

Modeling of Transport and Reaction in a Catalytic Bed Using a Catalyst Particle Model.

F. Allain^{*,1}, A.G. Dixon¹

¹Worcester Polytechnic Institute - Chemical Engineering Department, Worcester, MA, USA

*Corresponding author: Worcester Polytechnic Institute, Chemical Engineering Dpt. – 100 Institute Road, Worcester, MA 1609, USA. Email: florent.allain@wpi.edu

Abstract: A packed bed reactor consisting of spherical catalyst particles in a tube was simulated numerically. The steady state pseudo-heterogeneous model consisted of a pseudo-continuum representation for the heat and mass transfer in the reactor tube. The reaction source terms were evaluated by explicitly solving a 1D spherical pellet model at each discretization point. The use of coupling variables between two geometries was crucial in this study. A test case was first run against literature results for carbon monoxide conversion (1). The model was then run for methane steam reforming for comparison to 3D CFD.

The test case gave satisfactory results when compared to the literature, giving similar profiles but slightly different values for temperature and concentrations.

Keywords: packed bed, catalyst, particle, reaction engineering .

1. Introduction

Tubular packed bed reactors are amongst the most commonly used reactors in the industry, for reactions such as CO combustion, or methane steam reforming. Mass and heat transfer between the fluid phase and the catalytic solid phase represent the main problem when considering these reactors in reaction engineering. Many models have been proposed and studied throughout the 20th century, improving one after another the coupling between the two phases. From a simple pseudo-homogeneous model where both fluid and solid are considered at the same temperature, to pseudo-heterogeneous models using effectiveness factors to account for diffusion limitations between the two phases, a lot of progress has been made in the description of tubular packed bed reactors. Computational power limitation was a great factor of influence in the simplifications that had to be made in order to be able to solve these models. These limitations having been greatly overcome, we

can now use more sophisticated models where the reaction source terms are evaluated by explicitly solving a 1D spherical pellet model at every discretization point of the bed, without the use of an effectiveness factor. One of these steady-state pseudo-heterogeneous models, with pseudo-continuum representations for heat and mass transfer is used in this paper to solve 2 cases: the carbon monoxide combustion and the methane steam reforming (MSR).

2. Reactor model.

The pseudo-heterogeneous model used in this paper is described in this section.

The system consists of a bed of catalyst particles and a fluid phase. The fluid phase is described by a set of 2D partial differential equations, accounting for the heat and mass balances in the fluid, and the solid phase by the same number of 1D differential equations, accounting for the balances in the catalyst particles. The catalyst particles are supposed spherical and surrounded by the uniform concentration and temperature of the fluid at that same point. The model is pictured in Figure 1.

2.1 Fluid equations

Mass balance: (one for each species i)

$$-\frac{\partial C'_i}{\partial z'} + \frac{1}{Pe_{m_r,i}} \left(\frac{\partial^2 C'_i}{\partial r'^2} + \frac{1}{r'} \frac{\partial C'_i}{\partial r'} \right) + \frac{1}{Pe_{m_a,i}} \frac{\partial^2 C'_i}{\partial z'^2} = St_{m,i} (C'_i - C'_{i,s})$$

Heat balance:

$$-\frac{\partial T'}{\partial z'} + \frac{1}{Pe_{h_r}} \left(\frac{\partial^2 T'}{\partial r'^2} + \frac{1}{r'} \frac{\partial T'}{\partial r'} \right) + \frac{1}{Pe_{h_a}} \frac{\partial^2 T'}{\partial z'^2} = St_h (T' - T'_s)$$

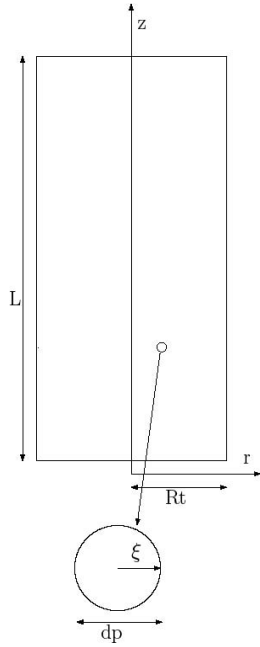


Figure 1. 2D bed and 1D particle models.

2.2 Solid equations

Mass balance: (one for each species i)

$$-\frac{\partial^2 C'_{s,i}}{\partial \xi'^2} = \frac{2}{\xi'} \frac{\partial C'_{s,i}}{\partial \xi'} + \varphi^2 \text{rate}$$

Heat balance

$$-\frac{\partial^2 T'_s}{\partial \xi'^2} = \frac{2}{\xi'} \frac{\partial T'_s}{\partial \xi'} + \beta \varphi^2 \text{rate}$$

2.3 Boundary conditions

Solid phase:

$$\xi' = 1 \quad -\frac{\partial C'_{s,i}}{\partial \xi'} = Sh_{s,i}(C'_{s,i} - 1),$$

$$-\frac{\partial T'_s}{\partial \xi'} = Bi_s T'_s$$

$$\xi' = 0 \quad \text{Axis symmetry.}$$

Fluid phase:

The set of boundary conditions for the temperature were different in the two studies. The CO combustion (case 1) was done at a constant wall temperature, the MSR (case 2) was

conducted in a reactor with a gradient of temperature along the walls.

$$z' = 0 \quad -\frac{\partial C'_i}{\partial z'} = Pe_{m,a,i}(C'_i - C'_{i,in})$$

$$-\frac{\partial T'}{\partial z'} = Pe_{h,a}(T' - T'_{in})$$

$$z' = \frac{L}{Rt} \quad \text{Convective fluxes for } C \text{ and } T,$$

$$r' = 0 \quad \text{Axis symmetry for } C \text{ and } T$$

$$r' = 1 \quad \frac{\partial C'_i}{\partial r'} = 0 \quad (\text{insulation})$$

$$-\frac{\partial T'}{\partial r'} = Bi_s(T' - T'_w)$$

3. Use of COMSOL Multiphysics

The previously described equations were entered in the chemical engineering module of COMSOL Multiphysics, as steady state analysis. The fluid equations were entered as convection diffusion equations and the solid ones as conduction for the heat balance, and diffusion for the mass balances. The simulations were done with dimensionless parameters.

The 2 sets of equations had to be coupled. The solid equations had to be solved at every discretization point of the fluid bed, in order to get the solid surface conditions. These are then used to evaluate the transfer between the two phases at the pellets surface. To do so, a 3D geometry was created. Two of the coordinates of this geometry stand for the 2D bed coordinates (the same as for the fluid equations), and the last one as the pellet radial coordinate. Therefore, we only use one of the dimensions of this 3D model to implement the 1D equations of the solid at every point of the fluid bed.

Then, as shown in Figure 2, extrusion coupling variables are added to the model, to transfer the 2D bed conditions to the 3D geometry providing the conditions surrounding the pellets at every point, and to transfer the pellet surface conditions to the 2D geometry, in order to evaluate the exchange terms between fluid and solid surface.

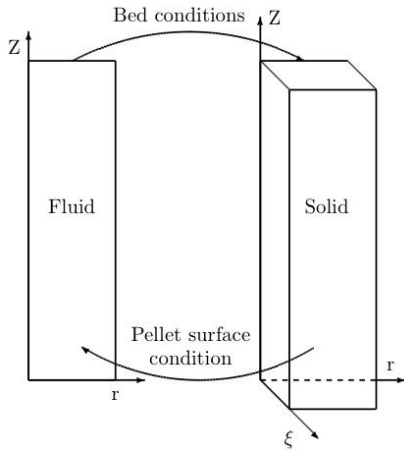


Figure 2. Coupling between 2D (Fluid bed) and 3D (Solid particles) geometries.

The following tables will give the parameters of the equations as they were entered in COMSOL for the CO conversion case. The MSR case used the same kind of equations, slightly modified because of the 3 different reactions and the different wall boundary condition for the heat equation. Also, the MSR case was simulated without axial dispersion to simplify calculations. The convergence was set at 10^{-3} .

D (anisotropic)	1/Pemr 0 0 1/Pema
R	-Stm*(c-cssf)
u	-1/r*1/Pemr
v	1
z=0	Flux: $N_0=1$
z=L/Rt	Convective flux
r=0	Axial symmetry
r=1	Insulation/Symmetry

Table 1. COMSOL parameters for the mass convection and diffusion model in the fluid.

k (anisotropic)	1/Pepr 0 0 1/Pepr
ρ, C_p, γ	1, 1, 1
Q	-Sth*(T-Tssf)
u	-1/r*1/Pepr 1
z=0	Heat Flux: $q_0=1-T$
z=L/Rt	Convective flux
r=0	Axial Symmetry
r=1	Heat Flux: $q_0=Bi/Pepr*(1-T)$

Table 2. COMSOL parameters for the heat convection and conduction model in the fluid.

D (anisotropic)	1/phisqr 0 0 0 0 0 0 0
R	2/x*csx*1/phisqr-rate
$\xi=0$	Insulation/Symmetry
$\xi=1$	Flux: $N_0=0, c_b=1,$ $k_c=Shs/phisqr$
r=0	Insulation/Symmetry
r=1	Insulation/Symmetry
z=0	Insulation/Symmetry
z=1	Insulation/Symmetry

Table 3. COMSOL parameters for the mass diffusion model in the solid.

k (anisotropic)	1/(beta*phisqr) 0 0 0 0 0 0 0
Q	2/x*Tsx*1/(beta*phisqr)+rate
$\xi=0$	Insulation/Symmetry
$\xi=1$	Heat Flux: $q_0=0,$ $h=Bi/(phisqr*beta), T_{inf}=1,$ $Const=0, T_{amb}=0$
r=0	Insulation/Symmetry
r=1	Insulation/Symmetry
z=0	Insulation/Symmetry
z=1	Insulation/Symmetry

Table 4. COMSOL parameters for the heat conduction model in the solid.

Our model will be referred to as the “single pellet model” in the rest of the paper.

4. Results

4.1 CO conversion

The set of parameters used for the study and simulation of CO conversion were found in different sources (1, 2). Amongst others, the inlet concentration is set at 0.5 mol/m^3 for CO. The concentration of O_2 is fixed at 30.6 mol/m^3 and considered constant. Its diffusion in the particle is also neglected, and we consider that there are no limitations to the transfer at the surface of the pellet, and therefore the concentration is constant and the same in the pellet as in the fluid. The inlet temperature, as well as the wall temperature, is set at 385K.

The fluid temperature profile is provided in Figure 3. The results compare with the literature. The profile is similar, the hot spot appearing at the same place; however the highest temperature is lower (by 30 K). This can be explained by the transfer between the two phases being represented more accurately in our case, with

more limitations at the surface of the pellet and therefore a less effective transfer.

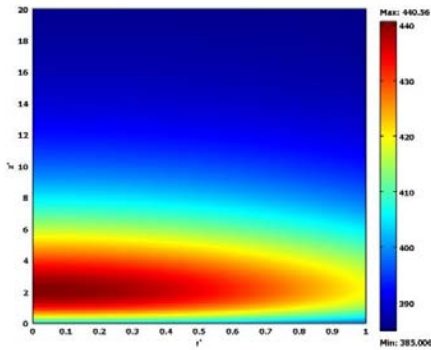


Figure 3. Temperature profile in the fluid obtained with the single pellet model for the reaction of CO conversion (K). Actual tube goes from $z'=0$ to 38.

Figure 4 shows the difference between solid surface and fluid temperature. When compared to previous work, this difference is higher in our case. They showed a maximum difference of approximately 20K, where we get a 45K difference. This difference is due to the better evaluation of the solid parameters through the solving of the heat diffusion equation in the entire solid particles. Also it supports the idea of a bigger limitation for heat transfer between the two phases. It is also important to note that this difference in temperature depends a lot on the diffusivity of CO in the catalyst and this parameter might need some adjustments.

The profile of temperature in the solid particles is given in Figure 5. We can see that the profile of temperature in a pellet is relatively flat, and follows the shape of the profile in the fluid, with higher values.

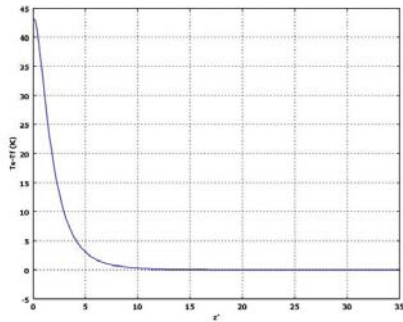


Figure 4. Temperature difference between solid and fluid at $r'=0.5$ obtained with the single pellet model. (K)

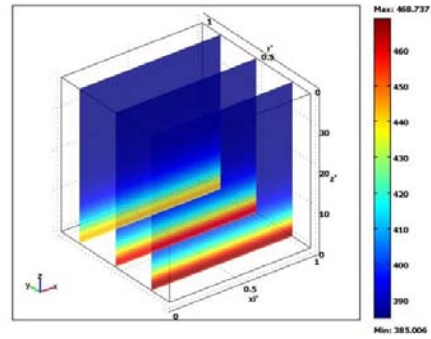


Figure 5. Temperature profile in the solid particles obtained with the single pellet model. (K) Case of CO conversion.

When looking at the CO concentration profiles (Figures 6 and 7), we can clearly see that the reaction occurs very fast at the inlet of the tube.

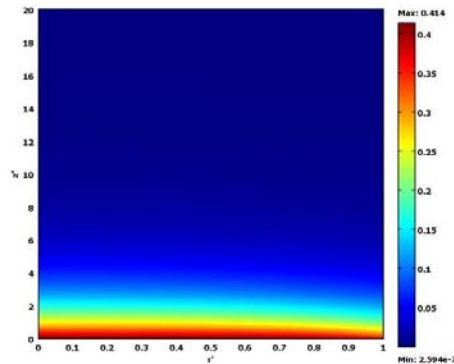


Figure 6. CO concentration profile in the fluid, obtained with the single pellet model. (mol/m^3) Actual tube goes from $z'=0$ to 38.

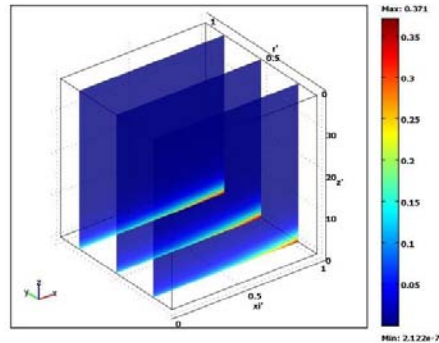


Figure 7. CO concentration in the solid particles, obtained with the single pellet model. (mol/m^3)

Most of the CO is consumed before $z'=5$. The values for CO concentration in the fluid

phase that we obtained in the study are close to the ones from the literature. This indicates a good evaluation in the previous study of the transfer between the two phases and a good evaluation of the diffusion in the pellets, which was completely solved in our case.

The results we obtained in our case are globally close to the one from the literature. However we have to keep in mind the fact that the concentration of oxygen was supposed constant in the fluid, but also in the solid. The implementation of at least a diffusion equation for the oxygen in the pellets might improve the results, for both the concentration and the temperature profiles.

4.2 MSR reaction

Once the model was validated with the reaction of CO conversion, the case of methane steam reforming was studied. This case presents several challenges, in particular the fact that no concentration can be considered constant, and that we therefore need to solve a mass balance for each species in both the solid and fluid phases. The parameters used for the reaction rates are from Hou and Hughes (3). The fluid and tube properties were taken from simulations done by Johnson Matthey.

Figure 8 shows the temperature profile in the fluid. We can see that the heating through the wall takes place, but the diffusion through the entire fluid is not efficient. This probably comes from a problem in the evaluation of the effective heat transfer coefficients at the wall.

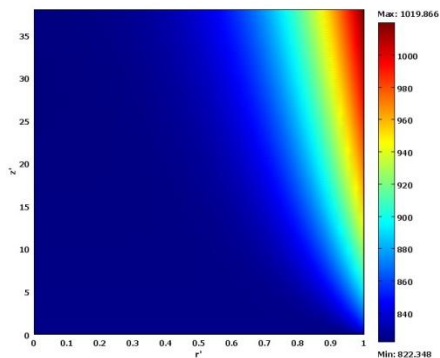


Figure 8. Temperature profile in the fluid obtained with the single pellet model for the MSR reaction (K).

When looking at the temperature profile in the pellets of catalyst in Figure 9, we can see as

in the previous case, that the temperature profile in one pellet is relatively flat. Once again, we will have to reevaluate the parameters for the heat and mass transfer between the pellet and the fluid, because we can see a temperature difference that goes up to 180K between the two phases, which is clearly not realistic.

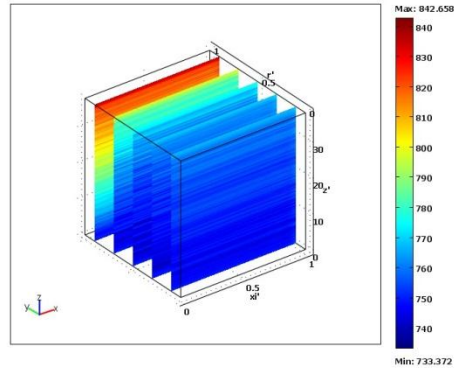


Figure 9. Temperature profile in the solid particles obtained with the single pellet model. (K) MSR Case.

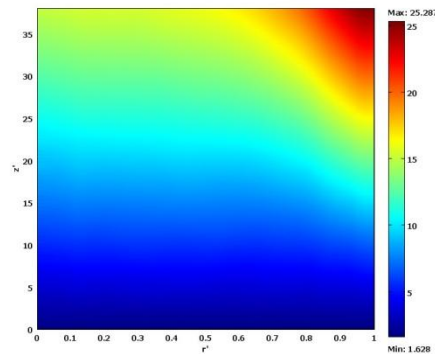


Figure 10. H₂ concentration profile in the fluid, obtained with the single pellet model. (mol/m³)

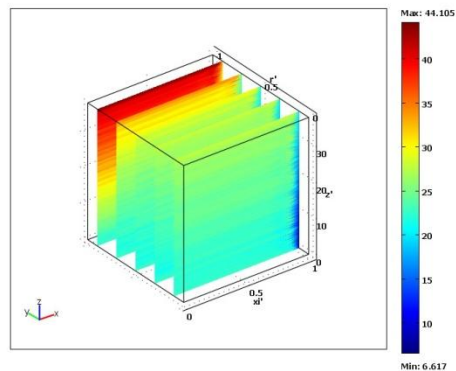


Figure 11. H₂ concentration in the solid particles, obtained with the single pellet model. (mol/m³)

Figures 10 and 11 show the H₂ concentration profiles in the fluid and in the solid. As the temperature profile shows a high gradient near the wall, so does the concentration profiles. Also the concentration differences between solid and fluid seems to be too high (up to 14 mol/m³) to be realistic, which clearly shows that parameters need to be adjusted.

The mesh needs some refining as well. Calculations were first conducted on a coarse mesh, which was then refined. However, computer power might become a limitation, because a better mesh is still required.

5. Conclusions

This study successfully simulated the reaction of CO conversion using a single pellet model implemented in COMSOL. The temperature and concentration profiles were consistent with previous studies with other reaction engineering models, showing a hot spot near the inlet of the tube, and a reaction occurring at the inlet. The case of the MSR reaction needs adjustments, as it is more complex and involves 3 stoichiometries and 5 species, leading to a number of 12 equations. Parameters need to be adjusted and the mesh needs to be refined in order to get consistent results.

6. Nomenclature

a_p	Catalyst specific surface area (m ⁻¹),
$Bi_i = \frac{d_p h_f}{2k_s}$	Biot number for specie i,
C_i	Fluid concentration of specie i (mol/m ³),
C_{in}	Total fluid inlet concentration (mol/m ³),
$C_i' = \frac{C_i}{C_{in}}$	Reduced fluid concentration of specie i,
C_i^s	Solid surface concentration of specie i, fluid phase (mol/m ³),
$C_{s,i}$	Solid concentration of specie i (mol/m ³),
$C_{i,s}^s$	Solid surface concentration of specie i, solid phase (mol/m ³),
$C'_{s,i} = \frac{C_{i,s}^s}{C_i^s}$	Reduced solid concentration of specie i,

C_{p_f}	Specific fluid heat capacity (J/kg/K),
d_p	Pellet diameter (m),
$D_{a,i}$	Axial fluid diffusivity for specie i (m/s),
$D_{r,i}$	Radial fluid diffusivity for specie i (m/s),
$D_{e,i}$	Diffusivity of specie i in the catalyst particle (m/s),
h_f	Heat transfer coefficient W/(m ² K),
k_a	Axial fluid thermal conductivity (W/K/m),
k_r	Radial fluid thermal conductivity (W/K/m),
$k_{r,j}$	Reaction j rate constant,
$k_{g,i}$	Mass transfer coefficient (m/s),
k_s	Catalyst thermal conductivity (W/K/m),
$Pe_{h_a} = \frac{uRt}{k_a}$	Axial heat Peclet number,
$Pe_{h_r} = \frac{uRt}{k_r}$	Radial heat Peclet number,
$Pe_{m_{a,i}} = \frac{uRt}{D_{a,i}}$	Axial mass Peclet number for specie i,
$Pe_{m_{r,i}} = \frac{uRt}{D_{r,i}}$	Radial mass Peclet number for specie i,
r	Bed radial coordinate (m),
Rt	Bed radius (m),
$r' = \frac{r}{Rt}$	Reduced bed radial coordinate,
$rate$	Reaction rate
$Sh_{i,s} = \frac{d_p k_{g,i}}{2D_{e,i}}$	Catalyst Sherwood number for specie i,
$St_h = \frac{a_p h_f Rt}{u \rho_f C_{p_f}}$	Fluid heat Stanton number,
$St_{m,i} = \frac{a_p k_{g,i} Rt}{u}$	Fluid mass Stanton number,
T	Fluid temperature (K),
T_{in}	Inlet temperature (K),
T_w	Wall temperature (K),
$T' = \frac{T}{T_{in}}$	Reduced fluid temperature,
$T'_w = \frac{T_w}{T_{in}}$	Reduced wall temperature,
T_s	Temperature in the solid (K),
T_s^s	Temperature at the surface of the solid (K),
$T'_s = \frac{T_s}{T_s^s}$	Reduced temperature in the solid,
u	Inlet velocity (m/s),
z	Bed length coordinate (m),

$$z' = \frac{z}{Rt} \quad \text{Reduced bed length coordinate,}$$

Greek letters

$$\beta_i = \frac{\Delta H_j C_i^s D_{e,i}}{T_s k_s} \quad \text{Adiabatic temperature rise in the pellet for specie i,}$$

$$\Delta H_j \quad \text{Enthalpy of reaction j (kJ/mol)}$$

$$\varphi_{i,j} = \left(\frac{d_p^2 k_{r,j} \rho_s}{4 C_i^s D_{e,i}} \right)^{1/2} \quad \text{Thiele modulus for specie i, reaction j,}$$

$$\rho_f \quad \text{Fluid density (kg/m}^3\text{),}$$

$$\rho_s \quad \text{Catalyst density (kg/m}^3\text{)}$$

$$\xi \quad \text{Pellet radial coordinate (m),}$$

$$\xi' = \frac{\xi}{d_p/2} \quad \text{Reduced pellet radial coordinate,}$$

7. References

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