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IMPROVING THE MATHEMATICAL MODEL OF A HETEROCATALYTIC TUBE REACTOR

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In recent decades the applicability and usefulness of mathematical models in the solution of many industrial problems have been shown. There are many cases when the correct answer can not be given because of the complexity of the problem however CFD approaches can be applied to dig deeper and improve the reliability of results. In this work the improvement of the first-principle model of a tubular fixed-bed reactor is shown applying COMSOL Multiphysics. Mathematical models of tubular fixed bed catalytic reactors to simulate their operation are well known and the formulation of such models is well documented. In most cases the aim of modeling is the development of the simpliest model which can be applied to solve the modeling task. However, nowadays these modeling problems can be more complicated and require more accurate models, e.g. in case of model based diagnostic systems, early detection systems. After the model with the adequate complexity was developed it must be solved with the necessary accuracy. In general, as the complexity of the model increases, so does the chance of encountering numerical difficulties. Our purpose is to apply the most appropriate software methodology to solve problems at each level of the model hierarchy, therefore a proccess model of an industrial heterocatalytic reactor has been extended with integrating transport processes on micro level. The idea is the integration of a model of a single catalyst pellet implemented in COMSOL Multiphysics into the steady-state process simulator of the reactor developed in MATLAB. The proposed approach makes possible to develop the model of a whole catalyst bed from the particle models. The first step to accomplish our purpose is the implementation of the pellet model in the applied CFD code. Then the pellet model can be integrated into the process simulator at the higher model hierarchy level.

Keywords: heterocatalytic tube reactor, mechanistic modeling, computational fluid dynamics, catalyst pellet

Introduction

The aim of all production technologies is formation of a more valuable material through some chemical reactions. The reactor is a place where reactions generally take place. Hence, a reactor must be able to convert the necessary amount of raw materials into products with desired quality in given amount of time. A chemical technology can not be imagined without a reactor consequently the design process of a reactor has a really important role in generating a well profitable technology. Furthermore the planing of instrumentation and optimization of operating variables is also crucial. Main steps in development of a well functioning reactor are the following:

- defining desired performance of reactor operation;
- collecting all a prior information and physical constraints;
- determining and/or investigating velocity field in the reactor;
- assigning all operating variables.

Nowadays development of flow field in process equipments is a key issue in planning of process unit. With a well designed flow field the overall process performance and safety of operation can be increased at the same time. To support this step, different modeling softwares 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 methods has significantly grown since the first computer was switched on [1].

CFD is 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. Coupling of mathematical models of different physical and chemical processes with efficient numerical solvers makes possible to analyze chemical engineering and other kind of engineering problems in much more details. Of course, as in other modeling technics, CFD models must be validated before it can be used to predict the behavior of invesigated system. Validation of models is based on comparing simulation results with measured variables, i.e. developing an adequate CFD model, because of the complexity of model, needs well-designed and precisely carried out experiments.

In recent years many papers applying CFD technics to analyze some phenomenon or to design a reactor have been published. The most frequently investigated phenomenon are the transport processes between a stationary and a moving phase, or two moving phases, such as heat transfer [2] and mass transfer [3] in a fluidized bed. Another interesting field of application of CFD models is the modeling of bubble columns [4-8]. CFD models can be applied not only in reactor and column design but in solving other kind of engineering problems, e.g. designing a protective suit [9]. These examples show that CFD is capable to simulate transport processes and it can be applied as a part of complex mathematical model.

In this paper the concept of a detailed mathematical model of an industrial used heterocatalytic reactor will be introduced. The former version of reactor model was applied in a Operator Support System [10] to support process operators in choosing appropriate values of important operating variables to keep the production in safe and efficient regime. To improve the accuracy of our reactor model mass and heat transfer processes between solid catalyst pellets and moving gas are considered. In previous investigations a small difference was noticed between the characteristic of measured and calculated temperature profiles but model relability couldn't be furher improved without increasing model complexity. However, to improve our quasi-single phase model solid phase and all coupled transport processes are considered.

Our idea is the integration of the model of a single catalyst pellet implemented in COMSOL Multiphysics into the steady-state process simulator of the reactor developed in MATLAB. The proposed approach makes possible to build up catalyst bed from particles which have different size. The first step to accomplish our purpose is the implementation of the pellet model in the applied CFD code. Then pellet model can be integrated into the process simulator at the higher model hierarchy level. After short introduction regarding the most frequently applied CFD codes and some CFD application examples in model development the investigated case study is presented, than simulation results obtained at this level of work are evaluated and finally conclusions are drawn and future steps are outlined.

Case study

Our approach is to apply the most appropriate software to solve problems at each level of model hierarchy, therefore a mathematical model of an industrial heterocatalytic reactor was developed with integrating processes at the level of thermodynamic phases.

Reactor model

The investigated, vertically positioned reactor contains a large number of tubes filled with catalyst as shown in *Fig. 1.* A highly exothermic reaction takes place as reactants are rising up in tubes passing through the fixed bed of catalyst particles while generated heat by reaction is removed through tube walls by cooling media. The reaction has equalibrium and since temperature is increasing in reactor more and more product decomposed. Due to the highly exothermic reaction it has a great chance to develop hot spots somewhere in catalyst bed which increase the rate of catalyst ageing. Direction of the flow of cooling media is not important in this process because there is only 7-8 K difference between the inlet and outlet temperature of cooling media. Selection of appropriate operating conditions is important to avoid the development of reactor runaway and to increase lifetime of catalyst.

The investigated reactor is a heterocatalytic tube reactor where gas phase is the moving phase while catalyst is the stationary phase. In our previous work a quasi-single phase mathematical description of the reactor was introduced [10]. Since model accuracy couldn't be improved without increasing model complexity the quasi-single phase must be divided into solid and gas phases as it shown in *Fig. 2.* State variables are calculated in both phases which are coupled by mass and heat transport processes. As it can be seen at components level in Fig. 2 the reaction is considered only in solid phase so the produced heat by the highly exothermic reaction is removed by cooling media in jacket.

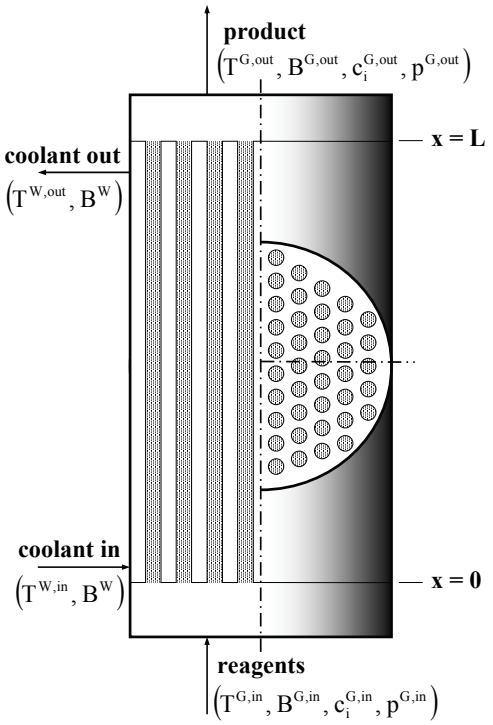


Figure 1: Simplified scheme of reactor

As it can be seen in the model structure in Fig. 2 process variables calculated in two phases in the tubes. Thermodynamic phases are coupled by mass and heat transport processes. Steps of the assumed overal process are summarized in *Fig. 3.* First steps, the adsorption of reagents take place simultanously and it is called competitive adsorption because two components are competing to get to the same active sites on the surface

of the catalyst. After both reagents adsorb a second order reaction takes place and generates the product which leaves the surface of catalyst by desorption process. Developed model calculates changes only along the reactor, i.e. model is one dimensional and it doesn't consider the diffusivity along the radius of catalyst bed. Before the introduction of model equations some simplifications must be considered to simplify the real problem. These simplifications are summarized as follows:

- gas and solid phases are considered in tubes, which are connected by the mass and heat transport processes;
- highly exothermic, second order reaction takes place in solid phase;
- diffusivity along radius of the reactor is neglected;
- all catalyst pellets have the same size and spherical shape;
- to calculate pressure drop in catalyst bed a modified Ergun-equation is applied.

A steady-state model based on the overall rate of all mass transport processes and reaction with detailed description of applied simplifications can be found in [10]. That model was solved in MATLAB and calculated temperature profiles were compared to measured ones in order to determine missing model parameters. It was concluded that accuracy of developed model was appropriate, although some minor differences could be experienced between characteristics of calculated and measured profiles. To further improve model accuracy, overall rate was substituted for by a CFD model of a catalyst pellet to simulate basic steps introduced in Fig. 3. Steady-state reactor model is not introduced in this paper, a detailed description can be found in [10].

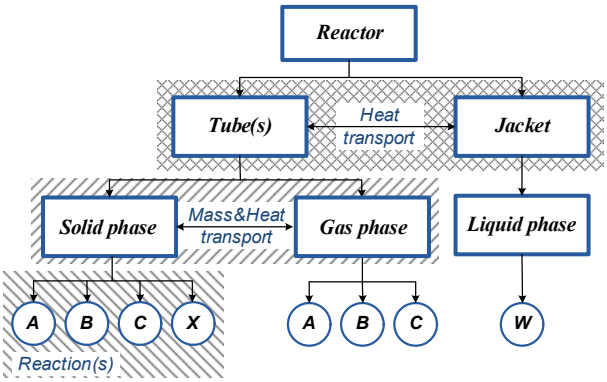


Figure 2: Structure of two phases model

Our concept is the integration of a catalyst pellet model implemented in COMSOL Multiphysics into the reactor simulator developed in MATLAB. The first step to accomplish our objective is the implementation of pellet model in the applied CFD code. As it can be seen in Fig. 2 processes at the micro level can be simulated and developed CFD model can be integrated into higher hierarchy level.

COMSOL is more than just a software which uses a CFD code because mathematical models of many processes in different area of science are collected and classified; consequently the necessary time to solve an engineering problem is less than with applying other CFD software. COMSOL applies the finite element method [1] to discretize the investigated object and to solve model.

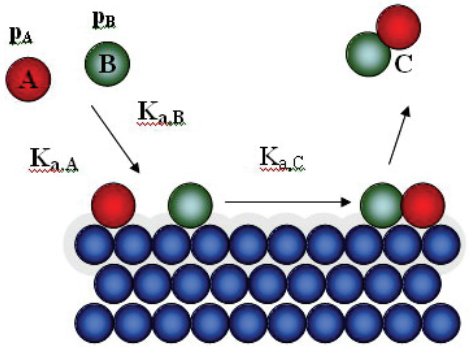


Figure 3: Basic steps of the assumed overall process

Catalyt pellet model in COMSOL Multiphysics

The first step of model building in COMSOL is the selection of the necessary correlations from the model collection. Of course there is a possibility to introduce new correlations. To investigate complex geometries an interactive graphical interface helps the user to define it or the user can import it from a CAD software.

Our COMSOL model contains only one catalyst pellet with the narrow surroundings of the particle. The surrounding is flowing around the pellet and the transport processes make the connection between two phases. MATLAB simulator runs this simulator and builds the whole catalyst bed. Difference between each pellet is considered by changing boundary conditions before solving the pellet model. To describe the whole catalyst bed the MATLAB simulator of the reactor evaluates boundary conditions based on the position of the acual pellet in the catalyst bed. Because of the axial symmetry of tubes and the spherical symmetry of the catalyst pellet the COMSOL model is two dimensional.

Based on the introduced simplifications and the introduced pellet model the following equations were applied to calculate the state variables in both phase. 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:

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

where

B^G – flow rate of gas phase;
c_i^G – concentration of i-component in gas phase; $i = \{A; B; C\}$;
x – reactor length;
D_i^G – diffusion coefficient of i-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-component;
c_i^S – concentration of i-component in solid phase.

Of course the convective term in solid phase is missing:

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

where

D_i^S – diffusion coefficient of i-component in solid phase;

V^S – the volume of solid phase;

ν_i – the stoichiometric coefficient of i-component;

r – reaction rate which is calculated by the following correlation:

$$r = k_0 \cdot e^{-\frac{E_A}{R \cdot T^S}} \cdot \left(c_A^S \cdot c_B^S - \frac{c_C^S \cdot c_X^S}{K} \right),$$

where

k_0 – preexponential factor;

E_A – activation energy;

R – ideal gas constant;

T^S – temperature of solid phase;

c_x^S – concentration of active sites on catalyst;

K – reaction eqaulibrium constant which is a function of the temperature.

As it can be seen in the last equation the effect of temperature on reaction rate is considered therefore changes of temperature of gas and solid phase are calculated too. Terms in both equations are the same as those considered in component balances:

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

where

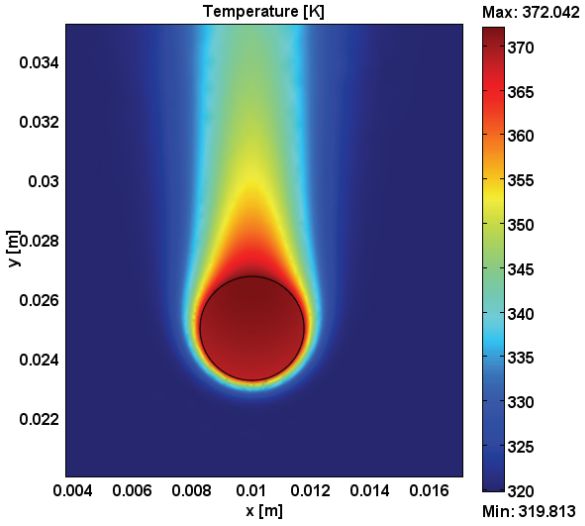
ρ^G – density of gas phase;

$c_G{}^G$ – heat capacity of gas phase;

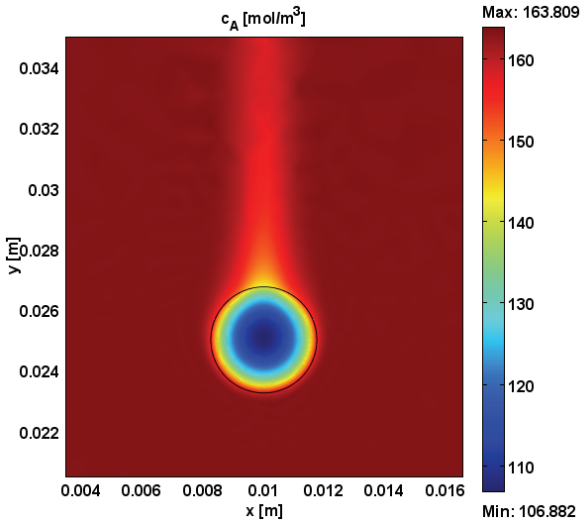
T^G – temperature of gas phase;

λ^G – heat conduction coefficient in gas phase;

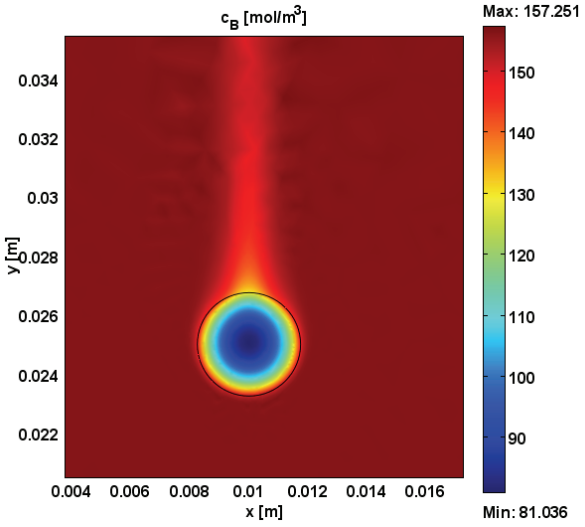
α^{GS} – heat transfer coefficent between the gas and solid phase.



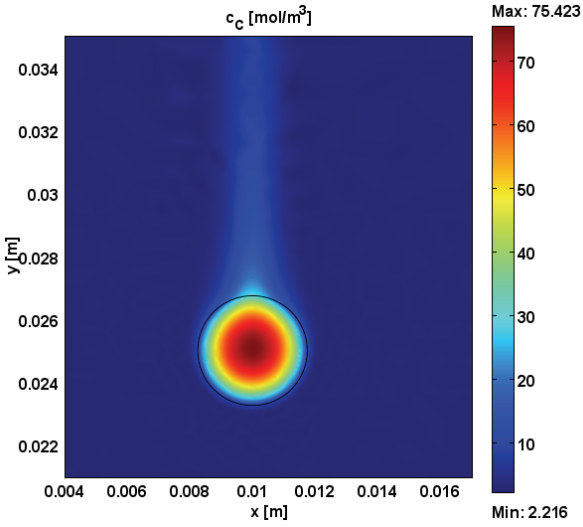
a) Temperature in catalyst pellet and in surroundings



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

Figure 4: Changes in the value of state-variables along the investigated part of reactor in steady-state

And finally the heat balance of solid phase:

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

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 eqautions were implemented in COMSOL to develop a pellet model which replaces the reaction rate of overall catalyst processes of earlier developed reactor simulator. Integration of reactor simulator made in MATLAB and the pellet model implemented in COMSOL is just a vision yet, still as it can be seen in next chapter that pellet model gives good results.

Results and discussions

To check the applicability of the developed COMSOL Multiphysics pellet model in our modeling approach, the value of state variables in front of reactor were given as boundary conditions in the solution of the pellet model. Generated results are plotted in *Fig. 4*.

In Fig 4a temperature surface can be seen and as it was expected the highly exothermic reaction taking place in catalyst increases the temperature of pellet and it warms up the flowing gas. Due to the diffusion in catalyst pellet the concentration of reagents decrease in the direction to the centre of the pellet (check Fig. 4b and Fig. 4c.) while the concentration of the product changes in the opposite direction as shown in Fig. 4d.

In this model all components can be connected to the same active sites on the catalyst but in reality there is a competition between components and the rate and the equalibrium of the adsorption determine the concentration in the catalyst. Since the temperature profile and properties of inlet and outlet flow are measured during the reactor operation the catalyst pellet model can not be validated without integrating it into the reactor simulator.

As it can be seen in Fig. 4d the outlet concentration of product from the investigated part of the reactor is very low and it 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.

Conclusions and future work

To follow an operation of a tube reactor usually process operators do not have any more information but some temperature measurements along the reactor and composition of inlet and outle flow. Hence, a reactor simulator can be very useful to follow the operation and to help process operators, e.g. to avoid development of reactor runaway or to optimize reactor operation. To achieve this aim an adequate reactor model with correct model parameters is needed. The paper proposed a possible way to improve a former developed mathematical model of a heterocatalytic tube reactor applied in the process industry to detect reactor runaway.

At this phase of our work applicability of COMSOL Multiphysics in modeling a catalyst pellet and its narrow surroundings is investigated. The developed model and the applied software can be applied to generate and simulate state variables in the whole catalyst bed.

Integration of pellet model into an earlier developed reactor simulator is our next step. After the success integration a model validation must be performed comparing the calculated temperature profiles with the measured ones. Finally the accurate model can be built into an operator support system to improve reliablility of runaway detection.

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