rout@nt.ntnu.no

Steady-state Packed Bed Reactor Modeling for Methanol Synthesis

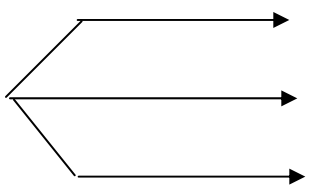
K. R. Rout, H. A. Jakobsen*
NTNU, Norway

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Contents

- Motivation of methanol synthesis
- Types of reactor model



Pseudo-homogeneous model

Conventional heterogeneous model

Simplified heterogeneous model

- Comparasion of Psedu-homogeneous-, conventional- and simplified heterogeneous model
- Numerics: least squares spectral element method.
- Results and Discussion
- Conclussion

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Process evaluation for methanol synthesis

- Net power
- Total input
- Total output

Reactor Simulation for methanol synthesis

- Reactor type design/size
- Best operating conditions
- Transport phenomena

Kinetic study for methanol synthesis

- Catalyst preparation
- Kinetic rate
- Catalytic activity

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Motivation for the process

- METHANOL is multipurpose based chemical.
- It can be used as chemical intermidiates.
- Easy for transportation.
- It has high octane number.
- Good antiknock performance.

Future renewable energy sources

Fuel
(Methanol + Gasoline) ⟶ combustion engine

Methanol: Fuel cell

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Motivation for steady-state reactor modeling

METHANOL synthesis:

- Feed treatment purification
- Reforming
- Methanol synthesis
- Product purification and storage

Intrinsic nonlinerity + complex phenomena = Computer Simulation

Dynamic simulation:
Start-up and shut down investigation
System identification
Safety, control, optimization
Catalytic activity

Reactor modeling ?

Pseudo-homogeneous

Conventional- and simplified Heterogeneous

Steady-state model

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Reactions involved in Methanol synthesis

- $CO + 2H_2 = CH_3OH$·····(1)

  $CO_2 + H_2 = CO + H_2O$·····(2)

  $CO_2 + 3\,H_2 = CH_3OH + H_2O$·····(3)

  The over all reaction is exothermic.

- Side reactions (even through they are inhibited by high catalyst selectivity under normal operating conditions):

  $CO + 3H_2 = CH_4 + H_2O$·····(4)

  $nCO + 2nH_2 = C_nH_{2n+1}OH + (n\text{-}1)\,H_2O$·····(5)

  $2CH_3OH = CH_3OCH_3 + H_2O$·····(6)

  This reaction occurs at 570 K; might lead to reactor instabilites due to of its high exothermicity.

- Catalyst: $Cu/Zn/Al_2O_3$ (life cycle: 2 year)

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Packed bed reactor models

Derivation of Reactor model

Mass based model : ρ

Mole based model : C
Assumption of total numer of moles
along the reactor axis is constant: this is not true

Modeling of packed bed reactor

Pseudo-homogeneous model

do not account explicitly the presence of pellet

Heterogeneous model

seperate equation for the solid and interstitial fluid.

Simplified Mass transport: Efficiency factors

Conventional Mass transport: Multicomponent diffusion models

1. Wilke Model
2. Maxwell-Stefan Model
3. Dusty gas model

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Pseudo-homogeneous reactor model

- Species Mass balance: $$\rho_g u_z \frac{\partial \omega_j}{\partial z} = (1-\varepsilon)\sum_k \eta_k R_k \upsilon_{jk}$$
- Total continuity equation: $$\frac{\partial}{\partial z}(u_z \rho_g) = 0$$
- Energy balance: $$\rho_g Cp_g u_z \frac{\partial T}{\partial z} = (1-\varepsilon)\sum(-\Delta H_{rk})\eta_k R_k + \frac{4U}{d_t}(T_w - T)$$
- Ergun Equation: $$\frac{\partial P}{\partial z} = -\left(1.75 + 150\left(\frac{1-\varepsilon}{\mathrm{Re}}\right)\right)\frac{u_z^2 \rho_g}{d_p}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)$$

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Heterogeneous Model

Conventional

a) Fluid phase equations:

Mass balance: $\rho_g u_z \frac{\partial \omega_i}{\partial z} = k_{gi} a_v \rho_g (\omega_{is} - \omega_i)$

Energy: $\rho_g Cp_g u_z \frac{\partial T}{\partial z} = h_f a_v (T_s - T) + \frac{4U}{d_t}(T_w - T)$

Ergun Eq.: $\frac{\partial P}{\partial z} = -(1.75 + 150(\frac{1-\varepsilon}{\mathrm{Re}}))\frac{u_z^2 \rho_g}{d_p}(\frac{1-\varepsilon}{\varepsilon^3})$

b) Solid phase equations (Wilke, Maxwell-Stefan, Dusty gas model):

Mass balance:

$\frac{\partial J_{i,r}}{\partial r} = (1-\varepsilon)\sum_k \eta_k R_k \upsilon_{ik}$ where $J_{i,r} = -\rho_{g,s} D_{r,i} \frac{\partial \omega_{i,s}}{\partial r}$

Energy:

$\frac{\partial Q_s}{\partial r} = (1-\varepsilon)\sum(-\Delta H_{rk})\eta_k R_k$ where $Q_s = -\lambda_s \frac{\partial T_s}{\partial r}$

Simplified

a) Fluid phase equations:

Mass balance: $\rho_g u_z \frac{\partial \omega_i}{\partial z} = k_{gi} a_v \rho_g (\omega_{is} - \omega_i)$

Energy: $\rho_g Cp_g u_z \frac{\partial T}{\partial z} = h_f a_v (T_s - T) + \frac{4U}{d_t}(T_w - T)$

Ergun Eq.: $\frac{\partial P}{\partial z} = -(1.75 + 150(\frac{1-\varepsilon}{\mathrm{Re}}))\frac{u_z^2 \rho_g}{d_p}(\frac{1-\varepsilon}{\varepsilon^3})$

b) Solid phase equations:

Mass balance:

$a_v \rho_g k_{g,i}(\omega_i - \omega_{i,s}) + (1-\varepsilon)\sum_k \eta_k R_k \upsilon_{ik} = 0$

Energy:

$a_v h_f (T - T_s) + (1-\varepsilon)\sum(-\Delta H_{rk})\eta_k R_k = 0$

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Numerical scheme

- Least square spectral method (LSM)*.

  Because, for a given accuracy the high order spectral method requires only a few collocation points where as the low order methods such as the finite volume method (FVM), require a large number of grid points.

- The basic idea in the LSM is to minimize the integral of the square of the residual over the computational domain.

*Rout K. R., Solsvik J., Nayak A. K., Jakobsen H. A. (2011) A numerical study of multicomponent mass diffusion and convection in porous pellets for the SE-SMR and desorption processes. Chemical Engineering Science 66:4111-4126

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

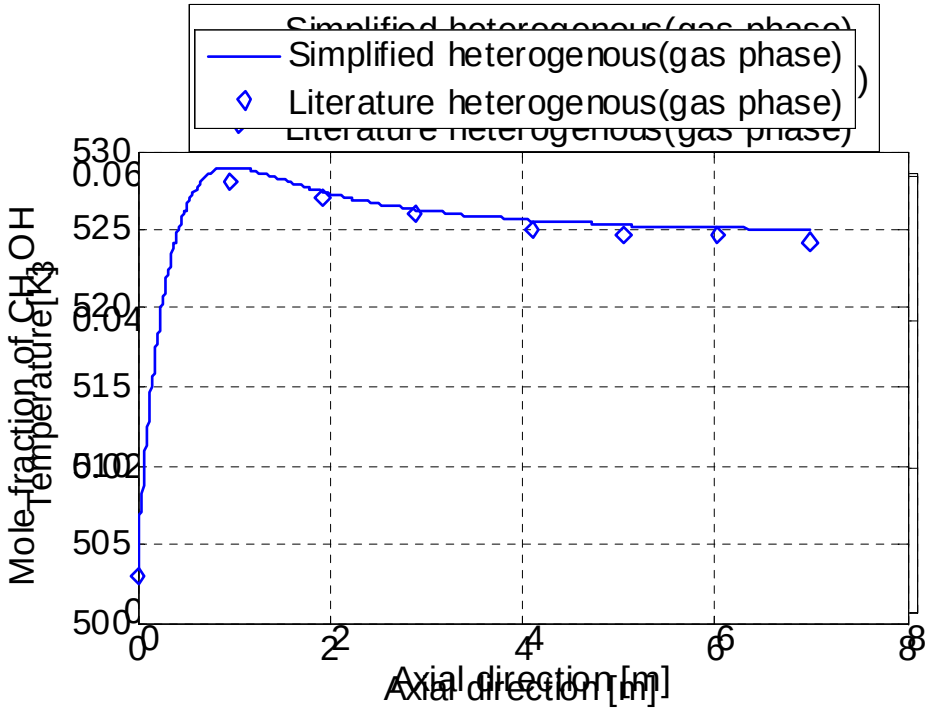
Overall Purpose

- Comparison of pseudo-homogeneous reactor model, conventional- and simplified heterogeneous reactor models with experimental data.
- The proposal of best suitable reactor model under normal operating conditions of fixed bed Lurgi reactor.
- Comparasion of different multicomponent diffusion models.

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Comparasion with Rezaie et al.

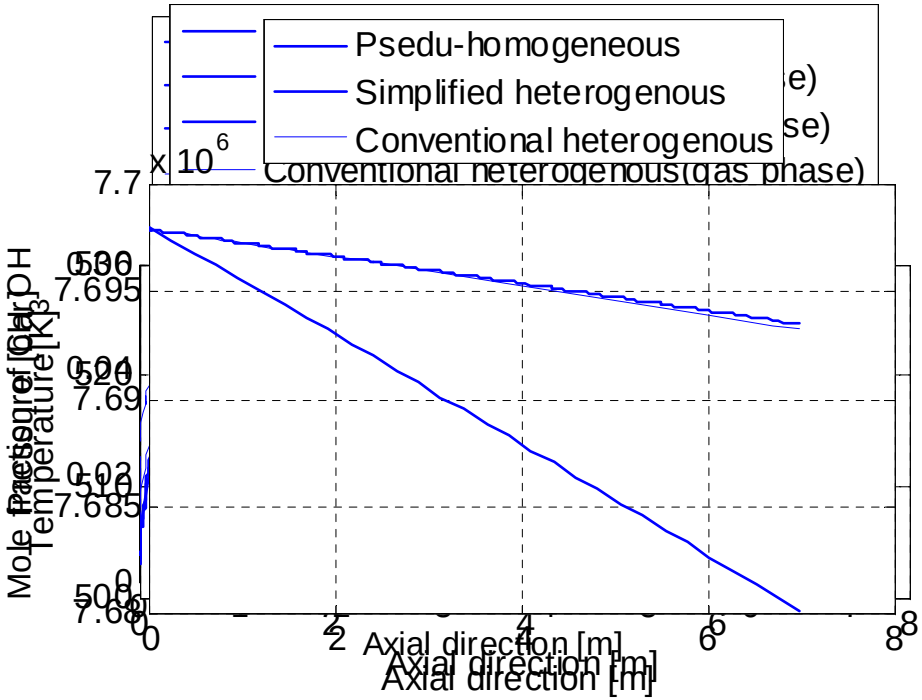


Rezaie N., Jahanmiri A., Moghtaderi B. Rahimpour M.R (2005) A comparasion of homogeneous and heterogeneous dynamic models for industrial methanol Reactors in the presence of catalyst deactivation. Chemical Engineering and Processing 44: 911-921

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Comparasion with different packed bed reactor models



rout@nt.ntnu.no

Comparasion with Experimental data by Rezaie et al

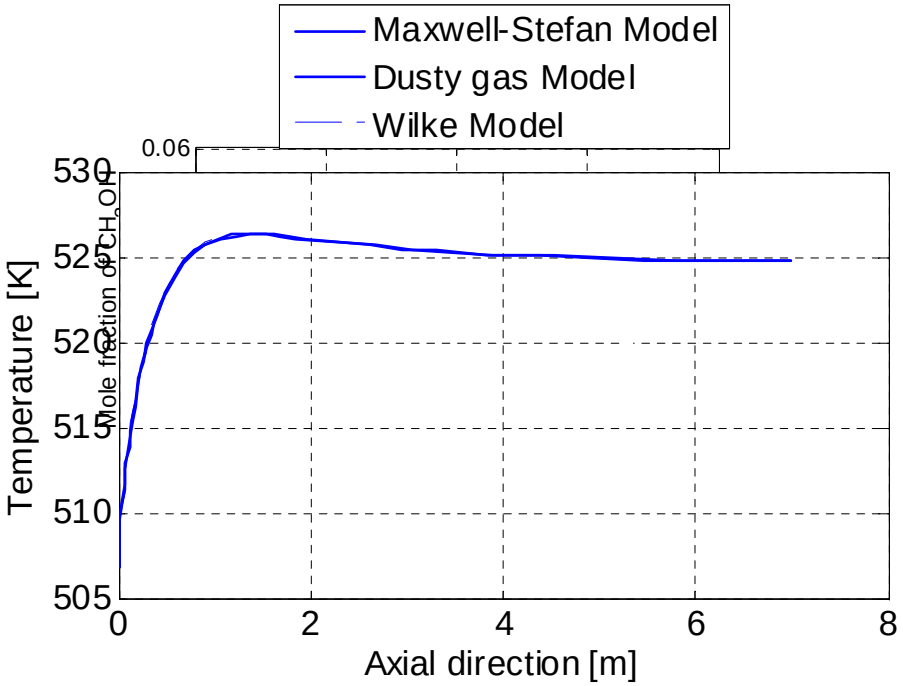
Time (day)	Plant (tonne/day)	Pseudo-homogeneous (tonne /day)	Simplified heterogeneous (tonne/day)	Conventional heterogeneous (tonne/day)
0	295.0	308.86	308.80	300.00

Rezaie N., Jahanmiri A., Moghtaderi B. Rahimpour M.R (2005) A comparasion of homogeneous and heterogeneous dynamic models for industrial methanol Reactors in the presence of catalyst deactivation. Chemical Engineering and Processing 44: 911-921

NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Comparasion of different multicomponent diffusion models in conventional heterogeneous model



NTNU
Norwegian University of Science and Technology

rout@nt.ntnu.no

Conclusion

- Both Pseudo-homogeneous- and simplified heterogeneous reactor model slightly overestimates with experimental data.
- However, the percentage of deviation is quite small.
- Conventional heterogeneous model is computationally expensive.
- As there is no significant deviation between gas- and solid phase concentrations of different components along the reactor axis, the pseudo-homogeneous reactor model seems to be best choice for methanol synthesis process.

rout@nt.ntnu.no

Thank You

NTNU
Norwegian University of Science and Technology