Reactor Technology, TKP4145, Project 4

In this project you are asked to extend the pseudo-homogeneous model you made in project 2 to a heterogeneous model. That is, you should include the two extra ODEs for the calculation of the processes occurring within the catalyst pellets as in project 3. The reactions take place on the active sites within the pores of the particles, hence there will be heat- and mass transfer between the gas in the bulk and the catalyst particles.

The implementation in MATLAB is similar to that of the pseudo-homogeneous model in project 2, but in addition, the equations for the particles must be solved as in project 3. The equations for the bulk gas in the reactor should still be integrated in the axial direction by use of `ode15s`, but in addition to the discretized equations for radial dispersion and conduction in the reactor the particle equations have to be solved in each point of the reactor calculations. The pellet equations should be discretized by the finite difference method. The resulting set of algebraic equations can either be solved by the 2nd order Newton-Raphson method (e.g., using the `fsolve` function in MATLAB) or by the first order Picard method as performed in project 3. The subroutines `dss020` and `dss042` can be used to approximate the radial derivatives both for the reactor- and pellet equations.

First you have to derive the governing equations comprising a set of differential- and algebraic equations on mass basis. The pellet equations should be formulated in spherical coordinates, but due to symmetry only the r-coordinate is considered.

Then, you should implement the equations in MATLAB. The report handed in must contain the complete set of equations, printout of the MATLAB implementation and the results from the simulations in form of 3D-plots of the variable fields.

In addition you should include a comparison of the results from project 4 with the results from project 2. In project 2 the pellet diffusion limitations were estimated by use of an efficiency factor, whereas a more rigorous model was employed in project 4. Discuss whether the efficiency factor approximation gave a sufficient description of the diffusion limitations or not. Is there any other diffusion limitations not accounted for in the model used in project 2?

Information

The divergence of a vector in spherical coordinates is defined as:

$$\nabla \cdot \mathbf{v} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 v_r\right) + \frac{1}{r^2 sin\theta}\frac{\partial}{\partial \theta}\left(v_\theta sin\theta\right) + \frac{1}{r^2 sin\theta}\frac{\partial v_\phi}{\partial \phi} \tag{1}$$

The gradient of a scalar is defined as:

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

Boundary Conditions

$$\left.\frac{\partial \omega_i}{\partial r}\right|_{r=0} = 0 \qquad \text{for all } z$$

$$\left.\frac{\partial \omega_i}{\partial r}\right|_{r=R} = 0 \qquad \text{for all } z$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=0} = 0 \qquad \text{for all } z$$

$$\left.\frac{\partial T}{\partial r}\right|_{r=R} = -\frac{U}{\lambda_{er}}\left(T|_{r=R} - T_0\right) \qquad \text{for all } z$$

$$\left.\frac{\partial u_z}{\partial r}\right|_{r=0} = 0 \qquad \text{for all } z$$

$$\left.\frac{\partial u_z}{\partial r}\right|_{r=R} = 0 \qquad \text{for all } z$$

$$\left.\frac{\partial \omega_i}{\partial \xi}\right|_{\xi=0} = 0 \qquad \text{for all } z \text{ and } r$$

$$-D_i\left.\frac{\partial \omega_i}{\partial \xi}\right|_{\xi=r_p} = k_i\left(\omega_i - \omega_{i,bulk}\right) \qquad \text{for all } z \text{ and } r$$

$$\left.\frac{\partial T}{\partial \xi}\right|_{\xi=0} = 0 \qquad \text{for all } z \text{ and } r$$

$$-\lambda_p\left.\frac{\partial T}{\partial \xi}\right|_{\xi=r_p} = h\left(T - T_{bulk}\right) \qquad \text{for all } z \text{ and } r$$

Recall that the boundary conditions are algebraic equations, and shall therefore not be integrated. These equations can elegantly be implemented in MATLAB by use of a so-called mass matrix.

The catalyst data are given in table 1:

Table 1: Catalyst data

Catalyst density	2355.2	$[kg/m^3]$
Particle diameter	0.0173	$[m]$
Void in bulk	0.528	
Heat transfer coefficient	30000	$[W/m^2K]$
Particle conductivity	50	$[W/mK]$

Some useful relations are given in appendices 1-2.

Predefined functions in MATLAB

Some functions are implemented to simplify the work and these can be found on *Blackboard*. You may still use the functions given for project 2, in addition a new function can be obtained.

- `masscoef.m` - A function which computes the binary diffusivities and the mass transfer coefficients for the different species.

Hint

Assume that the averaged molecular mass of the mixture is not changing significantly (neglecting changes in the number of moles) and that the effective radial diffusivity and conductivity are constant over the cross-section. The molecular diffusivities for gases may be assumed constant within the pores of the pellets, and the conductivity of the solid particle may also be assumed constant. The iterations in `fsolve` are very sensitive to the start estimates that you provide. It is therefore important that you try to estimate these values with reasonable accuracy. Moreover, these simulations will take some time, but 10-15 minutes should be sufficient provided that you use relatively few discretization points in the radial direction in the reactor (i.e., 6-7 points are sufficient) and in the pellet (i.e., 6-7 points are sufficient).

Appendix I: Calculation of diffusivities and mass transfer coefficients

The molecular diffusivities may be computed from the relation:

$$D_i = \frac{1.0 \times 10^{-4} \left(0.00143 \cdot T^{1.75}\right)}{\left(P \cdot M_{ib}^{1/2} \left(\left(\sum \nu_i\right)^{1/3} + \left(\sum \nu_b\right)^{1/3}\right)\right)^2} \qquad (1)$$

in which M_{ib} is given as:

$$M_{ib} = 2\left(\frac{1}{M_a} + \frac{1}{M_b}\right)^{-1} \qquad (2)$$

The molecular constants $\sum \nu_b$ are listed in table 2. The mixture diffusivity can be calculated from the Wilke equation (See Jakobsen, 2008; page 274 (molar) or 289 (mass based).

Table 2: Molecular sums for diffusivity computations

i	$\sum \nu$
CH_4	25.14
CO	18.01
CO_2	26.90
H_2	6.12
H_2O	13.10
N_2	18.50

The mass transfer coefficients may for example be computed from the empirical relation:

$$k_i = u_z^s \times 1.17 \times \left(\frac{D_p u_z^s \rho_g}{\mu} \right)^{-0.42} \times \left(\frac{\mu}{\rho_g D_i} \right)^{-0.67} \tag{3}$$

This parameter is computed by the `masscoef.m` function.

Symbols

k_i	$[m/s]$	Mass transfer coefficient, gas-solid
ν	$[-]$	Diffusion volumes