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DEVELOPMENT OF CFD BASED MATHEMATICAL MODELS TO STUDY HETEROCATALYTIC SYSTEMS

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Nowadays mathematical models are applied in almost every field of our life to predict how real systems behave. Computational Fluid Dynamics (CFD) has become a standard tool for analyzing various situations where fluid flow has a significant effect on the studied processes. Complex models can be implemented and solved in commercial CFD packages (e.g. COMSOL Multiphysics). The goal of this paper is to model a catalytic bed based on the model of individual catalyst pellets. The proposed model takes into account the mass, heat and momentum transport as well as the reactions in a catalytic pellet of an industrial fixed-bed tube reactor. Different ways for aggregating pellet models were compared and evaluated applying COMSOL Multiphysics [1]. The catalytic pellet model was exported using MATLAB-COMSOL connection, and the catalytic bed model was implemented and tested using MATLAB.

Keywords: CFD, heterocatalytic system, pellet model, reactor bed model.

Introduction

Characteristics of flow field in process equipments are key issues in design of process units. With a well designed flow field the overall process performance and the safety of operation can be increased at the same time. To support this step, different modelling software packages and flow sheet simulators have been developed in last decades. As computational capacity of computers has being increased the role of computational fluid dynamics (CFD) among the applied modelling techniques and a method has significantly grown since the first computer was switched on [1].

CFD can be considered as a collection of numerical solvers for partial differential equations. With applying CFD codes more complicated problems in more complex structures can be investigated in details than with other modelling techniques. In recent years many papers applying CFD techniques to analyze the processes or to design reactors have been published. The most frequently investigated topics are the pressure drop, flow profile [2,3], heat transfer and mass transfer [4,5,6] for a reactor, the same for a catalytic pellet [8] as well as intra-particle diffusion effects [9]. These examples show that CFD is capable to simulate transport processes and it can be applied as a part of complex mathematical models.

Our purpose was to study heterocatalytic systems. The model development process will be introduced in case of an industrial heterocatalytic reactor with highly exothermic reaction. COMSOL Multiphysics can give an effective support since it can be applied to solve models which consist of higher order partial differential equations with finite elements method. In this article COMSOL Multiphysics is applied to calculate the development of state variables in a packed bed tube reactor.

Case Study

The simplest reactor models studied here were the one-dimensional quasi-single phase steady-state and dynamical models. It was followed by a two-phase dynamical model since heterocatalytic processes can be more adequately described by applying separate solid and gas phases.

These models can be applied in the analysis of any possible situation in the system, such as reactor runaway. In 1D model the state-variables are calculated along the catalyst bed. However the radial diffusion cannot be considered without expanding dimensions. 2D axial symmetry models take into consideration the geometry and the evolved flow field in the system while requiring only moderate calculation cost during the solution of models. The analysis shows the significant heat sources (hot spots) and the unusual flow fields (back mixing, turbulent waves). These types of results can be suitable to increasing of reactor efficiency [5, 6].

The most complex model studied here was the 2D axial symmetry, two-phase model. In this model both solid and gas phases are considered. The detailed mathematical description of the pellet was implemented in COMSOL Multiphysics. It can be applied to investigate the influence of diffusion and the velocity

field on the reactor temperature and the rate of transport processes between the considered phases.

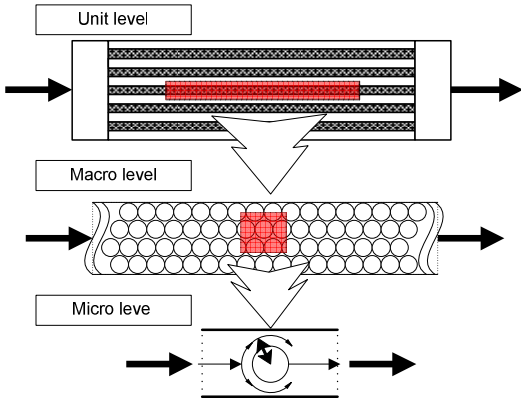


Fig. 1. Hierarchy of the reactor modelling

The pellet model can be applied to design the shape and size distribution of catalyst pellets, to get a closer look to specific locations of the catalyst bed, to analyze the possible development of runaway in a single catalyst pellet, and to build a catalytic bed from them. Unfortunately, for solving of this type of complex reactor model requires horrible hardware capacity.

Pellet model

In our previous works, a quasi-single phase mathematical description of the reactor, and 2D models, which takes into consideration the geometry and the evolved flow field in the system were, introduced [4, 7, 10]. The investigated, vertically positioned reactor contains a large number of tubes filled with catalyst. Our concept is the integration of a catalyst pellet model, implemented in COMSOL Multiphysics, into the catalytic bed using a pellet by pellet building technique developed in MATLAB. The first step to accomplish our objective is the implementation of pellet model in the applied CFD code. The reaction taking place is
The reaction is an exothermic, equilibrium reaction with changing number of moles.

$$A + B \Leftrightarrow C$$

All component mass balances in the gas phase contain terms to calculate convective and conductive transport processes and naturally the mass transport process between the solid and gas phase:

$$\nabla(-D_A \cdot \nabla cA) = R - u \cdot \nabla cA \quad (1)$$

$$\nabla(-D_B \cdot \nabla cB) = R - u \cdot \nabla cB \quad (2)$$

$$\nabla(-D_C \cdot \nabla cC) = R - u \cdot \nabla cC \quad (3)$$

where u – flow rate of gas phase; i = {A; B; C}; c_i – concentration of i^{th}-component in gas phase; D_i – diffusion coefficient of i^{th}-component in gas phase; R is the component source (chemical reaction);

$$r = k_0 \cdot e^{-\frac{E_A}{R \cdot T}} \quad (4)$$

Where:
k_0 – preexponential factor
E_A – activation energy
R – ideal gas constant
T – temperature of solid phase

Terms in both equations are the same as those considered in component balances:

$$\nabla(-k\nabla T) = Q - \rho \cdot C_p \cdot u \cdot \nabla T \quad (5)$$

Where:
ρ – average density of gas phase;
C_p – average heat capacity of gas phase;
T_G – temperature of gas phase
k– heat conduction coefficient in gas phase

Finally the momentum balance:

$$\nabla = \frac{\partial}{dx} + \frac{\partial}{dy} + \frac{\partial}{dz} \quad (6)$$

$$\rho \cdot u \cdot \nabla u = \\ = \nabla \cdot [p \cdot I + \eta \cdot (\nabla u + (\nabla u)^T)] + F \quad (7)$$

$$\nabla u = 0 \quad (8)$$

Where:
η – viscosity
p – pressure
u – velocity.

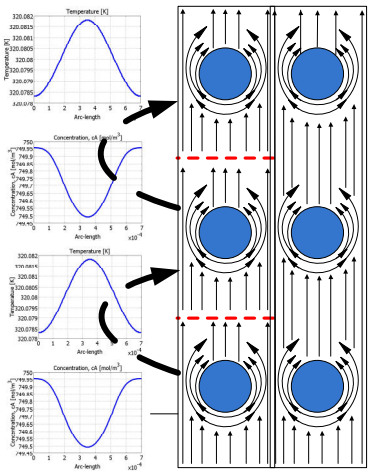
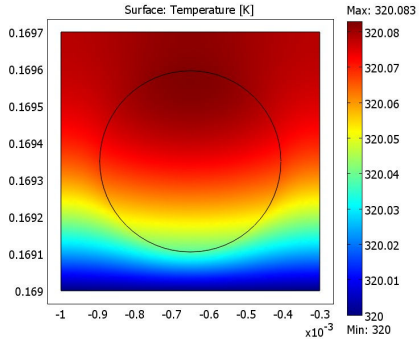
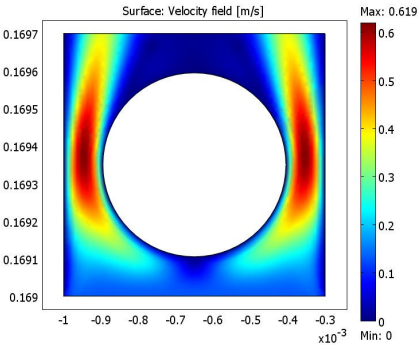


Fig. 2. The visualization of the implemented pellet structure

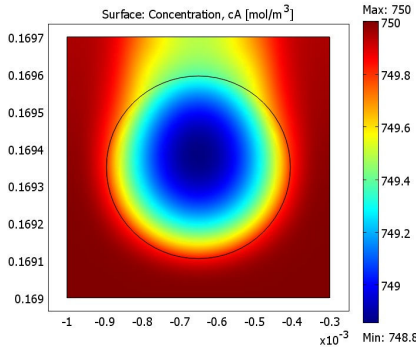
This is just a short description of model equations to illustrate the structure of pellet model. All physical properties are calculated as the function of temperature. These equations have been applied to implement a pellet model in COMSOL.



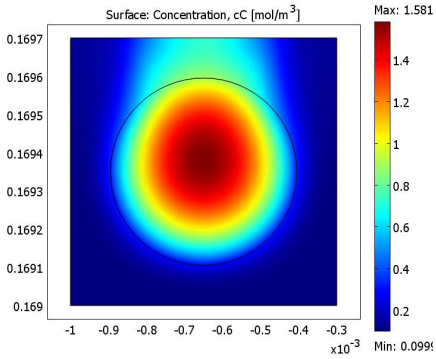
a) Temperature in the catalyst pellet and in its surroundings



b) Velocity field in the catalyst pellet and in its surroundings



c) Concentration of raw material A in the catalyst pellet and in its surroundings



d) Concentration of product component in the catalyst pellet and in its surroundings

Fig. 3. State-variables along the investigated part of reactor in steady-state

Catalytic bed model

In the following the pellet model implemented in COMSOL was used to build the model of the catalyst bed. Using the high-level connection between MATLAB and COMSOL, the implemented pellet model can be exported to MATLAB as a function. The user interface of MATLAB lets you to modify the pellet model, and to build up a structure from them. As [12] shown, the first pellet outlet properties are boundary averages, and these results become the next pellet inlet parameters. Finally, a linear catalytic bed was built and the first investigations were conducted on it.

Now, as *Fig* 2 shows, the concept of the examination is to make the same size model in two different ways, and to investigate the differences. The classical method was used as a reference; where diameters of the pellets were the same, and these pellets were taken into one domain, which domain's size was equal the aggregated domains of the built bed. The pellet by pellet model was compared to this model. The pellet by pellet model is working as a network of pellet models. The output parameter profiles of the first pellet models are the second pellets inlet parameters. It makes the model more accurate; because the pellet effect of the velocity field can be appear in the next pellet domain. A pellet and its surroundings were defined, and the scale was fixed during the examinations. When the pellet diameter was increased, the surrounding size was increase too. The differences between the data were examined in the end of every pellet element (the red doted line on the *Fig 2*). The difference was calculated as a relative square error:

$$\frac{(\mathrm{Reference\_profil} - \mathrm{Result\_profil})^2}{(\mathrm{Max\_value} - \mathrm{Min\_value})^2} \qquad (9)$$

Results and discussions

For the COMSOL Multiphysics pellet model the value of state variables entering the reactor were given as boundary conditions in the solution of the pellet model. Obtained results of the pellet model are plotted in *Fig* 3.

In *Fig* 3.a the temperature surface can be seen and as it was expected the highly exothermic reaction taking place in catalyst increases the temperature of the pellet and it warms up the flowing gas.

Due to the diffusion in the catalyst pellet the concentration of reagents decreases in the direction to the centre of the pellet (see *Fig* 3.c); while the concentration of the product changes in the opposite direction as shown in *Fig* 3.d. In this model all components can be connected to the same active sites on the catalyst, however in practice there is a competition between components and the reaction rate and the equilibrium of the adsorption determine the concentration in the catalyst. Since only the temperature profile and properties of inlet and outlet flows are

measured during the reactor operation, the catalyst pellet model cannot be validated without being integrated into the reactor simulator.

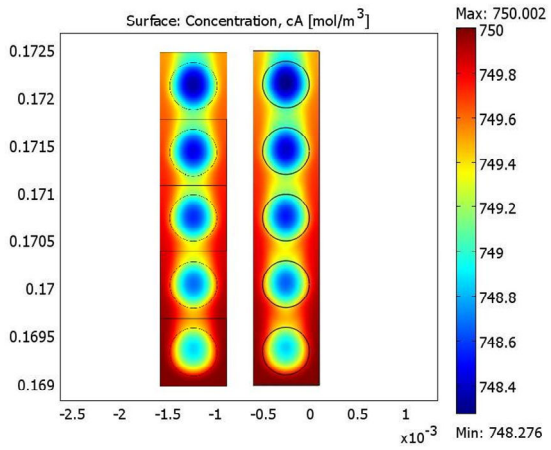


Fig. 4. Raw material (A) component concentration surfaces of the different modelled bed (pellets diameter: 7e-4 m)

As it can be seen in *Fig* 3.d the outlet concentration of the product is very low. This suggests that the parameters applied to calculate the rate of adsorption must be modified. Still the tendencies of changes in case of all the calculated state variables are the same as we expected.

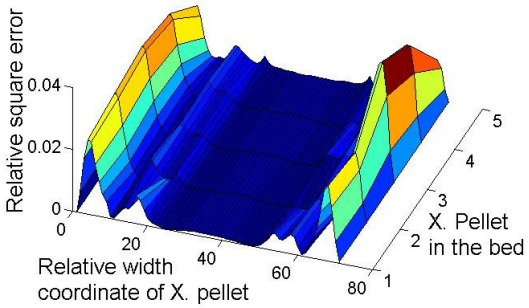


Fig. 5. Difference between the velocity profiles

This pellet model have been exported to MATLAB, and used as a function. The MATLAB software ensures wide freedom for its users, and with its built-in function it makes possible to implement a catalytic bed pellet by pellet.

The effect of the catalyst volume distribution on the conversion was analyzed [12]. This time five pellet in six different diameter were examined. The difference of the "classical" and the network models A component concentration surfaces with 7e-4 m pellet diameter was shown by *Fig* 5. The diameters of the modelled pellets were 7e-4m-12e-4 m.

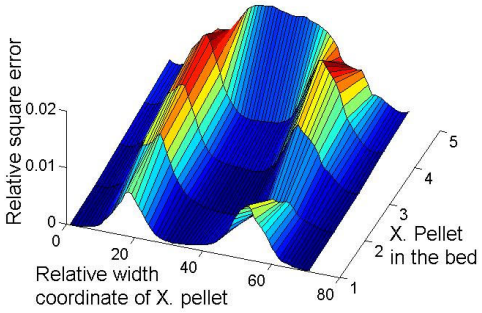


Fig. 6.. Difference between the concentration of raw material (A,B) profiles (pellets diameter: 7e-4 m)

The differences were examined at the end of every pellet. The difference was calculated as a relative square error. The relative square differences of each parameter were shown on *Fig* 5-8. As *Fig* 5 shows, the highest values of velocity difference are regularly near the wall.

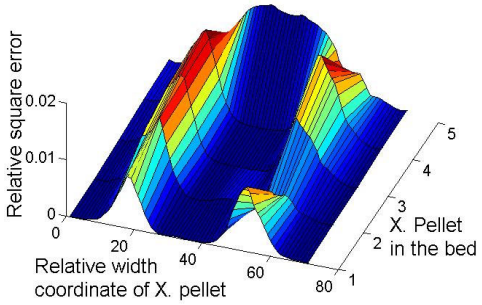


Fig. 7. Difference between the concentration of the product (C) profile (pellets diameter: 7e-4 m)

The component profile differences are shown on *Fig* 6-7. When the flow leaves the pellet, the convective effect depends on the flow and it is a good reason why the profiles differ. As you can see on the *Fig* 4, the wags of the pellets show noticeable difference.

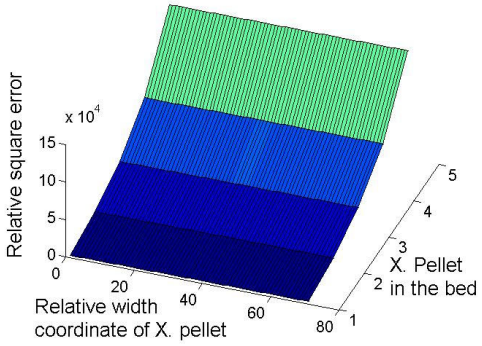


Fig. 8. Difference between the temperature profile (pellets diameter: 7e-4 m)

The temperature difference profile has significantly higher relative values, because there were very little differences between the max and min values.

By the theory, different concentration results in different reaction rate, and in case of a significantly exothermic reaction this difference appears in the temperature values.

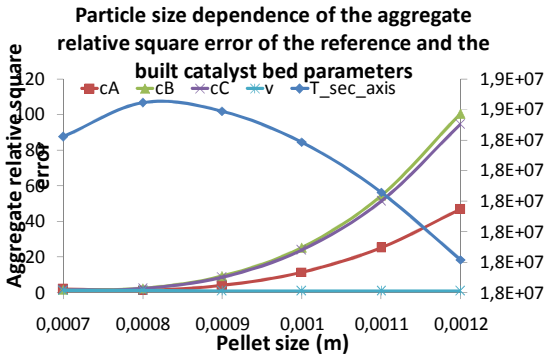


Fig. 9. Particle size dependence of the aggregate relative square error of the reference and the built catalyst bed parameters

6 different pellet diameters were examined. As *Fig* 9 shows, the aggregated error of the components is increasing with the pellet size, and aggregated error of the velocity and the temperature is decreasing with growing pellet size.

Conclusions

To monitor an operation of a tube reactor the process operators usually do not have much information, just some temperature measurements along the reactor and composition of inlet and outlet flows. Hence, a reactor simulator can be very useful to follow the operation and to help process operators, e.g. to avoid development of reactor runaways or to optimize reactor operation. The two dimensional model of catalyst pellet with its close surroundings was implemented into COMSOL Multiphysics. This pellet model can be utilized to design the shape and diameter distribution of catalyst pellets, to get a closer look to specific locations of the catalyst bed, and to build a catalytic bed from them. The catalytic bed was implemented pellet by pellet and the validation of results has been started. Our vision is a flexible, pellet by pellet catalytic bed model, which can be used for the design, study and development of catalytic pellets and beds with reduced calculation cost. If we find the solution of the difference reduction, this network modelling system would be applicable for modelling tube systems with complex elements, for example flow meters, heaters etc. on a PC.

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