1 Symbol List

Table 1: Symbol list

symbol	name	unit
$k_{L,i}$	Liquid side mass transfer coefficient	$m\,s^{-1}$
a_L	Gas-liquid interfacial area per unit liquid volume	$m^2/m^3 = m^{-1}$
$k_{L,i}a$	Liquid side volumetric mass transfer coefficient	$m^{-1}\,m\,s^{-1} = s^{-1}$
y_i	Gas phase mole fraction of component i	$-$
x_i	Liquid phase mole fraction of component i	$-$
y_i^*	Gas phase mole fraction of component i at the phase boundary	$-$
x_i^*	Liquid phase mole fraction of component i at the phase boundary	$-$
k_i	"Constant" describing the relationship y_i^*/x_i^* at given conditions	$-$
$\omega_{i,G}$	Gas phase weight fraction of component i	$-$
$\omega_{i,G}^*$	Gas phase weight fraction of component i at the phase boundary	$-$
$\omega_{i,L}$	Liquid phase weight fraction of component i	$-$
$\omega_{i,L}^*$	Liquid phase weight fraction of component i at the phase boundary	$-$
z	Reactor height	m
ρ_L	Total density, liquid phase	$kg\,m^{-3}$
ρ_G	Total density, gas phase	$kg\,m^{-3}$
$\rho_S = \rho_{\text{cat}}$	Catalyst density density	$kg\,m^{-3}$
ρ_{SL}	Slurry density	$kg\,m^{-3}$
v_G	Gas velocity	$m\,s^{-1}$
v_L	Liquid velocity	$m\,s^{-1}$
v_{SL}	Slurry velocity	$m\,s^{-1}$
v_G^s	Gas superficial velocity	$m\,s^{-1}$
v_L^s	Liquid superficial velocity	$m\,s^{-1}$
v_{SL}^s	Slurry superficial velocity	$m\,s^{-1}$
$\overline{M_G}$	Gas phase average molar mass	$kg\,kmol^{-1}$
$\overline{M_L}$	Liquid phase average molar mass	$kg\,kmol^{-1}$
ϵ_L	Liquid volume fraction	$-$
ϵ_G	Gas volume fraction	$-$
ϵ_S	Solid volume fraction	$-$
ϵ_{SL}	Slurry volume fraction	$-$
ϕ_L	Liquid mass fraction	$-$
ϕ_G	Gas mass fraction	$-$
ϕ_S	Solid mass fraction	$-$
ϕ_{SL}	Slurry mass fraction	$-$
ν_i	Stochiometric coefficient for component i	$-$
r_{CO}	Reaction rate in terms of CO conversion	$kmol\,s^{-1}\,kg_{cat}^{-1}$
$M_{w,i}$	Molecular weight of component i	$kg\,kmol^{-1}$
ρ_{cat}	Density of catalyst	$kg_{cat}\,m^{-3}$
T	Temperature	K
T_G	Temperature, Gas Phase	K
T_L	Temperature, Liquid Phase	K
T_{SL}	Temperature, Slurry Phase	K
T_{surr}	Temperature, Surroundings	K
p	Pressure	Pa

Table 1: Symbol list

symbol	name	unit
p_G	Gas phase pressure	Pa
p_L	Liquid phase pressure	Pa
h	Height of dispersion	m
R	Gas constant (value: 8.314×10^3)	$J\,K^{-1}\,kmol^{-1}$
L	Total height of dispersion	m
g	Standard acceleration of gravity	ms^{-2}
$D_{\text{eff,z,G}}$	Eff. axial dispersion coefficient, gas	m^2s^{-1}
$D_{\text{eff,z,L}}$	Eff. axial dispersion coefficient, liquid	m^2s^{-1}
$C_{p,G}$	Spec. heat (at constant pressure), Gas	$Jkg^{-1}K^{-1}$
$C_{p,S}$	Spec. heat (at constant pressure), Solid	$Jkg^{-1}K^{-1}$
$C_{p,L}$	Spec. heat (at constant pressure), Liquid	$Jkg^{-1}K^{-1}$
$C_{p,SL}$	Spec. heat (at constant pressure), Slurry	$Jkg^{-1}K^{-1}$
U	Thermal Transmittance Number	$Wm^{-2}K^{-1}$
d_t	Diameter of tube	m
h_L	Heat transfer coefficient between slurry and gas	$Wm^{-2}K^{-1}$
a	Interfacial area density	$m^2m^{-3} = m^{-1}$
$\lambda_{\text{eff,z,G}}$	Eff. thermal conductivity, gas	$Wm^{-1}K^{-1}$
$\lambda_{\text{eff,z,L}}$	Eff. thermal conductivity, liquid	$Wm^{-1}K^{-1}$
$\lambda_{\text{eff,z,S}}$	Eff. thermal conductivity, solid	$Wm^{-1}K^{-1}$
$\lambda_{\text{eff,z,SL}}$	Eff. thermal conductivity, slurry	$Wm^{-1}K^{-1}$
λ_G	Thermal conductivity, gas	$Wm^{-1}K^{-1}$
λ_L	Thermal conductivity, liquid	$Wm^{-1}K^{-1}$
λ_{SL}	Thermal conductivity, slurry	$Wm^{-1}K^{-1}$
μ_G	Viscosity, gas	$Pa\,s = kgs^{-1}m^{-1}$
μ_L	Viscosity, liquid	$Pa\,s = kgs^{-1}m^{-1}$
μ_{SL}	Viscosity, slurry	$Pa\,s = kgs^{-1}m^{-1}$
ΔH_r	Reaction heat	$Jkmol^{-1}$
h_W	Heat transfer coefficient between slurry and wall	$Wm^{-2}K^{-1}$
S_I	Perimeter	m
S_c	Perimeter of column	m
S_t	Perimeter of cooling tube	m
A	Area	m^2
D_c	Diameter of column	m
A_t	Area of cooling tube	m^2
N_t	Number of cooling tubes	$-$
d_s^*	Sauter mean diameter	m

Table 2: Subscript and Superscript list

symbol	name
$*$	At the phase boundary
0	Initial (at the inlet)
i	Component number (or name)
s	Superficial
c	Column
t	Cooling tube
p	Constant pressure
w	Column wall
G	Gas Side / Phase
L	Liquid Side / Phase
S	Solid (catalyst) Side / Phase
SL	Slurry Phase (liquid + catalyst)
SK	Catalyst skeleton (material excluding pores)
z	Along the z direction
cat	Catalyst
eff	Effective (sum of molecular and turbulent contributions)

2 Starting point

The general axial dispersion model (ADM) for two-phase flow, with reaction in the liquid (slurry) phase and heat exchange in the liquid (slurry) phase, is taken from Jakobsen (2008) [8], section 8.4, page 767, equations 8.1 to 8.5. Equation 6 (liquid (slurry) phase mass balance), is added.

2.1 Gas Phase Equations

$$\frac{d}{dz}\left(\rho_G v_G^s \omega_{i,G}\right) = \frac{d}{dz}\left(\epsilon_G \rho_G D_{\text{eff,z,G}} \frac{d\omega_{i,G}}{dz}\right) - k_{L,i} a \rho_L(\omega_{L,i}^* - \omega_{L,i}) \tag{1}$$

$$\rho_G C_{p,G} v_G^s \frac{dT_G}{dz} = \frac{d}{dz}\left(\epsilon_G \lambda_{\text{eff,z,G}} \frac{dT_G}{dz}\right) - h_L a(T_G - T_{SL}) \tag{2}$$

$$\frac{d}{dz}\left(\rho_G v_G^s\right) = -\sum_i k_{L,i} a \rho_L(\omega_{L,i}^* - \omega_{L,i}) \tag{3}$$

2.2 Liquid Phase Equations

$$\frac{d}{dz}\left(\rho_L v_L^s \omega_{i,L}\right) = \frac{d}{dz}\left(\epsilon_L \rho_L D_{\text{eff,z,L}} \frac{d\omega_{i,L}}{dz}\right) + k_{L,i} a \rho_L(\omega_{L,i}^* - \omega_{L,i}) + \epsilon_L \sum_r \nu_{i,r} R_{L,r} \tag{4}$$

$$\rho_L C_{p,L} v_L^s \frac{dT_L}{dz} = \frac{d}{dz}\left(\epsilon_L k_{\text{eff,z,L}} \frac{dT_L}{dz}\right) + 4\frac{U}{d_t}(T_{\text{sur}} - T_L) + h_L a(T_G - T_L) + \epsilon_L \sum_r (-\Delta H_r) R_{r,L} \tag{5}$$

$$\frac{d}{dz}\left(\rho_L v_L^s\right) = \sum_i k_{L,i} a \rho_L(\omega_{L,i}^* - \omega_{L,i}) \tag{6}$$

2.3 Boundary Conditions

Boundary conditions are given in equations 8.6 to 8.9 in Jakobsen (2008) [8].

3 Assumptions

- Perfectly mixed slurry phase consisting of liquid with suspended catalyst particles.
- Constant volume fraction of solids, ϵ_S.
- Only the slurry phase exchanges heat with the wall.
- The pressure is the same in the gas and in the slurry phase; $p_G = p_L$, and follows a hydrostatic profile along the reactor height.
- Ideal gas law valid for gas phase, $pV = nRT$.
- Reaction takes place in the liquid.
- Neglecting mass transfer resistance in gas film, i.e. $\rho_{G,i}^* \approx \rho_{G,i}$

- Equilibrium at the phase boundary between gas and liquid; $y_i^* = k_i x_i^*$

- $k_{L,i} a(\rho_{L,i}^* - \rho_{L,i}) = k_{L,i} a \rho_L (\omega_{i,L}^* - \omega_{i,L})$

- Assume mass transfer resistance across liquid film surrounding catalyst pellet, and resistance inside pellet, much less than mass transfer resistance across phase boundary (GL).

- Constant liquid density, $\frac{d\rho_L}{dz} \approx 0$.

- Constant axial dispersion coefficient in both phases, $D_{\text{eff,z,L}}$ and $D_{\text{eff,z,G}}$.

- Constant liquid velocity $v_L = \frac{v_L^s}{\epsilon_L}$ (but **not** constant superficial velocity v_L^s, i.e. ϵ_L and v_L^s are changing, but v_L is constant).

- Constant thermal conductivity along z direction in both gas and slurry, $\lambda_{\text{eff,z,G}}$ and $k_{\text{eff,z,SL}}$

4   Kinetic Model

The kinetic model by Yates and Satterfield (1991) [13] is used.

$$r_{CO} = \frac{a p_{\text{CO}} p_{\text{H}_2}}{(1 + b p_{\text{CO}})^2} \tag{7}$$

The original units are

$$
\begin{aligned}
a &[=] \frac{mmol}{min\, g_{cat} MPa^2} \\
b &[=] \frac{1}{MPa} \\
r_{CO} &[=] \frac{\frac{mmol}{min\, g_{cat} MPa^2} MPa\, MPa}{1 + \frac{1}{MPa} MPa} = \frac{mmol}{min\, g_{cat}}
\end{aligned} \tag{8}
$$

Converting to SI units gives

$$
\begin{aligned}
a [=] & \frac{min}{60s} \frac{mol}{1000 mmol} \frac{kmol}{1000 mol} \frac{1000 g_{cat}}{kg_{cat}} \frac{mmol}{min\, g_{cat} MPa^2} \frac{MPa^2}{10^6 10^6 Pa^2} \\
= & \frac{10^3}{60\, 10^3\, 10^3\, 10^6\, 10^6} \frac{kmol}{s\, kg_{cat}\, Pa^2} \\
= & \frac{10^{-15}}{60} \frac{kmol}{s\, kg_{cat}\, Pa^2} \\
b [=] & \frac{1}{MPa} \\
= & \frac{1}{MPa} \frac{MPa}{10^6 Pa} \\
= & \frac{10^{-6}}{Pa} \\
r_{CO} [=] & \frac{\frac{10^{-15}}{60} \frac{kmol}{s\, kg_{cat}\, Pa^2} Pa\, Pa}{1 + \frac{10^{-6}}{Pa} Pa}
\end{aligned} \tag{9}
$$

Furthermore, it is desired to express the components CO and H_2 in terms of their fractions in the liquid phase. We have from the assumptions that

$$y_i^* = k_i x_i^* \tag{10}$$

and can then write

$$p_i^* = y_i^* p = k_i x_i^* p \tag{11}$$

The final reaction rate expression is thus:

$$\begin{aligned} r_{CO} &= \frac{10^{-15}}{60} \frac{a k_{CO} x_{CO}^* p \, k_{H_2} x_{H_2}^* p}{1 + b \, 10^{-6} \, k_{CO} x_{CO}^* p} \\ r_{CO} &= \frac{10^{-15}}{60} \frac{a k_{CO} x_{CO}^* \, k_{H_2} x_{H_2}^* p^2}{1 + b \, 10^{-6} \, k_{CO} x_{CO}^* p} \end{aligned} \tag{12}$$

5 Reaction Term

The reaction term from [8] was given as in equation 13.

$$\epsilon_L \sum_r \nu_{i,r} R_{L,r} \tag{13}$$

As the number of reactions in the chosen kinetic model is 1 (Yates and Satterfield (1991)) [13], we can remove the summation sign in 13 to obtain the expression given in 14

$$\epsilon_L \nu_i R_L \tag{14}$$

The reaction rate expression R_L taken from [13] and discussed in section 4 was finally obtained in equation 12 in the units $r_{CO}[=]\frac{kmol}{s\,kg_{cat}}$. Studying equations **??** and **??**, we see that the reaction term $\frac{\epsilon_L R_i}{\rho_L v_L^s}$ overall shall have the units $\frac{1}{m}$. This requires the units $\epsilon_L R_i[=]\frac{kg\,m}{m^3\,s}\frac{1}{m}$. We see that this requires the following expression for R_i:

$$\begin{aligned} [\epsilon_L R_i] &= \frac{kg\,m}{m^3\,s}\frac{1}{m} = [X][\epsilon_L \nu_i r_{CO}] = [X]\frac{kmol}{s\,kg_{cat}} \\ [X] &= \frac{[\epsilon_L R_i]}{[\epsilon_L \nu_i r_{CO}]} = \frac{\frac{kg\,m}{m^3\,s}\frac{1}{m}}{\frac{kmol}{s\,kg_{cat}}} = \frac{kg}{kmol}\frac{kg_{cat}}{m^3} = [M_{w,i}][\rho_{cat}] \end{aligned} \tag{15}$$

The final reaction rate term to be inserted into equation **??** is thus

$$\frac{\epsilon_L \nu_i r_{CO}}{\rho_L v_L^s} M_{w,i} \rho_{cat} \tag{16}$$

6 Mass Transfer Term

We have

$$k_{L,i} a \rho_L (\omega_{i,L}^* - \omega_{i,L}) \tag{17}$$

6

The equilibrium criterium at the phase boundary between gas and liquid is given in equation 18.

$$y_i^* = k_i x_i^* \tag{18}$$

The mole fraction x_i can be expressed in terms of mass fraction ω_i as given in equation 19.

$$x_i = \frac{\frac{\omega_i}{M_{w,i}}}{\sum_j \left(\frac{\omega_j}{M_{w,j}}\right)} \tag{19}$$

Inserting for y_i^* and x_i^* in equation 18 gives

$$\frac{\frac{\omega_{i,G}^*}{M_{w,i}}}{\sum_j \left(\frac{\omega_{j,G}^*}{M_{w,j}}\right)} = k_i \frac{\frac{\omega_{i,L}^*}{M_{w,i}}}{\sum_j \left(\frac{\omega_{j,L}^*}{M_{w,j}}\right)} \tag{20}$$

Recognising the definition for average molar mass (equation 21) in terms of mass fractions, we can write the equilibrium expression as in equation 22.

$$\overline{M_w} = \sum_i x_i M_{w,i} = \sum_i M_{w,i} \frac{\frac{\omega_i}{M_{w,i}}}{\sum_j \left(\frac{\omega_j}{M_{w,j}}\right)} = \sum_i \frac{\omega_i}{\sum_j \left(\frac{\omega_j}{M_{w,j}}\right)} = \frac{1}{\sum_j \left(\frac{\omega_j}{M_{w,j}}\right)} \tag{21}$$

$$\frac{\omega_{i,G}^*}{\sum_j \left(\frac{\omega_{j,G}^*}{M_{w,j}}\right)} = k_i \frac{\omega_{i,L}^*}{\sum_j \left(\frac{\omega_{j,L}^*}{M_{w,j}}\right)}$$
$$\overline{M_G}\,\omega_{i,G}^* = k_i \overline{M_L}\,\omega_{i,L}^* \tag{22}$$
$$\dots$$
$$\omega_{i,L}^* = \frac{1}{k_i} \frac{\overline{M_G}}{\overline{M_L}} \omega_{i,G}^*$$

The final form of the mass transfer terms is given in equation 23.

$$k_{L,i} a \rho_L \left(\frac{1}{k_i} \frac{\overline{M_G}}{\overline{M_L}} \omega_{i,G}^* - \omega_{i,L}\right) \tag{23}$$

6.1 Calculation of k_L and a

The correlation by Calderbank and Moo-Young [2], equation (2) for larger bubbles, was utilised:

$$k_L = 0.42(N_{Sc})^{-1/2} \left(\frac{\Delta\rho\mu_c g}{\rho_c^2}\right)^{1/3} \tag{24}$$

where $\Delta\rho = \rho_c - \rho_d$, i.e. density difference between continous (c) and dispersed (d) phase, and the dimensionless Schmidt number is defined as:

$$Sc = \frac{\mu_c}{\rho_c D_c} \tag{25}$$

Taking the liquid phase as the continous phase and the gas phase as the dispersed phase and adding the index "i" to denote component i, we get:

$$k_{i,L} = 0.42(N_{Sc})^{-1/2} \left(\frac{(\rho_L - \rho_G)\mu_L g}{\rho_L^2} \right)^{1/3}$$

$$Sc = \frac{\mu_L}{\rho_L D_{i,L}}$$

(26)

Diffusion coefficients for each of the components were calculated using the correlation by Erkey et al [6], table 5:

$$10^9 \frac{D_{12}}{\sqrt{T}} = \beta(V - V_D)$$

(27)

where

- D_{12} is the diffusion coefficient, m^2/s

- T is the temperature, T

- V is the molar volume of the solvent at the prevailing conditions, cm^3/mol

- V_D is a parameter in the correlation, cm^3/mol

Further,

$$\beta = \frac{94.5}{M_1^{0.239} M_2^{0.781} (\sigma_1 \sigma_2)^{1.134}}$$

$$V_D = bV_0$$

$$V_0 = \frac{N\sigma_2^3}{\sqrt{2}}$$

(28)

$$b = 1.206 + 0.0632(\sigma_1/\sigma_2)$$

$$V = \frac{M_w}{\rho_L}$$

where (1) is the solute and (2) is the solvent. σ is the hard sphere diameter, for which data were found in [6] and supplemented with [1] (lighter hydrocarbons) and [11] (water).

Experimental results by the same authors in earlier work suggest that the complex wax mixture (solvent) can be treated as a pure n-alkane with the average carbon number of the wax [7]. The average carbon number of the wax was 29. Octacosane was used as the solvent in their work and also here. The density of the solvent was also measured by [5] and thus used here.

The diffusion coefficients were reported to be only weakly dependent on pressure over the range of 0.1 - 3.40 MPa in previous work by the authors [5].

The resultant diffusion coefficients were well in line with those used by Maretto and Krishna [10] for CO and H_2 (only those two components).

7 Heat Transfer Terms

7.1 Heat transfer between slurry and gas

The heat transfer between slurry and gas is given by

$$h_L a (T_G - T_{SL}) \tag{29}$$

7.2 Heat transfer between slurry and wall (cooling)

The reaction is exothermal. Heat is removed by cooling tubes inside the reactor.

The heat transfer term denoting the cooling of the slurry by cooling tubes, $\frac{4U}{d_t}(T_{\mathrm{sur}} - T_{SL})$, must be re-written. The starting point from Jakobsen (2008) [8], section 8.4, page 767 considers heating on the outside of the reactor perimeter only, but for Fischer-Tropsch synthesis an arrangment of multiple coolant tubes inside the reactor is more common. A more general form of the heat transfer term by cooling is given in Jakobsen (2008) [8], equation 1.291:

$$- h_W \frac{S_I}{A} (\langle T \rangle_A - \langle T \rangle_W) \tag{30}$$

Considering a cooling arrangement with N_t coolant tubes with the same length as the dispersion having a constant cross-sectional area A_t, we can write the perimeter S_I and area A of the cooling surface at each level of z as:

$$
\begin{aligned}
S_I &= 2\pi \frac{D_c}{2} + N_t S_t = \pi D_c + N_t \pi d_t = \pi \left(D_c + N_t d_t \right) \\
A &= A_{\mathrm{column}} - A_{\mathrm{coolingtubes}} = \pi \left(\frac{D_c}{2} \right)^2 - N_t A_t = \frac{\pi}{4} D_c^2 - N_t \frac{\pi}{4} d_t^2 = \frac{\pi}{4} \left(D_c^2 - N_t d_t^2 \right)
\end{aligned}
\tag{31}
$$

This gives for the heat transfer term due to cooling of slurry:

$$- h_W \frac{S_I}{A} (\langle T \rangle_A - \langle T \rangle_W) = h_W \frac{\pi \left(D_c + N_t d_t \right)}{\frac{\pi}{4} \left(D_c^2 - N_t d_t^2 \right)} (T_{\mathrm{surr}} - T_{SL}) = h_W \frac{D_c + N_t d_t}{\frac{1}{4} \left(D_c^2 - N_t d_t^2 \right)} (T_{\mathrm{surr}} - T_{SL}) \tag{32}$$

7.3 Calculation of parameter h_W

The parameter h_W was calculated using the correlation by Deckwer [3], as re-stated by Jhawar and Prakash [9], equation (3). The thermal conductivity of the slurry was calculated by the equation proposed by Tareef [12]. For the viscosity, Einstein's relation was used:

$$\mu_{SL} = \mu_L (1 + K \epsilon_S) \tag{33}$$

where the constant K was found by Meisl for a suspension of a Hopcalite catalyst in paraffin, according to [4] (equation 13).

8 Mass and Species Mass Conservation equations

8.1 Total mass conservation: gas phase

For the total mass balance for the gas phase, equation 3, the left hand side is expanded and the equation is manipulated to obtain an expression for the change in superficial gas velcocity by reactor length $\frac{d}{dz}v_G^s$ alone on the left hand side.

$$\frac{d}{dz}\left(\rho_G v_G^s\right) = -\rho_L \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right)$$

$$\rho_G \frac{d}{dz}v_G^s + v_G^s \frac{d}{dz}\rho_G = -\rho_L \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right) \tag{34}$$

$$\frac{d}{dz}v_G^s = -\frac{v_G^s}{\rho_G}\frac{d}{dz}\rho_G - \frac{\rho_L}{\rho_G} \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right)$$

8.2 Species mass conservation: gas phase

Starting out from the axial dispersion model, the species mass balance for the gas phase is split into two equations; one for flux and one for weight fractions.

We define:

$$j_{i,G} = -\epsilon_G \rho_G D_{\text{eff,z,G}}\frac{d\omega_{i,G}}{dz} \tag{35}$$

We then get:

$$j_{i,G} + \epsilon_G \rho_G D_{\text{eff,z,G}}\frac{d\omega_{i,G}}{dz} = 0$$

$$\frac{d}{dz}\left(\rho_G v_G^s \omega_{i,G}\right) + \frac{dj_{i,G}}{dz} + k_{L,i} a \rho_L \left(\frac{1}{k_i}\frac{\overline{M_L}}{\overline{M_G}}\omega_{i,G}^* - \omega_{i,L}\right) = 0 \tag{36}$$

Finally, expanding the left hand side of the weight fraction equation.

$$\rho_G v_G^s \frac{d}{dz}\omega_{i,G} + \rho_G \omega_{i,G}\frac{d}{dz}v_G^s + v_G^s \omega_{i,G}\frac{d}{dz}\rho_G + \frac{dj_{i,G}}{dz} + k_{L,i} a \rho_L \left(\frac{1}{k_i}\frac{\overline{M_L}}{\overline{M_G}}\omega_{i,G}^* - \omega_{i,L}\right) = 0 \tag{37}$$

8.3 Total mass conservation: liquid phase

For the total mass balance in the liquid phase, we insert for the mass transfer term (equation 23) into equation 6. Further, we expand the left hand side and obtain an expression for $\frac{d}{dz}v_L^s$.

$$\frac{d}{dz}\left(\rho_L v_L^s\right) = \rho_L \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right)$$

$$\rho_L \frac{d}{dz}v_L^s + v_L^s \frac{d}{dz}\rho_L = \rho_L \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right) \tag{38}$$

$$\frac{d}{dz}v_L^s = -\frac{v_L^s}{\rho_L}\frac{d}{dz}\rho_L + \sum_i k_{L,i} a \left(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}\right)$$

8.4 Species mass conservation: liquid phase

Starting out from the axial dispersion model, the species mass balance for the liquid phase is split into two equations; one for flux and one for weight fractions.

We define:

$$j_{i,L} = -\epsilon_L \rho_L D_{\text{eff,z,L}} \frac{d\omega_{i,L}}{dz} \tag{39}$$

We then get:

$$j_{i,L} + \epsilon_L \rho_L D_{\text{eff,z,L}} \frac{d\omega_{i,L}}{dz} = 0$$
$$\frac{d}{dz}\left(\rho_L v_L^s \omega_{i,L}\right) + \frac{dj_{i,L}}{dz} - k_{L,i} a \rho_L \left(\frac{1}{k_i}\frac{\overline{M_L}}{\overline{M_G}}\omega_{i,G}^* - \omega_{i,L}\right) = \epsilon_L R_i \tag{40}$$

Finally, expanding the left hand side of the weight fraction equation.

$$\rho_L v_L^s \frac{d}{dz}\omega_{i,L} + \rho_L \omega_{i,L}\frac{d}{dz}v_L^s + v_L^s \omega_{i,L}\frac{d}{dz}\rho_L + \frac{dj_{i,L}}{dz} - k_{L,i} a \rho_L \left(\frac{1}{k_i}\frac{\overline{M_L}}{\overline{M_G}}\omega_{i,G}^* - \omega_{i,L}\right) = \epsilon_L R_i \tag{41}$$

8.5 Rate of Change in Volume Fraction

The rate of change in volume fraction is set to zero at the current model stage. This will be improved. The volume fraction of gas is estimated, see separate note.

8.6 Rate of Change in Density

Equations **??** and 34 require an expression for the rate of change in gas density, $\frac{d}{dz}\rho_G$.

The ideal gas law (42) was assumed to be valid in section 3. An expression for gas density given the ideal gas law valid is given in

$$pV = nRT \tag{42}$$

$$\rho_G = \frac{n}{V}\overline{M_G} = \frac{p\overline{M_G}}{RT} \tag{43}$$

This yields the expression shown in equation 44.

$$\frac{d}{dz}\rho_G = \frac{d}{dz}\left(\frac{p\overline{M_G}}{RT}\right) = \frac{p}{RT}\frac{d}{dz}\overline{M_G} + \frac{\overline{M_G}}{RT}\frac{dp}{dz} - \frac{p\overline{M_G}}{R}\frac{\frac{dT_G}{dz}}{T_G^2} \tag{44}$$

Equation 44 requires an expression for the rate of change in average molar mass for the gas phase $\frac{d}{dz}\overline{M_G}$ and for the pressure $\frac{dp}{dz}$. These are derived in sections 8.8 and 8.7, respectively.

11

8.7   Rate of Change in Pressure

A hydrostatic pressure profile is applied;

$$p(z) = \int_0^L \rho_{\text{tot}}(z)g dz \tag{45}$$

The total density ρ_{tot} is assumed constant and given by

$$\rho_{\text{tot}} = \epsilon_G^0 \rho_G^0 + \epsilon_L^0 \rho_L + \epsilon_s \rho_s \tag{46}$$

Inserting for $\rho_{\text{tot}}(z) = \rho_{\text{tot}}$ and utilising $h = L - z$

$$
\begin{aligned}
p(z) &= \int_0^h \rho_{\text{tot}}g dz \\
p(z) &= \rho_{\text{tot}}gh \\
p(z) &= \rho_{\text{tot}}g(L - z)
\end{aligned}
\tag{47}
$$

Differentiating with respect to z then gives

$$\frac{dp}{dz} = -\rho_{\text{tot}}g \tag{48}$$

8.8   Rate of Change in Average Molar Mass

Equation 21 provides us with an expression for $\overline{M_G}$, which we insert into equation 44 and differentiate. The result is given below.

$$\frac{d}{dz}\overline{M_G} = \frac{d}{dz}\left(\sum_i x_i M_{w,i}\right) = \sum_i M_{w,i}\frac{d}{dz}\left(\frac{\frac{\omega_i^G}{M_{w,i}}}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\right)$$

$$= \sum_i M_{w,i}\left[\frac{\omega_i^G}{M_{w,i}}\frac{d}{dz}\left(\frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\right) + \frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{1}{M_{w,i}}\frac{d\omega_i^G}{dz}\right]$$

$$= \sum_i\left[\omega_i^G\frac{d}{dz}\left(\frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\right) + \frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{d\omega_i^G}{dz}\right]$$

$$= \sum_i\left[\omega_i^G\left(-\frac{1}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\frac{d}{dz}\left[\sum_j \frac{\omega_j^G}{M_{w,j}}\right]\right) + \frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{d\omega_i^G}{dz}\right]$$

$$= \sum_i\left[\omega_i^G\left(-\frac{1}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\left[\sum_j \frac{\omega_j^G}{M_{w,j}}\frac{d\omega_j^G}{dz}\right]\right) + \frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{d\omega_i^G}{dz}\right] \qquad (49)$$

$$= \sum_i\left[\omega_i^G\left(-\frac{1}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\left[\sum_j \frac{\omega_j^G}{M_{w,j}}\frac{d\omega_j^G}{dz}\right]\right) + \frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{d\omega_i^G}{dz}\right]$$

$$= \sum_i\left[\frac{1}{\sum_j \frac{\omega_j^G}{M_{w,j}}}\frac{d\omega_i^G}{dz} - \omega_i^G\frac{\sum_j \frac{1}{M_{w,j}}\frac{d\omega_j^G}{dz}}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\right]$$

$$= \sum_i\left[\frac{\frac{d\omega_i^G}{dz}\sum_j \frac{\omega_j^G}{M_{w,j}} - \omega_i^G\sum_j \frac{\frac{d\omega_j^G}{dz}}{M_{w,j}}}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\right]$$

$$\frac{d}{dz}\overline{M_G} = \frac{1}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2}\sum_i\left[\frac{d\omega_i^G}{dz}\sum_j \frac{\omega_j^G}{M_{w,j}} - \omega_i^G\sum_j \frac{d\omega_j^G}{dz}\frac{1}{M_{w,j}}\right]$$

9 Energy Conservation

The starting point for the temperature equations was given in equations 2 and 5. As stated in the section of Assumptions, 3, the thermal conductivity coefficient is constant for both phases. The equations were re-written into a set of two equations per phase; one heat flux and one temperature equation.

9.1 Temperature equation: gas phase

$$\rho_G C_{p,G} v_G^s \frac{dT_G}{dz} = \frac{d}{dz}\left(\epsilon_G \lambda_{\text{eff,z,G}}\frac{dT_G}{dz}\right) - h_L a(T_G - T_{SL}) \qquad (50)$$

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We define:

$$q_G = -\epsilon_G \lambda_{\text{eff,z,G}} \frac{dT_G}{dz} \tag{51}$$

This yields:

$$q_G + \epsilon_G \lambda_{\text{eff,z,G}} \frac{dT_G}{dz} = 0$$
$$\rho_G C_{p,G} v_G^s \frac{dT_G}{dz} + \frac{dq_G}{dz} - h_L a(T_G - T_{SL}) = 0 \tag{52}$$

9.2 Temperature equation: slurry phase

$$\rho_{SL} C_{p,SL} v_{SL}^s \frac{dT_{SL}}{dz} = \frac{d}{dz}\left(\epsilon_{SL} \lambda_{\text{eff,z,L}} \frac{dT_{SL}}{dz}\right) + h_W \frac{S_I}{A}(T_{\text{surr}} - T_{SL}) + h_L a(T_G - T_{SL}) + \epsilon_L(-\Delta H_r) r_{CO} \rho_{\text{cat}} \tag{53}$$

We define:

$$q_{SL} = -\epsilon_{SL} \lambda_{\text{eff,z,SL}} \frac{dT_{SL}}{dz} \tag{54}$$

This gives:

$$q_{SL} + \epsilon_{SL} \lambda_{\text{eff,z,SL}} \frac{dT_{SL}}{dz} = 0$$
$$\rho_{SL} C_{p,SL} v_{SL}^s \frac{dT_{SL}}{dz} + \frac{dq_{SL}}{dz} - h_W \frac{S_I}{A}(T_{\text{surr}} - T_{SL}) - h_L a(T_G - T_{SL}) = \epsilon_L(-\Delta H_r) r_{CO} \rho_{\text{cat}} \tag{55}$$

10 Parameters

See separate note on the non-adjustable operating conditions.

11 Final Model Equations

$$\epsilon_L + \epsilon_G + \epsilon_S = 1 \tag{56}$$

$$\frac{d\epsilon_L}{dz} = 0$$
$$\frac{d\epsilon_S}{dz} = 0 \tag{57}$$
$$\frac{d\epsilon_G}{dz} = 0$$

$$\frac{d\rho_G}{dz} = \frac{p}{RT}\frac{d\overline{M_G}}{dz} + \frac{\overline{M_G}}{RT}\frac{dp}{dz} - \frac{\overline{M_G} p \frac{dT_G}{dz}}{RT_G^2} \tag{58}$$
$$\frac{d\rho_L}{dz} = 0$$

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$$\frac{d\overline{M_G}}{dz} = \frac{1}{\left(\sum_j \frac{\omega_j^G}{M_{w,j}}\right)^2} \sum_i \left[\frac{d\omega_{G,i}}{dz} \sum_j \frac{\omega_j^G}{M_{w,j}} - \omega_{i,G} \sum_j \frac{d\omega_{G,j}}{dz} \frac{1}{M_{w,j}} \right]$$

$$\frac{d\overline{M_L}}{dz} = \frac{1}{\left(\sum_j \frac{\omega_j^L}{M_{w,j}}\right)^2} \sum_i \left[\frac{d\omega_{L,i}}{dz} \sum_j \frac{\omega_j^L}{M_{w,j}} - \omega_{i,L} \sum_j \frac{d\omega_{L,j}}{dz} \frac{1}{M_{w,j}} \right] \tag{59}$$

Note! The rate of change in molar mass was implemented as follows:

$$\frac{d\overline{M_G}}{dz} = D_{ij}\overline{M_G} \tag{60}$$

where D_{ij} is the derivative matrix of the interpolation polynomials.

$$\frac{dv_G^s}{dz} = -\frac{v_G^s}{\rho_G}\frac{d}{dz}\rho_G - \frac{\rho_L}{\rho_G}\sum_i k_{L,i}a(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}^*)$$

$$\frac{dv_L^s}{dz} = -\frac{v_L^s}{\rho_L}\frac{d}{dz}\rho_L + \sum_i k_{L,i}a(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}^*) \tag{61}$$

Species mass balance: dispersion flux and weight fraction equations.
Gas phase:

$$j_{i,G} + \epsilon_G\rho_G D_{\text{eff,z,G}}\frac{d\omega_{i,G}}{dz} = 0$$

$$\rho_G v_G^s \frac{d\rho_G}{dz} + \rho_G v_G^s \frac{d\omega_{i,G}}{dz} + \rho_G\omega_{i,G}\frac{dv_G^s}{dz} + \frac{dj_{i,G}}{dz} + k_{L,i}a(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}) = 0 \tag{62}$$

Liquid phase:

$$j_{i,L} + \epsilon_L\rho_L D_{\text{eff,z,L}}\frac{d\omega_{i,L}}{dz} = 0$$

$$\rho_L v_L^s \frac{d\rho_L}{dz} + \rho_L v_L^s \frac{d\omega_{i,L}}{dz} + \rho_L\omega_{i,L}\frac{dv_L^s}{dz} + \frac{dj_{i,L}}{dz} - k_{L,i}a(\frac{1}{k_i}\frac{\overline{M_G}}{\overline{M_L}}\omega_{i,G}^* - \omega_{i,L}) = \epsilon_L\nu_i r_{CO}M_{w,i}\rho_{cat} \tag{63}$$

Energy balance: heat flux and temperature equations.
Gas phase:

$$\frac{q_G}{\epsilon_G\lambda_{\text{eff,z,G}}} + \frac{dT_G}{dz} = 0$$

$$\frac{dT_G}{dz} + \frac{1}{\rho_G C_{p,G}v_G^s}\frac{dq_G}{dz} + \frac{h_L a}{\rho_G C_{p,G}v_G^s}(T_G - T_{SL}) = 0 \tag{64}$$

Liquid phase:

$$\frac{q_{SL}}{\epsilon_{SL}\lambda_{\text{eff,z,SL}}} + \frac{dT_{SL}}{dz} = 0$$

$$\frac{dT_{SL}}{dz} + \frac{1}{\rho_{SL}C_{p,SL}v_{SL}^s}\frac{dq_{SL}}{dz} - h_W\frac{S_I}{A}\frac{(T_{\text{surr}} - T_{SL})}{\rho_{SL}C_{p,SL}v_{SL}^s} - \frac{h_L a(T_G - T_{SL})}{\rho_{SL}C_{p,SL}v_{SL}^s} = \frac{\epsilon_L\sum_r(-\Delta H_r)r_{CO}\rho_{cat}}{\rho_{SL}C_{p,SL}v_{SL}^s} \tag{65}$$

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