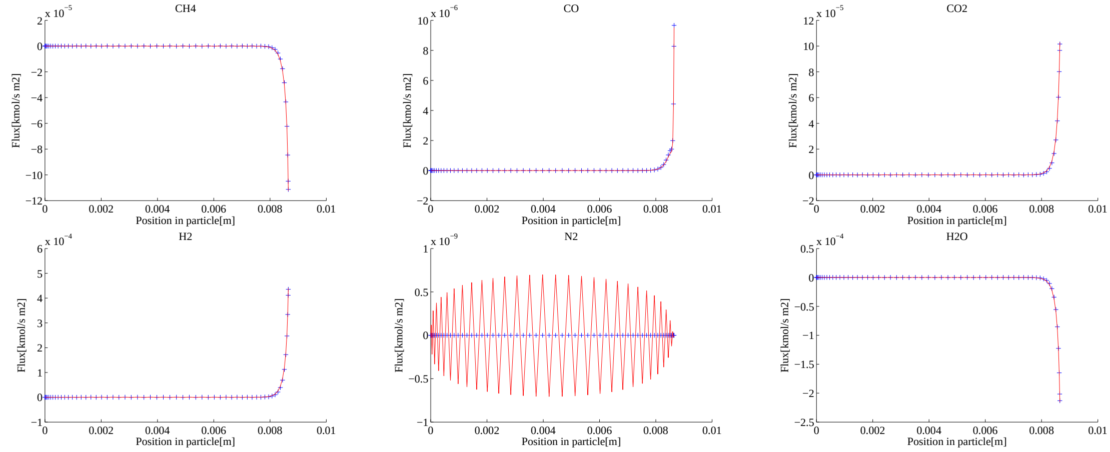


Figur 23: Mole based total fluxes

5.7.4 Wilke-Bosanquet - Rigorous

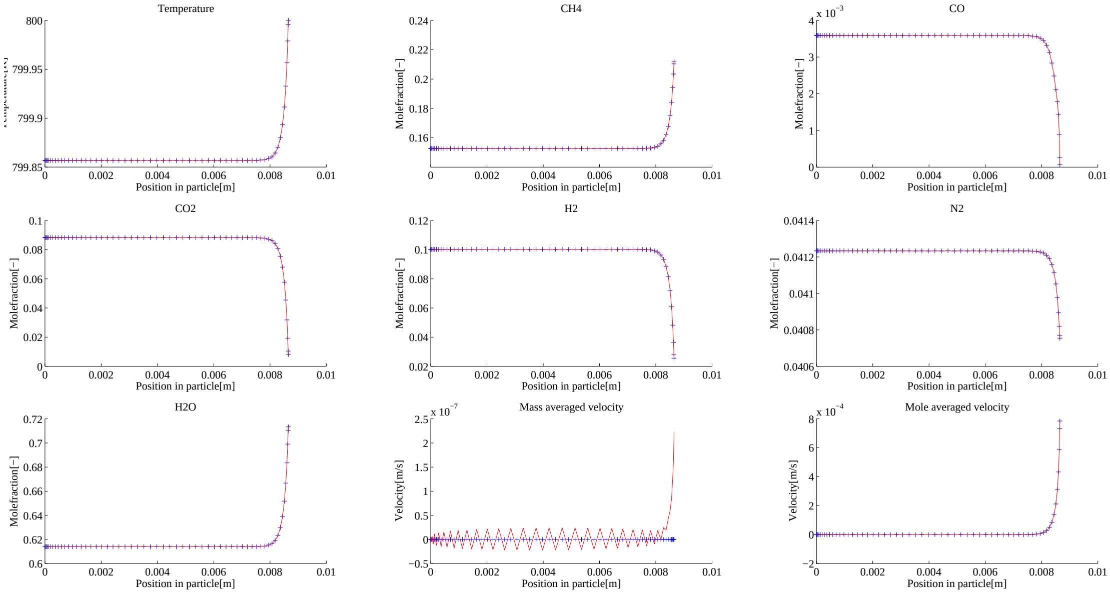


Figur 24: Comparison

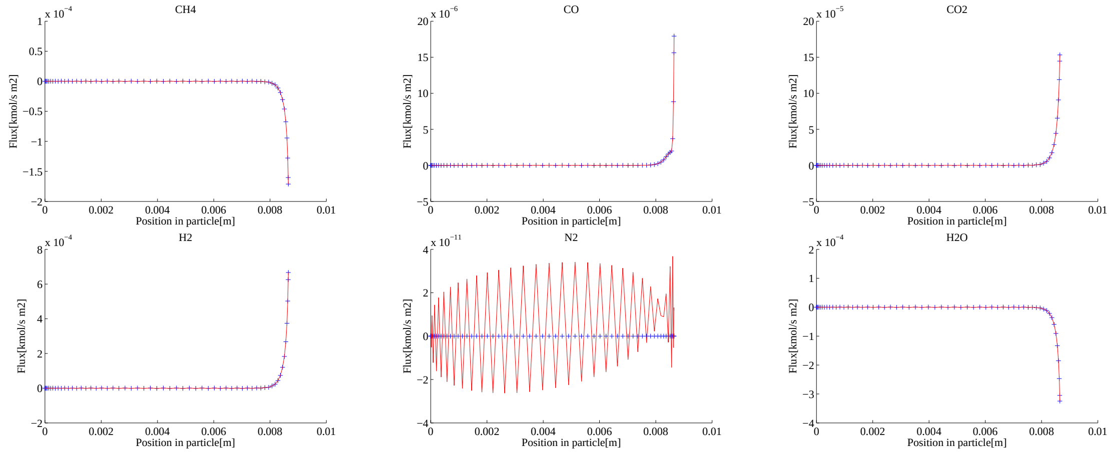


Figur 25: Mole based total fluxes

5.7.5 Maxwell-Stefan - No transfer limitations

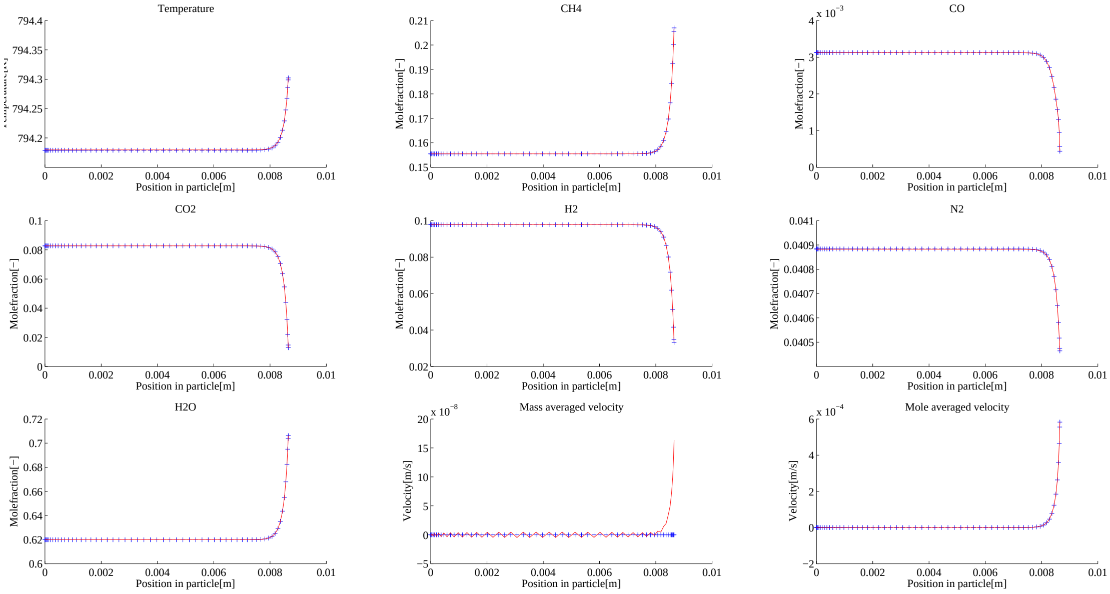


Figur 26: Comparison

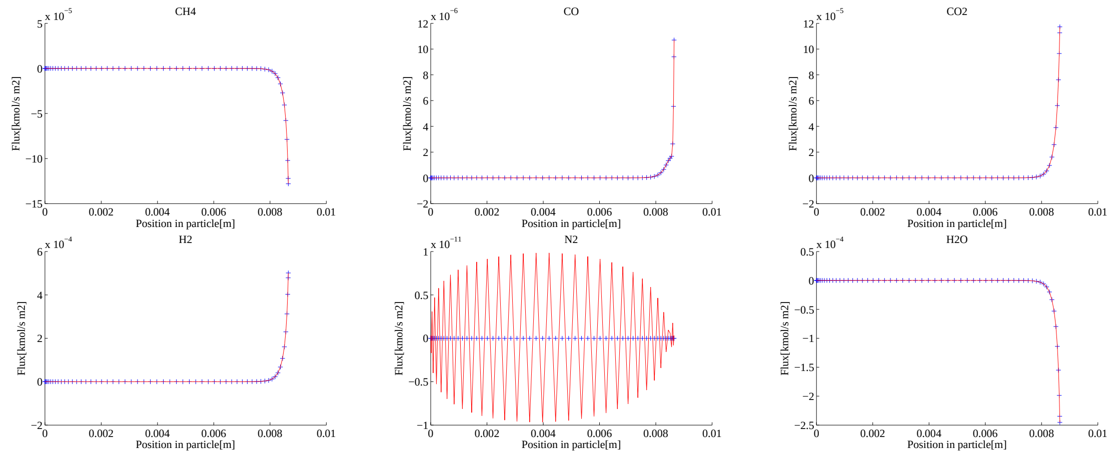


Figur 27: Mole based total fluxes

5.7.6 Maxwell-Stefan - Rigorous

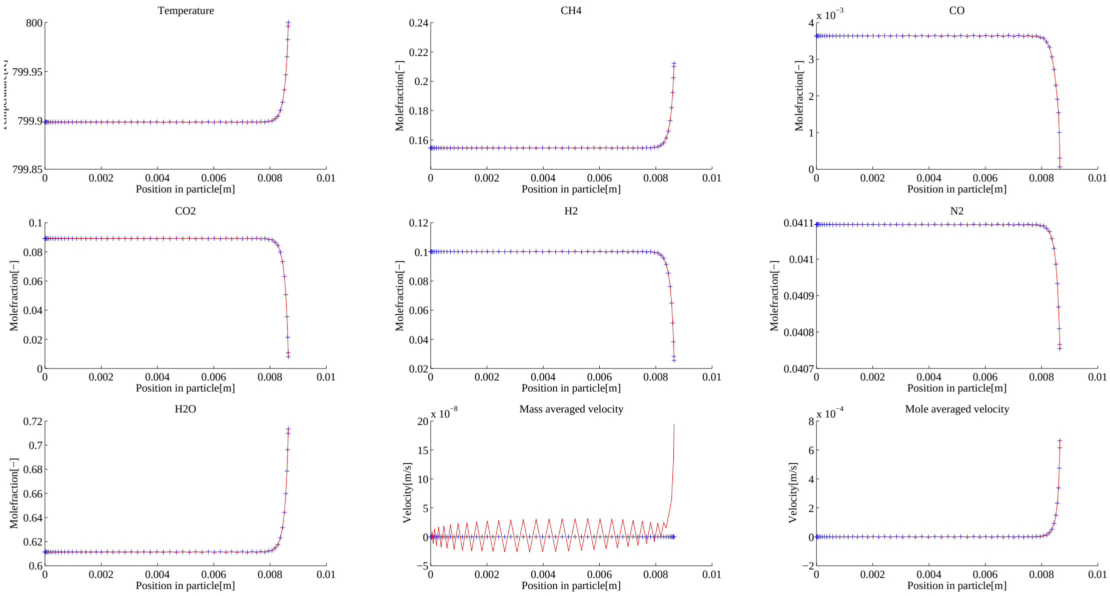


Figur 28: Comparison

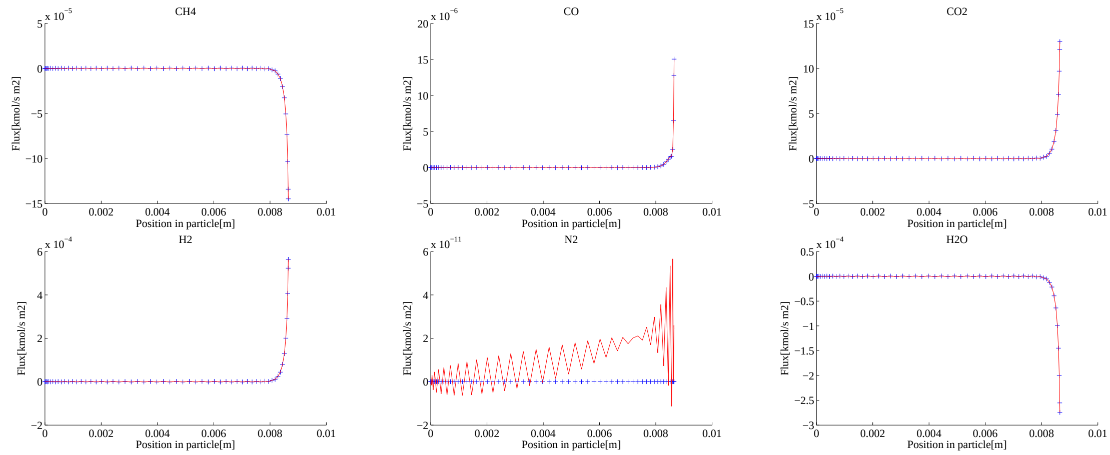


Figur 29: Mole based total fluxes

5.7.7 Dusty-gas - No transfer limitations

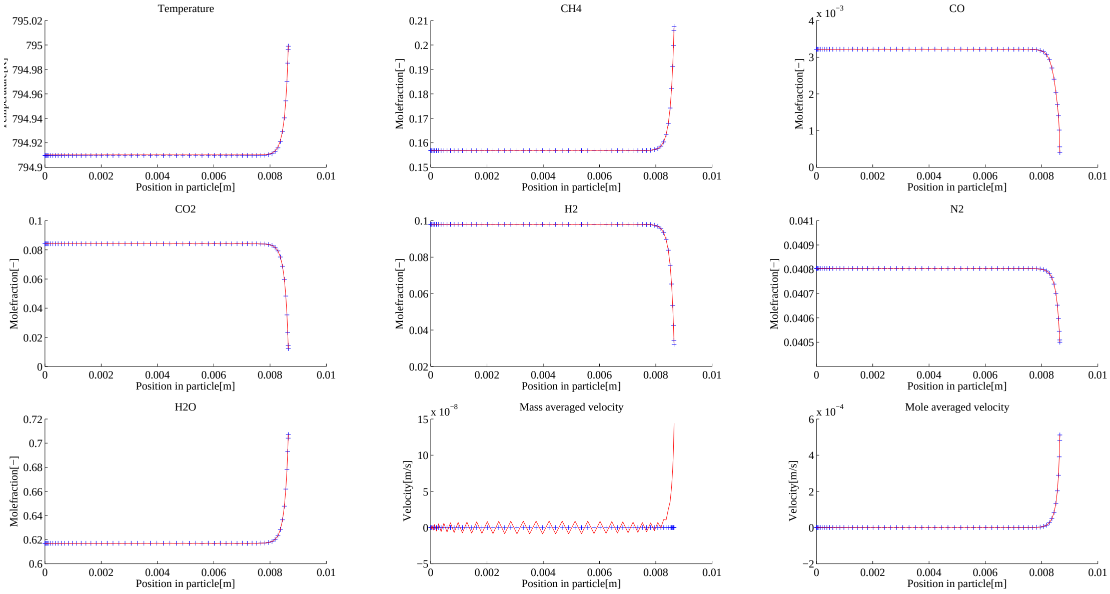


Figur 30: Comparison

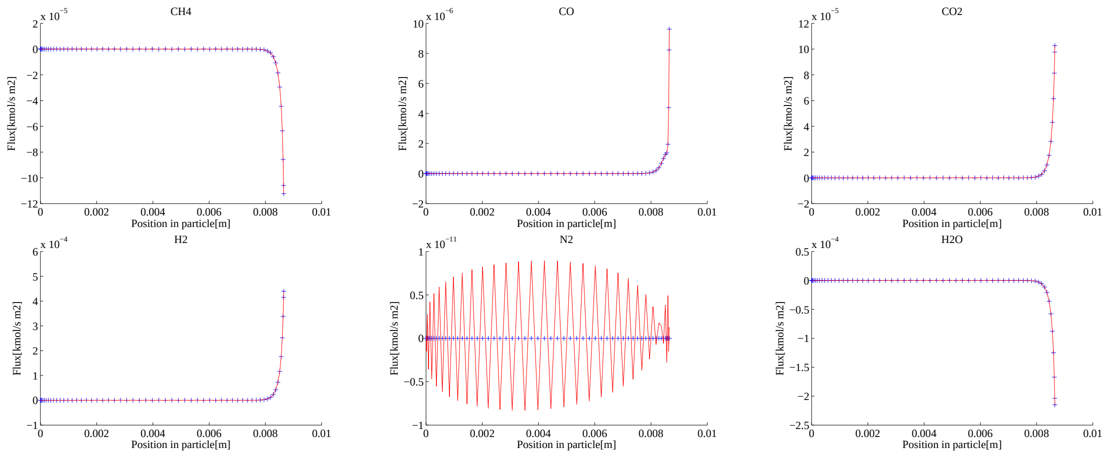


Figur 31: Mole based total fluxes

5.7.8 Dusty-gas - Rigorous

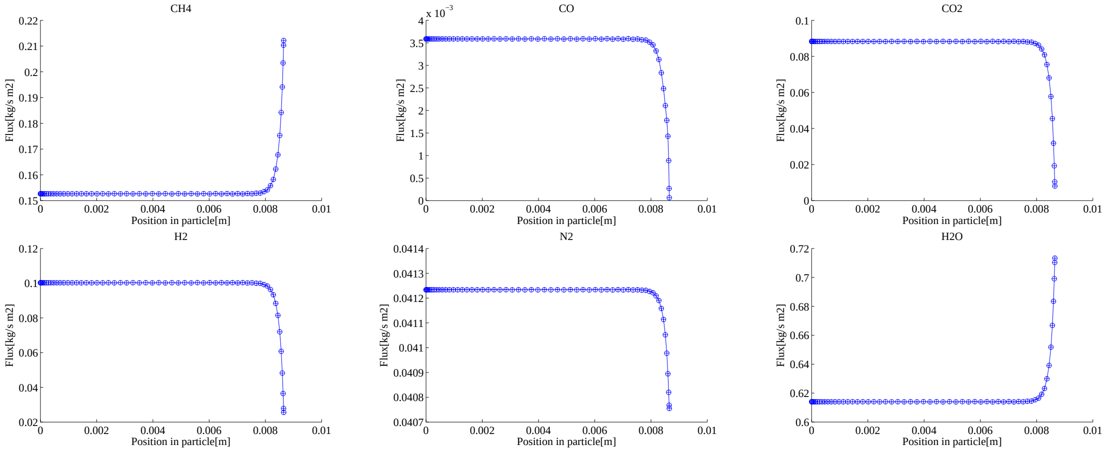


Figur 32: Comparison

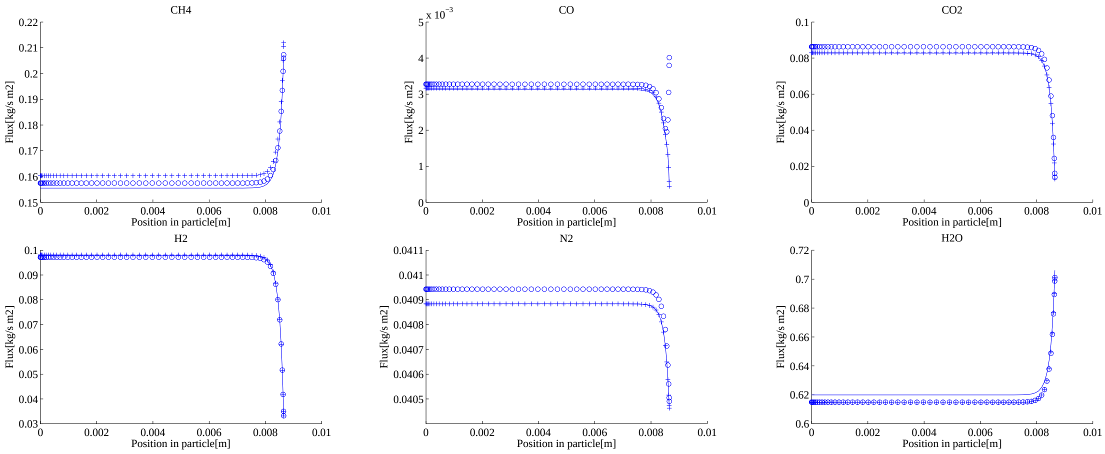


Figur 33: Mole based total fluxes

5.7.9 Effect of component solved with eqX



Figur 34: No transfer limitations ,– H2O ,+ CH4 ,o CO



Figur 35: Rigorous ,– H2O ,+ CH4 ,o CO

6 Alternative numerical method - Least squares

There are a numerous different numerical methods, so far only the method of orthogonal collocation has been used, in this part we will compare that method to the least squares method. The methods will be evaluated on the factor of robustness, speed and convergence.

6.1 Derivation of the equations to use in the model.

The LSQ model is to be solved identically with the fully rigorous steady state model solved with orthogonal collocation method in chapter XXX, and the model derivation can be seen there. However since the LSQ model appears to be more sensitive to the variable sequence in the solving matrix both the matrices for both the mass and mole based model will be showed to illustrate a working solution method.

In the solution method the variable T and q has changed places also the ω_i, x_i and J_i, j_i. This was needed to be done in order to obtain a stable matrix.

$$
\begin{bmatrix}
\frac{\partial}{\partial\xi^*} & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
T_1 & X_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial\xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & X_1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & Dl_1\bullet & \frac{\partial}{\partial\xi^*}
\end{bmatrix}
\begin{bmatrix}
T^* \\ q^* \\ \omega_{CH_4} \\ \omega_{CO} \\ \omega_{CO_2} \\ \omega_{H_2} \\ \omega_{N_2} \\ \omega_{H_2O} \\ j_{CH_4} \\ j_{CO} \\ j_{CO_2} \\ j_{H_2} \\ j_{N_2} \\ j_{H_2O} \\ v^* \\ p^*
\end{bmatrix}
=
\begin{bmatrix}
0 \\ T_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 1 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ 0 \\ MC_1 \\ 0
\end{bmatrix}
$$

Figur 36: Collocation matrix, mass based. Explanation on the labeled terms can be seen in table 35

Tabell 32: Terms in the collocation matrix

Label in matrix	Collocation matrix terms:	multiplied with:
X_1	$\frac{2}{\xi^*} + \frac{\partial}{\partial \xi^*}$	q^*, ω_i, v^*
T_1	$\frac{D_{ref}}{\lambda}\rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i Cp_i \frac{\partial}{\partial \xi^*}$	T^*
DM_1	Wilke: $\frac{D_{ref}}{D'_{im}\rho^*}$	j_i^*
DM_1	Wilke-Bosanquet: $\frac{D_{ref}}{D'_{i,eff}\rho^*}$	j_i^*
DM_1	Maxwell-Stefan: $\frac{\overline{M} D_{ref}}{\rho^*} \sum_{\substack{j=1 \\ j \neq i}}^{i} \frac{\omega_j}{M_j D_{ij}}$	j_i^*
DM_1	Dusty gas: $\frac{D_{ref}}{\rho^*}(\overline{M} \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{\omega_j}{M_j \tilde{D}_{ij}} + \frac{1}{D_{iK}})$	j_i^*
SB_1	$\rho^* v_\xi^* \frac{\partial}{\partial \xi^*}$	ω_i
Dl_1	$\frac{\mu}{B p_{ref}}$	v^*

Tabell 33: Terms in the source vector

Label in source vector	Source vector
	Source term temperature equation:
T_2	$$\frac{-\triangle H_r \xi_{ref}^2}{T_{ref}\lambda}$$
	Wilke:
DM_2	$$0$$
	Wilke-Bosanquet:
DM_2	$$0$$
	Maxwell-Stefan:
DM_2	$$\frac{-\omega_i}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*} + \frac{\overline{M} D_{ref}}{\rho^*}\omega_i \sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{j_j^*}{M_j D_{ij}}$$
	Dusty gas:
DM_2	$$\frac{\overline{M} D_{ref}}{\rho^*}\sum_{\substack{j=1 \\ j\neq i}}^{n} \frac{\omega_i j_j^*}{M_j \tilde{D}_{ij}} - \frac{\omega_i}{\overline{M}}\frac{\partial \overline{M}}{\partial \xi^*}$$
	Source term species balance:
SB_2	$$R_i \frac{\xi_{ref}^2}{D_{ref}\rho_{ref}}$$
	Source term continuity equation:
MC_1	$$-\frac{\partial \rho^*}{\partial \xi^*}\frac{v^*}{\rho^*}$$

6.2 Mole based model

$$
\begin{bmatrix}
\frac{\partial}{\partial \xi^*} & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
T_1 & X_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*} & 0 & 0 & 0 & 0 & 0 & DM_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & SB_1 & 0 & 0 & 0 & 0 & 0 & X_1\bullet & 0 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 1\bullet & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1\bullet & 0 & -\frac{p_{ref}}{RT} \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & MC_1 & X_1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \frac{\partial}{\partial \xi^*}
\end{bmatrix}
\begin{bmatrix}
T^* \\ q^* \\ x_{CH_4} \\ x_{CO} \\ x_{CO_2} \\ x_{H_2} \\ x_{N_2} \\ x_{H_2O} \\ J_{CH_4} \\ J_{CO} \\ J_{CO_2} \\ J_{H_2} \\ J_{N_2} \\ J_{H_2O} \\ c^* \\ u^* \\ p^*
\end{bmatrix}
=
\begin{bmatrix}
0 \\ T_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ DM_2 \\ 1 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ SB_2 \\ 0 \\ 0 \\ MC_2 \\ Dl_1
\end{bmatrix}
$$

Figur 37: Collocation matrix - Maxwell-Stefan, mole based

Tabell 34: Terms in the collocation matrix

Label in matrix	Collocation matrix terms:	multiplied with:
X_1	$\frac{2}{\xi^*} + \frac{\partial}{\partial \xi^*}$	q^*, x_i, u^*
T_1	$\frac{D_{ref}}{\lambda}\rho^* \rho_{ref} v_r^* \sum_{i=1}^{n} \omega_i Cp_i \frac{\partial}{\partial \xi^*}$	T^*
DM_1	Wilke: $\frac{D_{ref}}{D'_{im} c^*}, \qquad D_{im} = \frac{1 - x_i}{\sum_{j=1, j \neq i}^{n} \frac{x_j}{D_{ij}}}$	J_i^*
DM_1	Wilke-Bosanquet: $\frac{D_{ref}}{D'_{i,eff} c^*}, \qquad \frac{1}{D'_{i,eff}} = \frac{1}{\frac{1-x_i}{\sum_{j=1, j\neq i}^{n} \frac{x_j}{D_{ij}}}} + \frac{1}{D_{i,K}}$	J_i^*
DM_1	Maxwell-Stefan: $\frac{D_{ref}}{c^*} \sum_{j=1, j \neq i}^{i} \frac{x_j}{D_{ij}}$	J_i^*
DM_1	Dusty gas: $\frac{D_{ref}}{c^*} (\sum_{j=1, j \neq i}^{i} \frac{x_j}{D_{ij}}$	J_i^*
SB_1	$c^* u_\xi^* \frac{\partial}{\partial \xi^*}$	x_i
MC_1	$u^* \frac{\partial}{\partial \xi^*}$	c^*

Tabell 35: Terms in the source vector

Label in source vector	Source vector
	Source term temperature equation:
T_2	$$\frac{-\triangle H_r \xi_{ref}^2}{T_{ref}\lambda}$$
	Wilke:
DM_2	$$0$$
	Wilke-Bosanquet:
DM_2	$$0$$
	Maxwell-Stefan:
DM_2	$$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{J_j^* x_i}{D_{ij}}$$
	Dusty gas:
DM_2	$$\frac{D_{ref}}{c^*}\sum_{\substack{j=1\\j\neq i}}^{n}\frac{J_j^* x_i}{D_{ij}} - \frac{D_{ref} x_i u^*}{D_{iK}}$$
	Source term species balance:
SB_2	$$(R_i - x_i\sum_{i=1}^{n} r_i)\frac{\xi_{ref}^2}{D_{ref}c_{ref}}$$
	Source term continuity equation:
MC_2	$$(\frac{\xi_{ref}^2}{c_{ref}D_{ref}})\sum_{i=1}^{n} r_i$$
	Source term Darcy's law:
Dl_1	$$-\frac{v^*\mu D_{ref}}{Bp_{ref}}$$

6.3 Results and discussion

It has been looked into the differences when using a different numerical method for solving the pellet equations using the maxwell-stefan diffusion model. To make the methods comparable they are solved in a similar manner using four elements with three points in the first three elements and 20 points in the last element closest to the surface, bringing the total up to 26 points. Both models are run to a convergence residual of 10^-10 with similar under-relaxation parameters. It is worth mentioning that both models behaves similarly when changing the under-relaxation parameter, i.e. one of the models cant run with a higher underrelaxation value than the other.

The Least squares method is computationally costly compared to the orthogonal collocation method and more sensitive to the setup of the problem matrix. The method does however seem to give more stable results than orthogonal collocation using fewer calculation points, this is further explained in the next parts.

6.3.1 Results and discussion mass based models

By looking at the figure XXX and XXX, we can see that both numerical methods yield the same result for the mass based models with only some numerical differences for the LSQ model in the mass averaged velocity and the flux of nitrogen. The differences are however insignificant as the values are so small.

Comparing the pure numbers the LSQ model can obtain a total residual of $5*10^-11$ while the orthogonal collocation method obtains $4*10^-12$. In the matter of speed the methods were run to a residual of $1*10^-10$, the orthogonal collocation methods was the fastest with a simulation time of 16.5 minutes* vs 49.2 minutes* for the lsq model. Making the orthogonal collocation method a far better choice where speed is essential. In the terms of the amount of iterations neccessary to achieve convergence the least squares methods is slightly better than the orthogonal collocation method needing approximately 2.5% less iterations.

6.3.2 Results and discussion mole based models

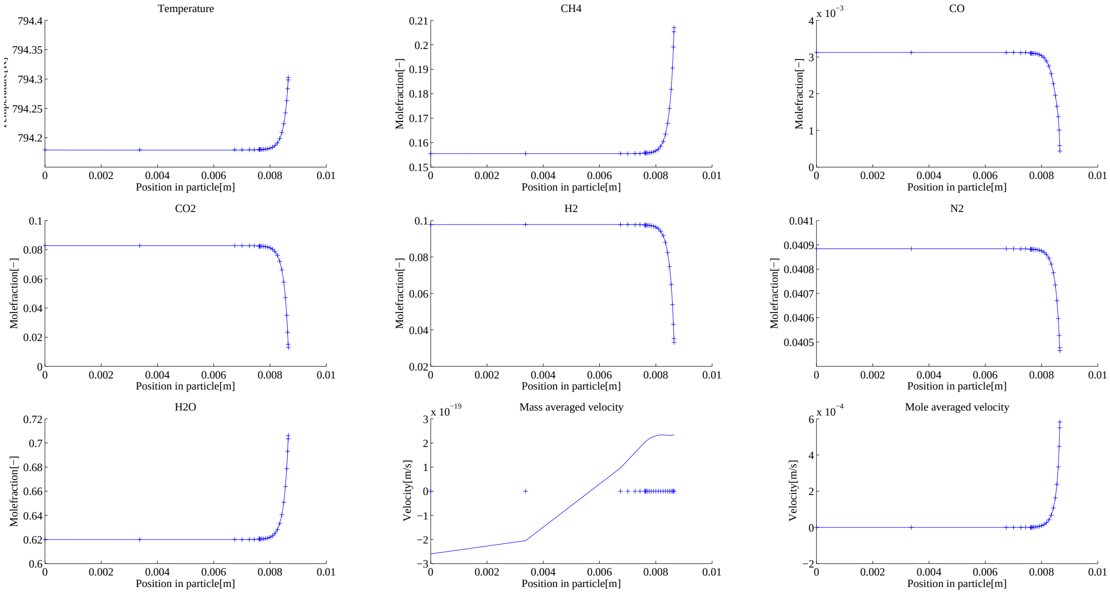
Looking into the more sensitive mole based model in figure XXX and XXX one can immediately see that the lsq model performs far better with the amount of points used in the simulation. The Lsq model yields a comparable result with the non-element version and the mass based element models, though this is not shown in a figure. This is especially noticable in the temperature plot and the nitrogen molefraction plot where the collocation method is noticably different from the Lsq method. The differences seen here will dissapear with additional collocation points for the orthogonal collocation method. Though it is aparant that LSQ performs better with fever points.

COMPARE to colloc in chapter XXX element method.

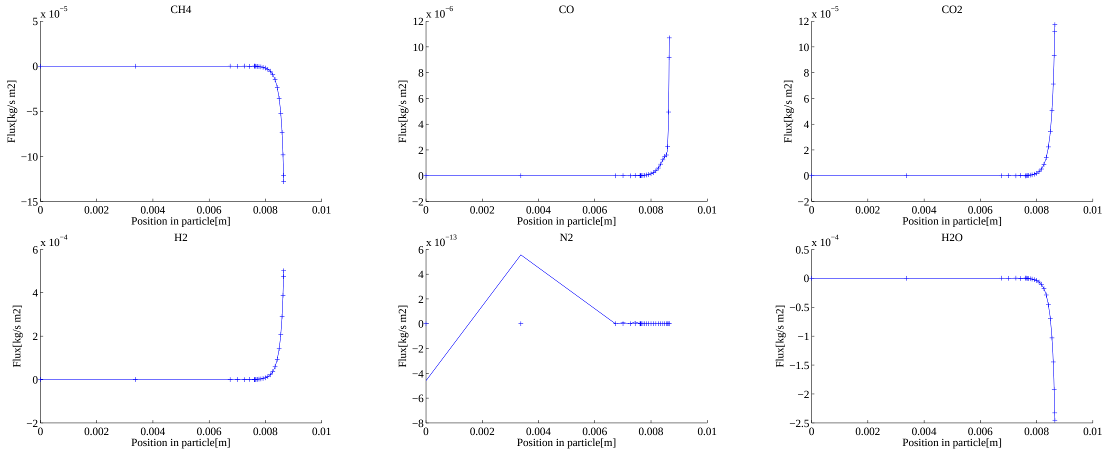
Comparing the different numerical methods for the mole based models the simulation time is 16 vs 58 minutes* for respectively the Orthogonal collocation and the least squares methods. The lsq model is only able to obain a convergene of $4 * 10^-9$ while the collocation method manages $5 * 10^-12$.

* Time obtained by the use of pulse iteration, described in tips chapter.

6.3.3 Maxwell-Stefan

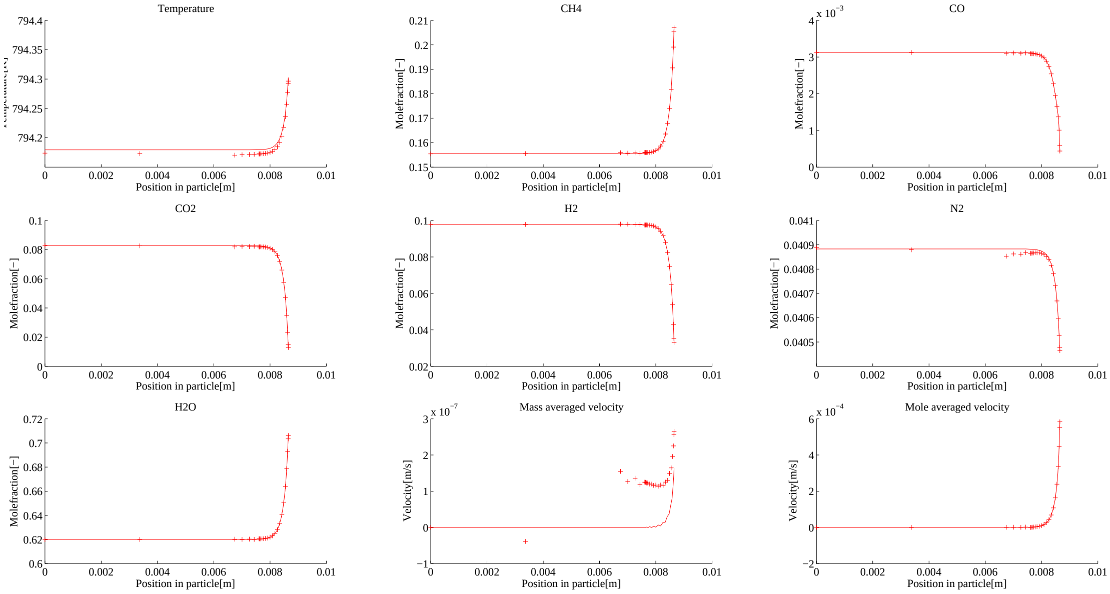


Figur 38: Comparison

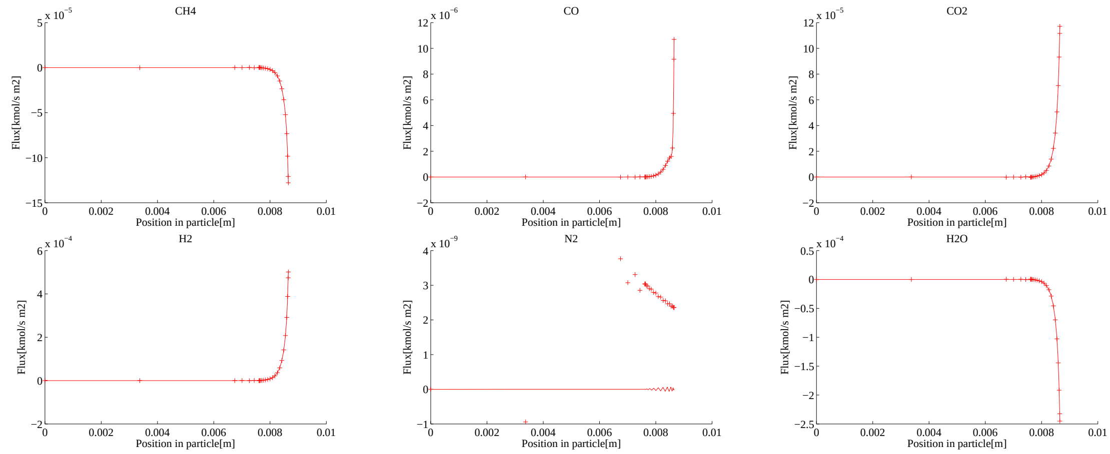


Figur 39: Mole based total fluxes

6.3.4 Maxwell-Stefan



Figur 40: Comparison



Figur 41: Mole based total fluxes

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