

# Supplementary material

## Bubbling fluidised reactor model according to (Kopyscinski et al., 2011; Witte et al., 2018)

A schematic of the one-dimensional two-phase reactor model is shown in Figure 1. The inlet gas stream to the reactor  $\dot{n}_{tot,0}$  is split into a stream going to the bubble phase  $\dot{n}_{b,0}$  and a flow in the dense phase  $\dot{n}_{e,0}$ . The flows are divided according to the volumetric fraction of the bubble phase  $\varepsilon_b$  and the emulsion phase  $\varepsilon_e = (1 - \varepsilon_b)$ . The initial fraction of the bubble phase is determined by superficial gas velocities  $u$  and bubble diameter  $d_b$ . The bubble diameter is determined by a correlation from Hilligart et al. (Hilligardt and Werther, 1985):

$$u_b = \psi(u - u_{mf}) + 7.11v\sqrt{gd_b}$$

$$\varepsilon_b = \frac{\psi(u - u_{mf})}{u_b}$$

The two parameters for the bubble rise velocity  $v$  and visible bubble flow  $\psi$  are dependent on the different types of Geldart particles, as well as the reactor height and diameter.

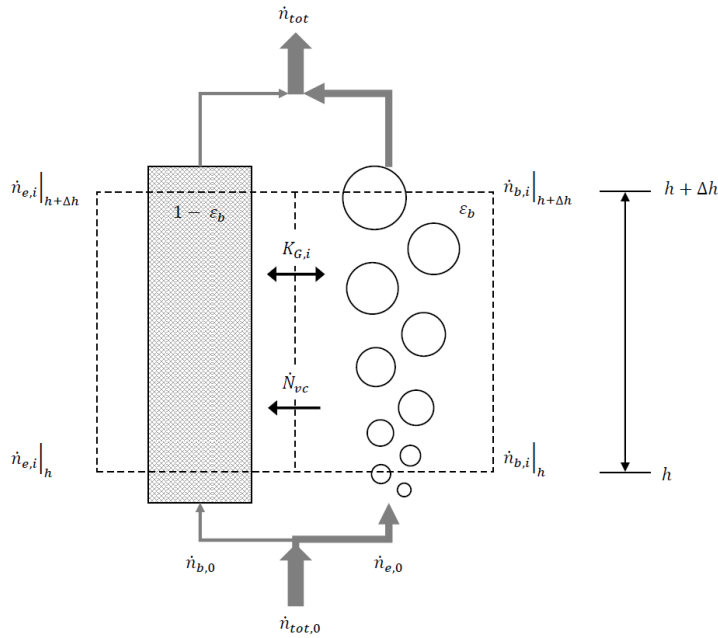


Figure 1: Scheme of the one-dimensional two-phase fluidised bed methanation model according to (Kopyscinski et al., 2011)

The molar balances of the two phases for each component  $i$  are as follows:

$$0 = -\frac{d\dot{n}_{b,i}}{dh} - K_{G,i} \cdot a \cdot A_{cross} \cdot (c_{b,i} - c_{e,i}) - \dot{N}_{vc} \cdot x_{b,i}$$

$$0 = -\frac{d\dot{n}_{e,i}}{dh} + K_{G,i} \cdot a \cdot A_{cross} \cdot (c_{b,i} - c_{e,i}) + \dot{N}_{vc} \cdot x_{b,i} + (1 - \varepsilon_b)(1 - \varepsilon_{mf}) \cdot \rho_P \cdot A_{cross} \cdot R_i$$

The volume fraction of the dense phase is represented by the factor  $(1 - \varepsilon_b)$ , while  $(1 - \varepsilon_{mf})$  expresses the volumetric fraction of particles in the emulsion phase at minimal fluidisation conditions. The overall reaction term is defined as:

$$R_i = \sum v_{ij} \cdot r_j$$

Where  $j$  represents the methanation and water-gas-shift reactions taking part.

The total bulk flow from the bubble to the dense phase is represented in factor  $\dot{N}_{vc}$ , which is the sum of the molar losses due to the reactions and the mass transfer to the dense phase:

$$\dot{N}_{vc} = \frac{\dot{n}_{vc}}{dh} = \sum_i K_{G,i} \cdot a \cdot A_{cross} \cdot (c_{b,i} - c_{e,i}) + (1 - \varepsilon_b)(1 - \varepsilon_{mf}) \cdot \rho_P \cdot A_{cross} \cdot \sum_i R_i$$

### Membrane model according to (Makaruk and Harasek, 2009)

The discretisation into  $c$  discrete points is done along the length of the membrane. The trans-membrane flow is expressed along the membrane length  $l$  by

$$\frac{d\dot{n}_p}{dl} = \dot{n}_{trans} = \Pi_i(x_i p_F - y_i p_P) A_L$$

Where  $\Pi_i$  refers to the permeance of the respective membrane material, the driving force of the separation is expressed as the partial pressure difference  $(x_i p_F - y_i p_P)$  and  $A_L$  refers to the available separation area per length.

The flow gradients are approximated by a first order upwind finite difference scheme. This allows the calculation of the molar flow on the retentate and permeate side of the membrane at a specific point  $j$  along the one-dimensional grid. The boundary conditions are defined at the points with index  $j = 1$ .

$$\dot{n}_{f,i,j}^{k+(1/2)} = \dot{n}_{f,i,j-1}^k - \Pi_{i,j}(x_{i,j}^k p_F^k - y_{i,c-j+2}^k p_P^k) A_L \cdot \Delta l$$

$$\dot{n}_{p,i,j}^{k+(1/2)} = \dot{n}_{p,i,j-1}^k + \Pi_{i,j}(x_{i,c-j+2}^k p_F^k - y_{i,j}^k p_P^k) A_L \cdot \Delta l$$

The iteration variable  $k$  denotes the state of the variables before the iteration and  $k + (1/2)$  the half-step variables. The full iteration step at  $k + 1$  is extrapolated by:

$$\dot{n}_{f,i,j}^{k+1} = \dot{n}_{f,i,j}^k - \omega \left( \dot{n}_{f,i,j}^{k+(1/2)} - \dot{n}_{f,i,j}^k \right)$$

$$\dot{n}_{p,i,j}^{k+1} = \dot{n}_{p,i,j}^k - \omega \left( \dot{n}_{p,i,j}^{k+(1/2)} - \dot{n}_{p,i,j}^k \right)$$

The initiation of the iteration requires an initial guess for the concentration profiles on the retentate a permeate side.

## Literature

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