

Reactor technology, TKP 4145, project 2

During the last 30 years several important gas fields have been discovered in the North Sea. As a consequence of this the oil- and gas companies have started to do more research on the the economical and technical aspects of utilizing the gas by applying different conversion plants. The most interesting gas conversion processes today are the methanol process and the Fischer-Tropsch process where natural gas is converted into fuels and/or waxes. Both processes contain two main steps: conversion of natural gas to synthesis gas and conversion of natural gas into fuels/waxes.

You are going to simulate the synthesis gas process in a multi-tube reactor. This process has several reactions, however the three most important reactions are described as follows:

No.	Reaction	$\Delta H_{298}, kJ/mol$
I	$CH_4 + H_2O = CO + 3H_2$	206.1
II	$CO + H_2O = CO_2 + H_2$	-41.15
III	$CH_4 + 2H_2O = CO_2 + 4H_2$	165.0

In this project a pseudo-homogeneous model should be employed including an internal efficiency factor in the reaction terms. That is, you may neglect the external heat and mass transfer resistances. You should develop stationary differential equations for how the temperature, gas velocity as well as mass fractions of the components change in both axial and radial direction of the reactor. In addition, you should find the total pressure in the axial direction (you can assume a uniform pressure in the radial direction). Then implement the equations in Matlab. Apply the discretization routines dss020 and dss042 to find the 1st- and the 2nd derivatives, respectively, in the radial direction and integrate along the in-dependable variable which is the reactor length by using ode15s.

First, formulate the necessary differential- and algebraic equations based on mass. Then implement the equations in Matlab. An example of how boundary conditions are treated in Matlab is given in chapter 6.2 in the “Fixed Bed Reactors” compendium. The dispersion coefficient can be computed from the Peclet number correlation for Pe_{mr} given in appendix 8.

The paper should include a complete set of equations, print-outs of the Matlab implementation and 3D plots of the variable fields from the simulation.

Information

Component balance based on mass:

$$\frac{\partial}{\partial t}(\rho\omega_j) + \nabla \cdot (\vec{u}_s \rho\omega_j) = \nabla \cdot (D_j \rho \nabla \omega_j) + R_i$$

Divergence of a vector in cylindrical coordinates:

$$\nabla \cdot \vec{v} = \frac{1}{r} \frac{\partial(rv_r)}{\partial r} + \frac{1}{r} \frac{\partial v_\theta}{\partial \theta} + \frac{\partial v_z}{\partial z}$$

Gradient of a scalar in cylindrical coordinates:

$$\nabla s = \frac{\partial s}{\partial r} \vec{i} + \frac{1}{r} \frac{\partial s}{\partial \theta} \vec{j} + \frac{\partial s}{\partial z} \vec{k}$$

Boundary conditions

$$\begin{aligned}
\frac{dw_i}{dr}|_{r=0} &= 0 & \text{for alle } z \\
\frac{dw_i}{dr}|_{r=R} &= 0 & \text{for all } z \\
\frac{dT}{dr}|_{r=0} &= 0 & \text{for all } z \\
\frac{dT}{dr}|_{r=R} &= -\frac{U}{\lambda_{er}}(T|_{r=R} - T_o) & \text{for all } z \\
\frac{du_z}{dr}|_{r=0} &= 0 & \text{for all } z \\
\frac{du_z}{dr}|_{r=R} &= 0 & \text{for all } z
\end{aligned}$$

The boundary conditions for u_z is introduced to ensure convergence as the radial convective term in the continuity is neglected as a simplification to avoid solving the momentum balance. Note that the boundary conditions are algebraic equations and shall therefore not be integrated. This can be done by applying a so-called mass matrix.

Inlet conditions are given in table 1:

Table 1: Inlet conditions		
Mass fraction of CH ₄	0.1911	
Mass fraction of CO	0.0001	
Mass fraction of CO ₂	0.0200	
Mass fraction of H ₂	0.0029	
Mass fraction of H ₂ O	0.7218	
Mass fraction of N ₂	0.0641	
Superficial inlet velocity	1.89	[m/s]
Inlet temperature	793	[K]
Inlet pressure	29	[bar]

Data for the reactor tubes are given in table 2:

Table 2: Tube data		
Inner tube diameter	0.102	[m]
Outer tube diameter	0.132	[m]
Tube length	7	[m]
Temperature on the outside of the wall	1100	[K]
Heat coefficient for the metal	52	[J/msK]

Catalyst data are given in table 3:

Table 3: Catalyst data		
Catalyst density	2355.2	[kg/m _s ³]
Particle diameter	0.0173	[m]
Void fraction in bulk region	0.528	
Internal efficiency factor, η , for all reactions	0.001	

Useful models and correlations for the project are given in appendix 1-8.

Implemented functions

Some of the models are already implemented and can be downloaded from the homepage of the course:

- reaction.m: The input arguments are temperature, mol fraction and total pressure. The function returns the production/consumption rate of the components and the reaction energy for the three reactions.
- heatcoef.m: Input arguments are the Reynold number, temperature and mol fractions. Output are the heat coefficient and effective radial conductivity.
- convert.m: The function takes mass fractions or the component densities as input arguments and returns mol fractions.
- ergun.m: Input arguments are total density, axial velocity, Reynold number and a radial positioning vector. The output is 1D axial pressure gradient.
- constant.m: Input file including all constants and parameters needed in the simulation.

Note! Be consistent and define all vectors in Matlab as column vectors. Otherwise these functions will not work.

Hints

Neglect axial dispersion and assume that the average molecular mass does not change in the axial direction. In addition, assume that the effective radial dispersion coefficient is constant through the cross-section and that radial convective (and advective) contributions can be neglected.

Appendix 1: Kinetics

Reaction rates computed in reaction.m are given as:

Reaction I:

$$r_1 = \frac{\frac{k_1}{p_{H_2}^{2.5}} \left(p_{CH_4} p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1} \right)}{(DENOM)^2}$$

Reaction II:

$$r_2 = \frac{\frac{k_2}{p_{H_2}} \left(p_{CO} p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2} \right)}{(DENOM)^2}$$

Reaction III:

$$r_3 = \frac{\frac{k_3}{p_{H_2}^{3.5}} \left(p_{CH_4} p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_3} \right)}{(DENOM)^2}$$

where the denominator, $DENOM$, in the three reactions is given as:

$$DENOM = 1 + K_{CO} p_{CO} + K_{H_2} p_{H_2} + K_{CH_4} p_{CH_4} + K_{H_2O} \frac{p_{H_2O}}{p_{H_2}}$$

The reaction rate coefficients can be calculated from the Arrhenius' equation:

$$k_i = A_i e^{-\frac{E_{ai}}{RT}} \quad i = 1, 2, 3$$

with the following data given in table 4:

Table 4: Data for reaction rate coefficients

i	A_i	E_{ai}
I	$4.255 \cdot 10^{15}$	240.1
II	$1.955 \cdot 10^6$	67.13
III	$1.020 \cdot 10^{15}$	243.9

Adsorption coefficients can be calculated by using the van't Hoff equation:

$$K_j = A_j e^{-\frac{\Delta H_j}{RT}} \quad j = \text{CO}, \text{H}_2, \text{CH}_4, \text{H}_2\text{O}$$

With the following data given in table 5:

Table 5: Data for adsorption coefficients

j	A_j	ΔH_j
CO	$8.23 \cdot 10^{-5}$	-70.65
H ₂	$6.12 \cdot 10^{-9}$	-82.90
CH ₄	$6.65 \cdot 10^{-4}$	-38.28
H ₂ O	$1.77 \cdot 10^5$	88.68

The equilibrium constants are given as:

$$K_1 = 10^{\left(-\frac{11650}{T} + 13.076\right)} \quad [\text{bar}^2]$$

$$K_2 = 10^{\left(\frac{1910}{T} - 1.784\right)} \quad [-]$$

$$K_3 = K_1 \cdot K_2 \quad [\text{bar}^2]$$

The production/consumption rates of the different components in the system are:

$$r_{CH_4} = -(r_1 + r_3)$$

$$r_{CO} = r_1 - r_2$$

$$r_{CO_2} = r_2 + r_3$$

$$r_{H_2} = 3r_1 + r_2 + 4r_3$$

$$r_{H_2O} = -(r_1 + r_2 + 2r_3)$$

List of symbols

r_1	[kmol/kg(cat) h]	Reaction rate for CO
r_2	[kmol/kg(cat) h]	Reaction rate for CO ₂
r_3	[kmol/kg(cat) h]	Reaction rate for CO ₂
k_1	[kmol bar ^{1/2} /kg(cat) h]	Hastighetskoeffisient for rx 1
k_2	[kmol bar/kg(cat) h]	Hastighetskoeffisient for rx 2
k_3	[kmol bar ^{1/2} /kg(cat) h]	Reaction rate coef. for rx 3
K_1	[bar ²]	Equilibrium constant
K_2	[-]	Equilibrium constant
K_3	[bar ²]	Equilibrium constant
K_{CO}	[bar ⁻¹]	Adsorption constant
K_{H_2}	[bar ⁻¹]	Adsorption constant
K_{CH_4}	[bar ⁻¹]	Adsorption constant
K_{H_2O}	[-]	Adsorption constant
p_i	[bar]	Partial pressure of component i
A_1	[kmol bar ^{1/2} /kg(cat) h]	Pre-exponential factor
A_2	[kmol bar/kg(cat) h]	Pre-exponential factor
A_3	[kmol bar ^{1/2} /kg(cat) h]	Pre-exponential factor
E_{ai}	[kJ/mol]	Activation energy for reaction i
R	[J/mol K]	Gas constant
T	[K]	Temperature
A_{CO}	[bar ⁻¹]	Pre-exponential factor
A_{H_2}	[bar ⁻¹]	Pre-exponential factor
A_{CH_4}	[bar ⁻¹]	Pre-exponential factor
A_{H_2O}	[-]	Pre-exponential factor
ΔH_j	[kJ/mol]	Formation enthalpy for component j

Appendix 2: Conductivity

The conductivity of the pure materials can be calculated as follows:

$$\lambda_i = A_i + B_i T + C_i T^2 + D_i T^3 \quad \text{where } i = \text{Component}$$

Linear dependency of the mixture conductivity and the conductivity of the pure materials is assumed:

$$\lambda_g = \sum_i y_i \lambda_i$$

This is calculated in heatcoef.m

The coefficients are given in table 6:

Table 6: Coefficients for calculation of conductivities				
i	A	B	C	D
CH_4	$-1.869 \cdot 10^{-3}$	$8.727 \cdot 10^{-5}$	$1.179 \cdot 10^{-7}$	$-3.614 \cdot 10^{-11}$
CO	$5.067 \cdot 10^{-4}$	$9.1025 \cdot 10^{-5}$	$-3.524 \cdot 10^{-8}$	$8.199 \cdot 10^{-12}$
CO_2	$-7.215 \cdot 10^{-3}$	$8.015 \cdot 10^{-5}$	$5.477 \cdot 10^{-9}$	$-1.053 \cdot 10^{-11}$
H_2	$8.099 \cdot 10^{-3}$	$6.689 \cdot 10^{-4}$	$-4.158 \cdot 10^{-7}$	$1.562 \cdot 10^{-10}$
H_2O	$7.341 \cdot 10^{-3}$	$-1.013 \cdot 10^{-5}$	$1.801 \cdot 10^{-7}$	$-9.100 \cdot 10^{-11}$
N_2	$3.919 \cdot 10^{-4}$	$9.816 \cdot 10^{-5}$	$-5.067 \cdot 10^{-8}$	$1.504 \cdot 10^{-11}$

List of symbols

λ_g	[W/mK]	Gas conductivity
λ_i	[W/mK]	Component conductivity
A_i	[W/mK]	Coefficient for calculation of conductivity for component i
B_i	[W/mK ²]	Coefficient for calculation of conductivity for component i
C_i	[W/mK ³]	Coefficient for calculation of conductivity for component i
D_i	[W/mK ⁴]	Coefficient for calculation of conductivity for component i

Appendix 3: Effective radial gas conductivity

The correlation for effective radial conductivity which is applied in heatcoef.m is given as:

$$\lambda_{er} = \lambda_{er}^0 + 0.14\lambda_g RePr$$

Static contribution to the radial conductivity, λ_{er}^0 can be expressed as:

$$\lambda_{er}^0 = \lambda_g \left[\epsilon \left(1 + \beta \frac{d_p \alpha_{rv}}{\lambda_g} \right) + \frac{\beta(1-\epsilon)}{\frac{1}{\phi + \frac{\alpha_{rs} d_p}{\lambda_g}} + \gamma \frac{\lambda_g}{\lambda_s}} \right]$$

where:

$$\begin{aligned} \alpha_{rv} &= \frac{0.227 \cdot 10^{-3}}{1 + \frac{\epsilon}{2(1-\epsilon)} \frac{1-p}{p}} \left(\frac{T}{100} \right)^3 \\ \alpha_{rs} &= 0.227 \cdot 10^{-3} \frac{p}{2-p} \left(\frac{T}{100} \right)^3 \end{aligned}$$

Here $\gamma = \frac{2}{3}$ while ϕ is dependent of the catalyst packing:

$$\phi = \phi_2 + (\phi_1 - \phi_2) \frac{\epsilon - 0.260}{0.476 - 0.260}$$

In our case the catalyst packing is low, that is, $\epsilon \approx 0.476 \Rightarrow \phi = \phi_1$. In the literature ϕ_1 in our case is $\phi_1 = 0.3$.

The catalyst conductivity is $\lambda_s = 0.243$ W/mK.

List of symbols

λ_{er}	[W/mK]	Radial conductivity
λ_{er}^0	[W/mK]	Static radial conductivity
λ_s	[W/mK]	Catalyst conductivity
ϵ	[-]	Catalyst packing

Appendix 4: Heat coefficient

The heat coefficient, U , calculated in `heatcoef.m` is given by:

$$\frac{1}{U} = \frac{1}{\alpha_w} + \frac{d_i}{2\lambda_{st}} \ln \frac{d_o}{d_i}$$

where the heat coefficient at the wall, α_w , is:

$$\alpha_w = \alpha_w^0 + 0.444 Re Pr \frac{\lambda_g}{d_p}$$

and static heat coefficient at the wall is:

$$\alpha_w^0 = \frac{8.694}{d_i^{4/3}} \lambda_{er}^0$$

List of symbols

U	[W/m ² K]	Heat coefficient
α_w	[W/m ² K]	Heat coefficient at the wall
α_w^0	[W/m ² K]	Static heat coefficient at the wall
λ_{st}	[W/mK]	Conductivity of the tube metal
d_i	[m]	Inner tube diameter
d_o	[m]	Outer tube diameter
T_o	[K]	Temperature on the outside of the wall

Appendix 5: Viscosity

The viscosity of the pure materials can be computed from

$$\mu_i = \frac{b_i T^{1.5}}{T + S_i} \quad \text{where} \quad i = \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{N}_2$$

Once again, linear dependency of the mixture viscosity and the viscosity of the pure materials is assumed:

$$\mu = \sum_i y_i \mu_i \quad \text{where} \quad i = \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{N}_2$$

The coefficients b_i and S_i are given in table 7:

Table 7: Coefficients for viscosity calculation

i	b_i	S_i
CH_4	$1.00 \cdot 10^{-6}$	168
CO	$1.50 \cdot 10^{-6}$	220
CO_2	$1.50 \cdot 10^{-6}$	220
H_2	$0.65 \cdot 10^{-6}$	67
H_2O	$1.75 \cdot 10^{-6}$	625
N_2	$1.40 \cdot 10^{-6}$	108

List of symbols

μ_i	[kg/ms]	Component viscosity
b_i	[kg/msK ^{0.5}]	Component viscosity coefficient
S_i	[K]	Component viscosity coefficient

Appendix 6: Heat capacity

The heat capacity of the pure materials can be calculated from:

$$Cp_i = A_i + B_i T + C_i T^2 + D_i T^3 \quad \text{where } i=\text{Component}$$

Linear dependency of the mixture heat capacity and the heat capacity of the pure materials is assumed:

$$Cp_g = \sum_i y_i \cdot Cp_i$$

where $i = \text{CH}_4, \text{CO}, \text{CO}_2, \text{H}_2, \text{H}_2\text{O}, \text{N}_2$.

The coefficients are given in table 8

Table 8: Coefficients for calculation of heat capacity of the pure materials

i	A	B	C	D
CH_4	$1.925 \cdot 10^4$	$5.213 \cdot 10^1$	$1.197 \cdot 10^{-2}$	$-1.132 \cdot 10^{-5}$
CO	$3.087 \cdot 10^4$	$-1.285 \cdot 10^1$	$2.789 \cdot 10^{-2}$	$-1.272 \cdot 10^{-5}$
CO_2	$1.980 \cdot 10^4$	$7.344 \cdot 10^1$	$-5.602 \cdot 10^{-2}$	$1.715 \cdot 10^{-5}$
H_2	$2.714 \cdot 10^4$	$0.927 \cdot 10^1$	$-1.381 \cdot 10^{-2}$	$0.764 \cdot 10^{-5}$
H_2O	$3.224 \cdot 10^4$	$0.1924 \cdot 10^1$	$1.055 \cdot 10^{-2}$	$-0.3596 \cdot 10^{-5}$
N_2	$3.115 \cdot 10^4$	$-1.357 \cdot 10^1$	$2.680 \cdot 10^{-2}$	$-1.168 \cdot 10^{-5}$

List of symbols

Cp_g	[J/kmolK]	Gas heat capacity
Cp_i	[J/kmolK]	Heat capacity of component i
A_i	[J/kmolK]	Coefficient for calculation of heat capacity for component i
B_i	[J/kmolK ²]	Coefficient for calculation of heat capacity for component i
C_i	[J/kmolK ³]	Coefficient for calculation of heat capacity for component i
D_i	[J/kmolK ⁴]	Coefficient for calculation of heat capacity for component i

Appendix 7: Useful relations

Average molecular mass

$$\overline{M} = \sum_i y_i \cdot M_i$$

Conversion from mass fraction into mol fraction

$$y_i = \frac{\frac{\omega_i}{M_i}}{\sum_i \frac{\omega_i}{M_i}}$$

Ideal gas law has been applied for the derivation of this expression.

Calculation of reaction enthalpy

The reaction enthalpies for the three reactions at a given temperature is calculated by linear interpolation between the reaction enthalpies at $T = 298$ and $T = 948$.

$$\Delta H_T = \Delta H_{298} + \frac{T - 298}{948 - 298} \cdot (\Delta H_{948} - \Delta H_{298})$$

Table 9: Reaction enthalpies for the three reactions at $T=298$ K and $T=948$ K

Reaction no.	ΔH_{298} [J/kmol]	ΔH_{948} [J/kmol]
1	$206.1 \cdot 10^6$	$224.0 \cdot 10^6$
2	$-41.15 \cdot 10^6$	$-37.30 \cdot 10^6$
3	$164.9 \cdot 10^6$	$187.5 \cdot 10^6$

List of symbols

\overline{M}	[kg/kmol]	Average mol mass
M_i	[kg/kmol]	Mol mass for component i
y_i	[-]	Mol fraction for component i
ω_i	[-]	Mass fraction for component i

Appendix 8: Dimensionless groups

Prandtl number:

$$Pr = \frac{\mu C p_g}{\lambda_g}$$

Reynold number:

$$Re = \frac{\rho u_z d_p}{\mu}$$

Peclet number:

$$\frac{1}{Pe_{mr}} = \frac{1}{1.1 Pe_r^d}$$

where

$$Pe_r^d = 8 \left[2 - \left(1 - \frac{2d_p}{d_i} \right)^2 \right]$$