CFD studies of heterocatalytic systems

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I. INTRODUCTION

Nowadays development of flow field in process equipments is a key issue 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 modeling 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) in applied modeling technics and 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 modeling technics. In recent years many papers applying CFD technique to analyze some phenomena or to design a reactor have been published. The most frequently investigated phenomena 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] and intra-particle diffusion effects [9] too. 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 reactor. COMSOL Multiphysics can give an effective support since it can be applied to solve models which consist 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.

II. CASE STUDY

The simplest developed reactor models 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 models the state-variables are calculated along the catalyst bed. However the radial diffusion cannot be considered without expanding dimensions. 2D models take into consideration the geometry and the evolved flow field in the system. Since the geometry of the reactor is symmetrical some simplifications can be applied to decrease the necessary 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 in optimization of reactor efficiency [5,6]. The most complex developed model is the 2D, two-phase model. In this model both solid and gas phases are

considered. The detailed mathematical description of the pellet has been performed 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. Based on the modelling possibilities 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 modesl requires horrible hardware capacity.

III. PELLET MODEL

In our previous works, a quasi-single phase mathematical description of the reactor, and 2D models, which take 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. 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:

$$\frac{d\left(B^G \cdot c_i^G\right)}{dx} + \frac{d\left(B^G \cdot c_i^G\right)}{dy} = -D_i^G \frac{d^2 c_i^G}{dx^2} + + -D_i^G \frac{d^2 c_i^G}{dy^2} A^{GS} \cdot \beta_i^{GS} \cdot \left(c_i^S - c_i^G\right) \quad (1)$$

where B^G – flow rate of gas phase; i = {A; B; C}; c_i^G – concentration of i^{th}-component in gas phase; x – reactor length; D_i^G – diffusion coefficient of i^{th}-component in gas phase; A^{GS} – interface area between the gas and solid phase; β_i^{GS} – mass transfer coefficient between the gas and solid phase of i^{th}-component; c_i^S – concentration of i^{th}-component in solid phase. Of course the convective term in solid phase is missing:

$$D_i^S \frac{d^2 c_i^S}{dx^2} + D_i^S \frac{d^2 c_i^S}{dy^2} = -A^{GS} \cdot \beta_i^{GS} \cdot \cdot \left(c_i^S - c_i^G\right) + V^S \cdot \nu_i \cdot r \qquad (2)$$

where D_i^S – diffusion coefficient of i^{th}-component in solid phase; V^S – the volume of solid phase; ν_i – the stoichiometric coefficient of i^{th}-component; r – reaction rate which is calculated by the following correlation:

$$r = k_0 \cdot e^{-\frac{E_A}{R \cdot T^S}} \qquad (3)$$

where k_0 – preexponential factor; E_A – activation energy; R – ideal gas constant; T^S – temperature of solid phase. Terms in both equations are the same as those considered in component balances:

$$\rho^G \cdot c_p^G \cdot B^G \cdot \left(\frac{dT^G}{dx} + \frac{dT^G}{dy}\right) = A^{GS} \cdot \alpha^{GS} \cdot \cdot \left(T^S - T^G\right) - \lambda^G \cdot \left(\frac{d^2 T^G}{dx^2} + \frac{d^2 T^G}{dx^2}\right) \qquad (4)$$

where ρ^G – density of gas phase; c_p^G – heat capacity of gas phase; T^G – temperature of gas phase; λ^G – heat conduction coefficient in gas phase; α^{GS} – heat transfer coefficient between the gas and solid phase. And finally the heat balance of solid phase:

$$\lambda^S \cdot \left(\frac{d^2 T^S}{dx^2} + \frac{d^2 T^S}{dy^2} \right) = -A^{GS} \cdot \alpha^{GS} \cdot \cdot \left(T^S - T^G \right) + V^S \cdot r \cdot \left(-\Delta H_r \right) \qquad (5)$$

where λ^S – heat conduction coefficient in solid phase; ΔH_r – reaction heat. This is just a short description of model equations to show 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.

IV. 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 let you to modify the pellet model, and to build up a structure from them. As Figure 1 shown, the first pellet outlet properties are boundary averages, and these results became the next pellet inlet parameters.

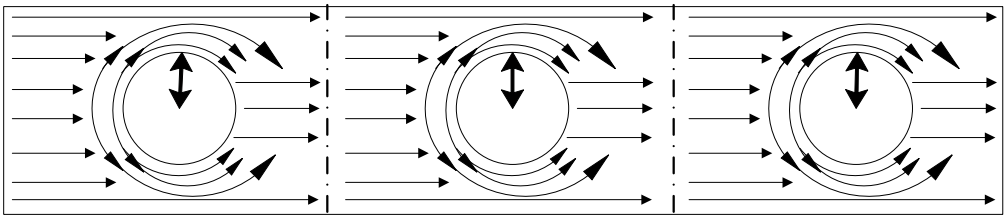


Figure 1. The visualization of the implemented pellet structure with average property connection

Then, the average outlet properties have been replaced with outlet profiles. Thus, it has become possible to take into account the effect of the established flow on the next pellet. Finally, a linear catalytic bed was built and the first investigations were conducted on it.

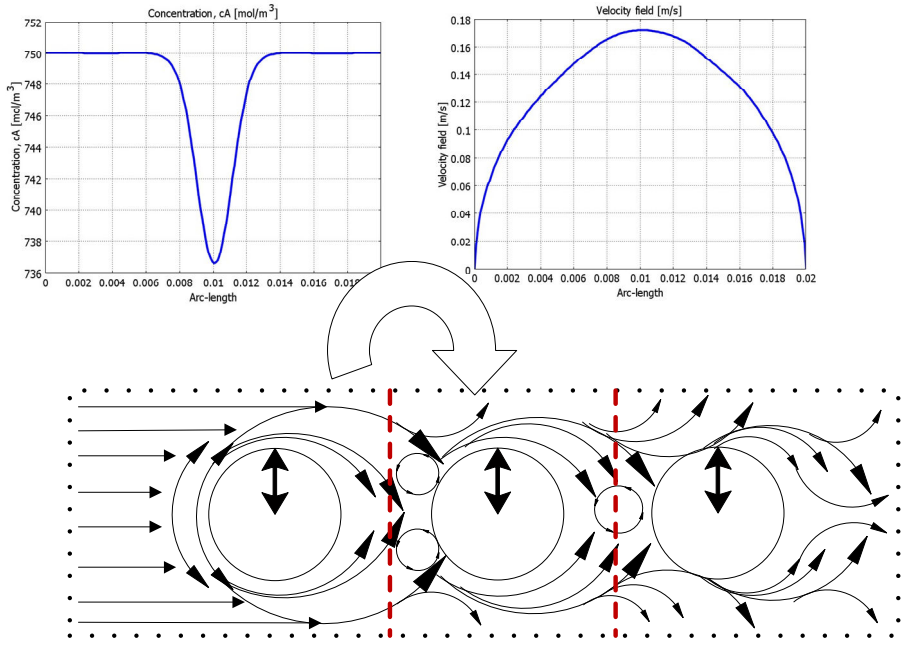
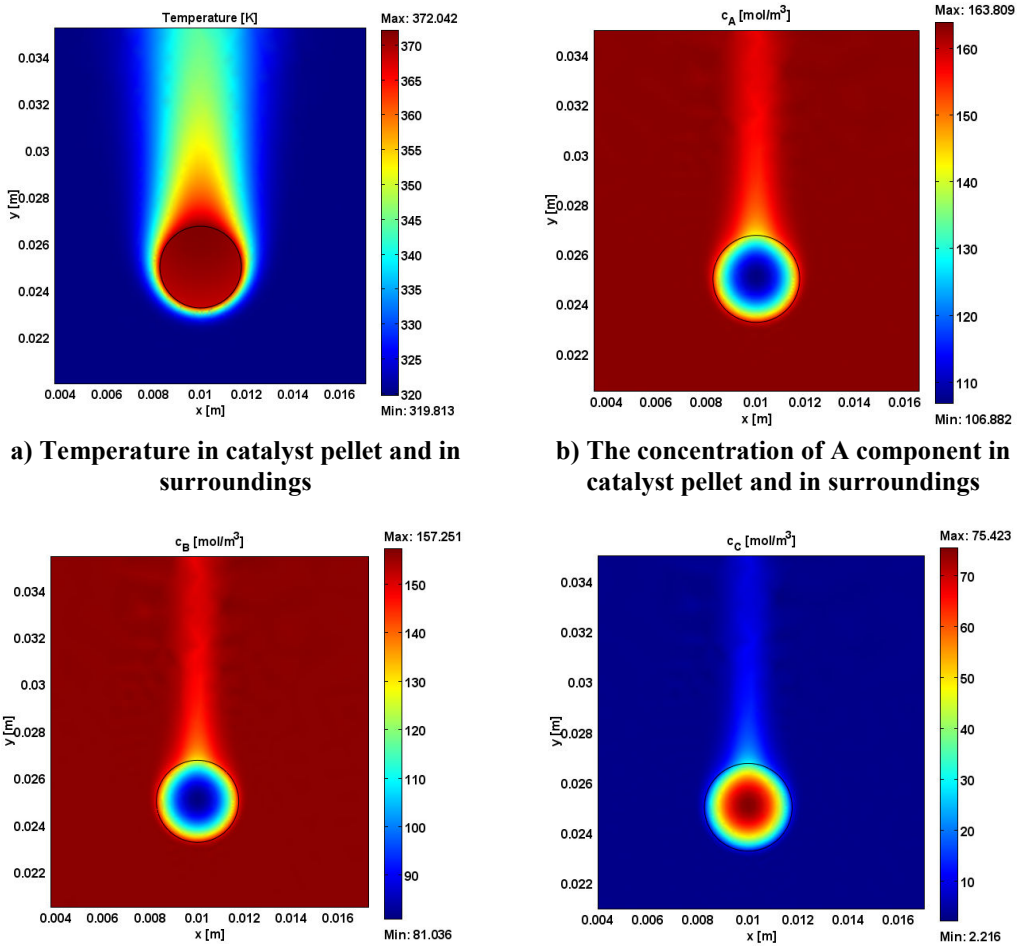


Figure 2. The visualization of the implemented pellet structure with property profile connection

V. RESULTS AND DISCUSSIONS

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

In Figure 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.



a) Temperature in catalyst pellet and in surroundings

b) The concentration of A component in catalyst pellet and in surroundings

c) Concentration of B component in catalyst pellet and in surroundings

d) Concentration of C component in catalyst pellet and in surroundings

Fig. 3: Changes in the value of state-variables along the investigated part of reactor in steady-state

Due to the diffusion in the catalyst pellet the concentration of reagents decrease in the direction to the centre of the pellet (see Figure 3.b and Figure 3.c); while the concentration of the product changes in the opposite direction as shown in Figure 3.d.

In this model all components can be connected to the same active sites on the catalyst, however in practise there is a competition between components and the 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.

As it can be seen in Figure 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 characteristic of changes in case of all the calculated state variables are the same as we expected.

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 analysed. In this investigation the first structute (see Figure1) was used. The number of pellets was increased at near constant catalytic volume. Experiments presented in literature [11] suggest the smaller the pellets are, the better the conversation/volume index is. Figure 4 and 5 show the reagent and Figure 6 the product concentration along the bed. As the number of particles is increasing higher and higher conversion can be achieved. Due to the exothermic reactions the temperature will be higher in the outlet than in the inlet. Figure 7 show that the temperature has a nearly linear relationship with the conversion.

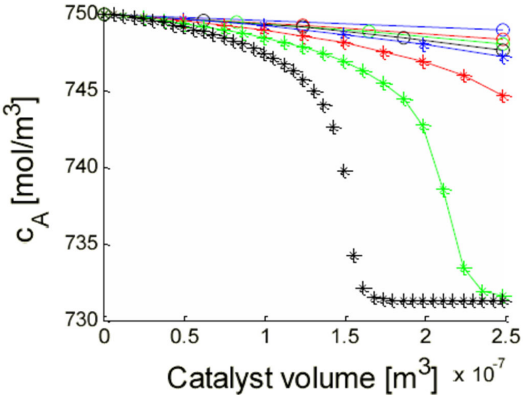


Figure 4. The concentration of A component in the catalytic bed

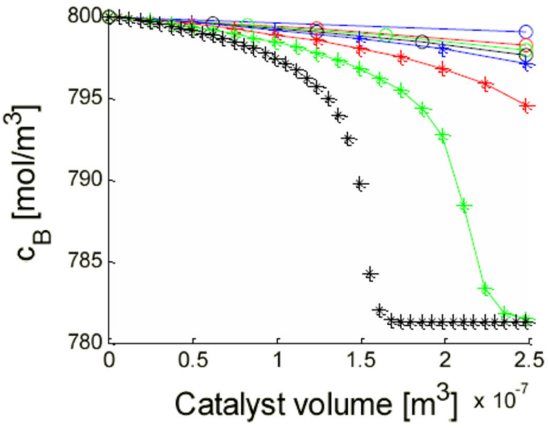


Figure 5. Concentration of B component in the catalytic bed

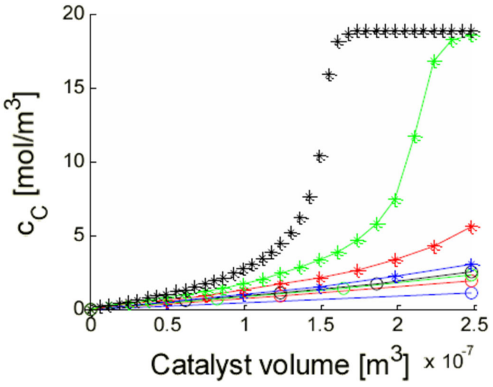


Figure 6. Concentration of C component in the catalytic bed

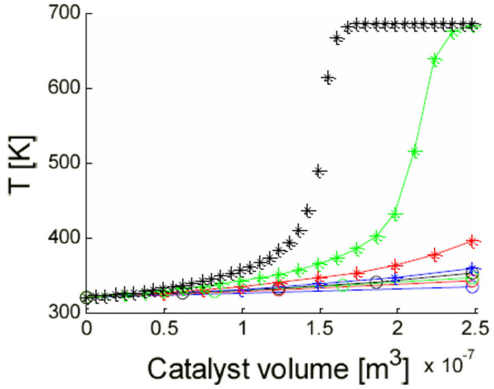


Figure 7. Temperature in the catalytic bed

VI. CONCLUSIONS AND FUTURE WORK

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 utilised to design the shape and size 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 result of the first tests fullfilled the expectations. 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.

VII. ACKNOWLEDGEMENT

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