Numerical investigation of the granule size effect on the reaction product yield in a catalyst fixed bed

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Numerical investigation of the granule size effect on the reaction product yield in a catalyst fixed bed

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Abstract. The research work presents the results of mathematical modeling of the ethylbenzene dehydrogenation process to styrene in a fixed catalyst bed. Calculations for the different length granule packaging are carried out. Calculated values of the reaction product yield (styrene) are in a wide range of gas velocities. There are significant differences in the yield of the product at high gas velocities for catalyst granules of different shapes. Of the considered catalyst granules forms, we got the best yield efficiency by the use of granules, which provide maximum surface area and porosity in the fixed bed catalyst.

1. Introduction

Catalytic processes with a fixed bed widely use in the chemical industry. Despite numerous developments in the field of application of structured packings catalyst [1], the random arrangement of granules is of particular interest, since such an arrangement presence in modern reactors. Accounting for the heterogeneity of the bed structure based on numerical modeling and experimental studies of chemical processes in cylindrical reactors was carried out in [2, 3]. Impressive results were obtained based on the averaged model and semi-empirical correlations.

Expanding the classical approach using the concepts of medium-radial porosity and medium-radial velocity profiles, the authors of [4-7] took into account the strong influence of the bed structural properties on heat and mass transfer as a whole. However, the use of such an average model may be incorrect if there are only a few granules in the reactor's cross section. For such cases, axial symmetry is not fulfilled, and it is impossible to describe local phenomena by the averaged model. Detailed research is possible using 3D-model [8]. The authors of [9] take into account the local features of the full three-dimensional structure of the fixed bed without simplification under the assumption of symmetry.

The primary requirement for conducting detailed numerical modeling is the creation of the porous structure geometry consisting of randomly spaced granules. To create a numerical model, use X-ray computed tomography data or magnetic resonance imaging methods as one of the suitable methods for creating a raster three-dimensional geometry image. These methods make it possible to digitize the geometry of existing samples, but do not allow the creation of environments with predetermined

parameters of a porous medium. Creating the porous medium geometry based on the Monte Carlo method, or the method of a separate element ("distinct element method" - DEM) allows to create a geometry with predetermined properties (size, granule shape, porosity), and, if necessary, print out objects in 3D the printer.

Detailed modeling has shown that the use of averaged flow models in porous media is often incorrect. To determine the model correctness in the case of direct numerical simulation, conduct experimental studies of the gas movement inside a porous medium created by a computer model using three-dimensional printing.

Optimization of a fixed catalyst bed chemical reactors is often carried out by numerical simulation using computational fluid dynamics (CFD) since in most cases hydrodynamics affect the course of a chemical reaction [11-13]. CFD modeling is based on the fundamental conservation laws of mass, momentum, energy and does not depend on the types of reactors and their scales, which allows us to consider multiscale phenomena occurring in reactors [10-12, 14].

In [15, 16], a detailed numerical study of the pressure drop during the gas flow through spherical granules randomly based on CFD modeling was performed. They compared the results obtained for different geometries and flow rates with the experimentally obtained dependencies. Finally, velocity and pressure fields calculated from CFD simulations are further used to interpret the differences between CFDs and empirical dependencies to determine the pressure drop value.

In this work, we constructed a mathematical model of the ethylbenzene dehydrogenation reaction to styrene in a fixed bed catalyst. The granular bed bases on the DEM. A granule model represents cylinders of different sizes. A comparative analysis of the catalyst granules shape and size influence on the reaction product yield is carried out by numerical simulation. The calculations were carried out in a wide gas velocity range, allowing us to estimate the product yield, both for laboratory installations and industrial reactors.

2. Mathematical models

2.1. Mathematical model of packing fixed catalyst bed granules

For the Eulerian-Eulerian approach, we write down the conservation laws for mass, momentum, and
The main methods of creating geometry with elements randomly located in space are the Monte Carlo method and the DEM, which is actively used to model bulk media with non-spherical granules. In the case of the fixed bed geometry creation, the use of the Monte Carlo method may be incorrect, since it does not take into account the additional forces acting on the granule, they must be connected separately. The DEM is a numerical method for solving problems that require a description of the bulk media mechanics. Presented in [17], DEM was developed to analyze the problems of rock movement using deformable polygonal blocks and then applied to soils [18].

We considered the dynamic process in which the flow velocity depends on the physical properties of a discrete system, and assumed that the speed and acceleration are constant in each time step. The solution scheme is identical to the scheme used by the explicit finite difference method. The DEM based on the idea that the selected time step can be so small that during a single time step, the disturbances cannot spread farther from any particle than its immediate neighbors. Then the forces acting on any particle at any time step are determined solely by its interaction with the particles with which it contacts. Since the rate at which a disturbance can propagate is a function of the discrete system physical properties, it is possible to calculate the time step to satisfy this constraint. The use of an explicit (as opposed to implicit) numerical scheme allows one to simulate the nonlinear interaction of a large number of particles without excessive requirements for RAM, as well as an iterative procedure.

The calculations performed by the DEM method alternate with the application of Newton's second law to particles and the law of the displacement force at the contact area. Newton's second law is used to determine the motion of each particle arising from the contact and volume forces acting on it, while

the law of displacement force is used to update the contact forces arising from the relative motion in each contact area. In this case, there is a constant update of the position of the walls coordinate.

At the beginning of each time step, the set of contacts updates relative to the known positions of the particles and walls. Then, for each contact, the force law of displacement is applied to update the contact forces based on the relative motion between two objects in the contact and the contact model. Then the motion law is applied to each particle in order to update its speed and position based on the resultant force and moment arising from the contact forces and other forces acting on the particle. Also, the position of the walls is updated depending on the specified velocity of the walls.

Fig. 1 shows a constructing example package of cylindrical catalyst granules for a model of a laboratory reactor 3 cm in diameter. The bed height is 4.6 cm, the granule diameter is 3 mm, and the granule length is 6 mm. After falling into the flask of the reactor, the granules are in a random order. This approach imitates well the poured catalyst granules in a laboratory reactor, as well as in a large-scale industrial reactor.

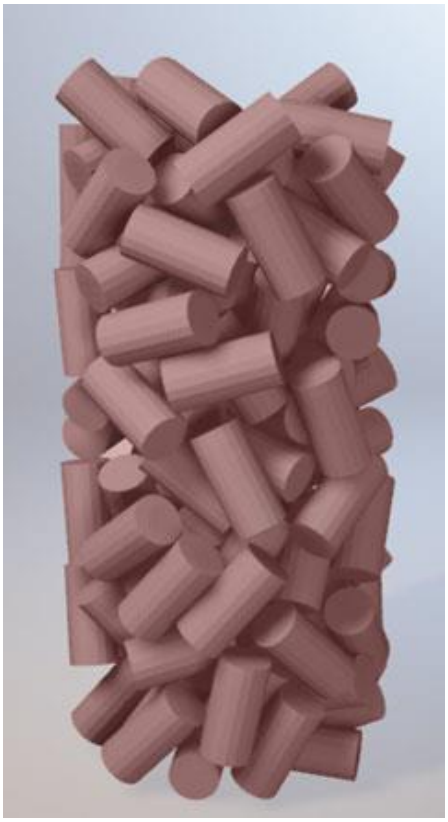

Figure 1. Packing model of cylindrical granules

2.2. Mathematical model for calculating the dynamics of the gas movement and heat and mass transfer processes

The described mathematical problem was solved by the finite volume method with a grid partition of the considered reactor region. For a multicomponent gas phase, the conservation laws of mass, momentum, and energy are satisfied. In the study of this problem, the following equations we solved.

The mass conservation equation for the gas phase:

$$\frac{\partial \rho_g}{\partial t} + \nabla \cdot \left(\rho \vec{v} \right) = 0, \tag{1}$$

where ρ is gas density, $\vec{v}$ is gas velocity.

The momentum conservation equation for the gas phase

$$\frac{\partial \rho \vec{v}}{\partial t} + \nabla \cdot \left(\alpha \rho \vec{v} \vec{v} \right) = -\nabla p + \nabla \cdot \bar{\bar{\tau}} + \rho \vec{g}, \tag{2}$$

where p is pressure, $\bar{\bar{\tau}}$ is gas phase stress tensor. In equation (2), the stress tensor

$$\bar{\bar{\tau}} = \mu \left(\nabla \vec{v} + \nabla \vec{v}^T \right) + \frac{2}{3} \mu \nabla \cdot \vec{v} \bar{\bar{I}}, \tag{3}$$

where μ is shear viscosity, $\bar{\bar{I}}$ is unit tensor.

The energy conservation equation for the gas phase

$$\frac{\partial \rho h}{\partial t} + \nabla \cdot \left(\rho \vec{v} h \right) + \nabla \cdot \vec{J} = \frac{\partial p}{\partial t} + \bar{\bar{\tau}} : \vec{v} \tag{4}$$

where h is gas enthalpy, $\vec{J}$ is diffusion flux, which arises due to gradients of concentration and temperature.

We divided the entire computing area of the reactor into finite elements of a triangular shape, the dimensions of which are sufficient to determine the characteristic factors of the phenomenon under study. In the calculations carried out in this paper, the typical number of finite elements ranged from 35,000,000 to 40,000,000 elements. Fig. 2 shows an example of a grid partition of the computational domain under consideration.

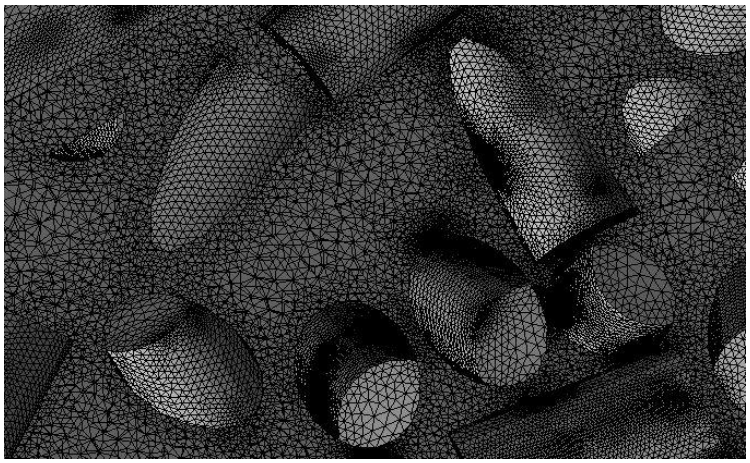

Figure 2. A grid partition example of a computational domain

To numerically solve the problem of hydrodynamics and heat and mass transfer in a catalyst fixed bed reactor for the ethylbenzene dehydrogenation to styrene, we need to specify conditions at the boundaries of the considered region. We set the boundary conditions following the mechanisms of operation of the calculated laboratory reactor and the solver used at all boundaries of the computational domain. So, we set the impenetrable wall condition on all impermeable surfaces, and a temperature equal to the temperature of the reactor heated walls on the outer wall of the area under consideration. At the site of the gas flow in the model of the reactor were set conditions for the gas mass flow. At the site in the reactor model, the conditions for external pressure outside the area under consideration we set for the gas outlet.

The considered gas phase flow is considered a multicomponent ideal incompressible gas consisting of raw material (ethylbenzene), water vapor, and the reaction products (styrene and hydrogen).

2.3. Mathematical model of the chemical reaction kinetics of the ethylbenzene dehydrogenation to styrene

The primary reaction of this process is the ethylbenzene dehydrogenation to styrene. Under the dehydrogenation understand the chemical processes associated with the elimination of hydrogen atoms from organic compounds. Dehydrogenation reactions are reversible, strongly endothermic, occurring with an increase in volume due to hydrogen evolution.

$$C_8H_{10} \leftrightarrow C_8H_8 + H_2 - Q. \tag{5}$$

For surface reactions, the rate of adsorption and desorption is determined both by chemical kinetics and by diffusion to and from the surface.

Consider the theoretical information from chemical kinetics used to build the model. The chemical reaction rate is usually known as the change in the amount of a substance reacting or resulting from a reaction per unit of time per unit volume.

$$\sum_i v_i B_i = \sum_j u_j A_j, \tag{6}$$

$$w = \frac{1}{V}\frac{dn}{dt} = \frac{dc}{dt},\ V = const, \tag{7}$$

where n is the number of moles, c is volume-mole or volume-molecular concentration of a substance.

In the case when the stoichiometric equation (6) of a simple reaction of type (7) is known, to determine the reaction rate should be in the form uniquely:

$$w = \frac{1}{v_i V}\frac{dn_i}{dt} = \frac{1}{u_k V}\frac{dn_k'}{dt},\ V = const, \tag{8}$$

where v_i and u_k refer to the stoichiometric coefficients of the starting materials and reaction products, respectively.

The central postulate of chemical kinetics says: "The rate of chemical reaction (with constant volume) is proportional to the product of current concentrations of the initial substances, raised to some degree."

$$w = -\frac{1}{v_i}\frac{dc_i}{dt} = \frac{1}{u_j}\frac{dc_j}{dt} = k\prod_i c_i^{p_i}. \tag{9}$$

The order and the molecular reaction. The numbers p_i in equation (10) are called reaction orders by substance, and their sum is called reaction order.

$$\sum_i p_i = n. \tag{10}$$

For reactions of type (6) the molecular is

$$v = \sum_i v_i. \tag{11}$$

In the case of elementary (one-step) reactions, the molarity coincides with its order. Thus, the molarity of the considered reaction (5) and its order are equal to unity: $v = 1$ and $n = 1$.

The general dependence of the rate constant on temperature gives the Arrhenius equation:

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2}, \tag{12}$$

where E_a is activation energy.

$$\ln k = -\frac{E_a}{RT} + const, \tag{13}$$

$$k = A\exp\left(\frac{-E_a}{RT}\right). \tag{14}$$

3. Results

Consider the model of a laboratory reactor for a granular catalyst bed for the ethylbenzene dehydrogenation to styrene. For comparison, we construct two models of cylindrical granule packages: 6 mm in length and 9 mm in length. The granule diameter is 3 mm. The granules are poured into a cylindrical flask with a diameter of 2.8 cm and are 4.6 cm in height. At the same time, longer granules can form larger free areas in which gas will move without contact with the catalyst surface.

Under laboratory conditions on small-sized reactors in the reaction of ethylbenzene dehydrogenation to styrene, the average velocity of the raw materials mixture and water vapor can be in the order of 0.1 m/s. In this case, for example, in industrial radial-type reactors, the average gas velocity can be in the order of 10 m/s. Therefore, we will perform calculations for a wide range of gas velocities.

Verification of the mathematical model was carried out for laboratory experiments with an average gas velocity of about 0.1 m/s. The product yield on the experimental setup ranged from 66-70%. The results of numerical calculations are presented in fig. 3.

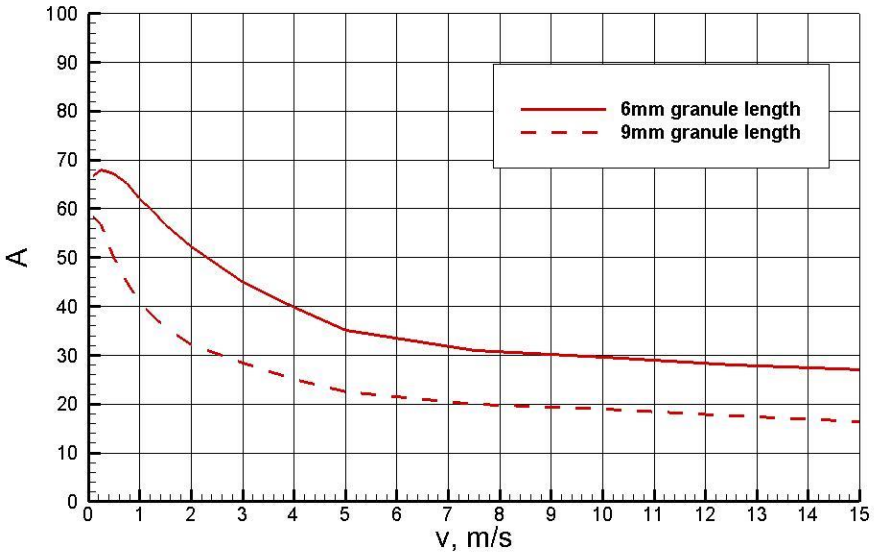

Figure 3. The calculated yield of the product depending on the gas velocity for cylindrical pellets

There is a significant decrease in product yield at high gas velocities, and this is due to the decrease in the time of gas contact with the catalyst granule surface. The use of larger granules allows for a lower yield of the dehydrogenation reaction product. Thus, the granule size and porosity of the catalyst bed can have a significant impact on the yield of the reaction product.

Fig. 4 shows the fields of mass fraction of the reaction product (styrene) for calculations at a gas velocity: (a) - 0.1 m/s, (b) - 15 m/s.

At a higher gas velocity due to the short time of gas contact with the surface, the mass fraction of the reaction product decreases significantly with increasing gas velocity.

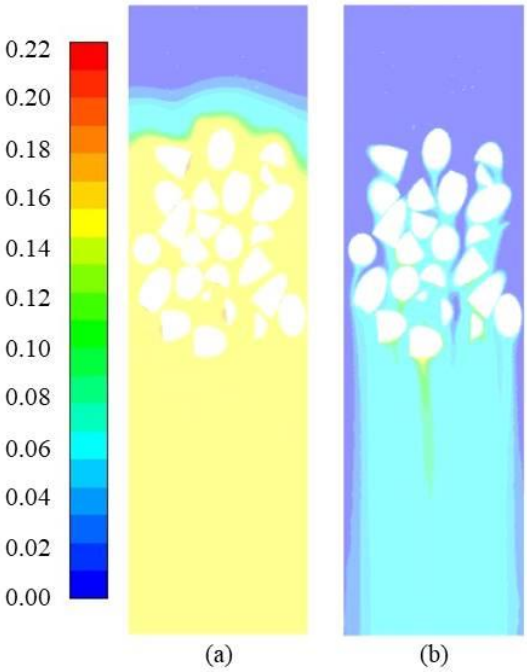

Figure 4. Mass content of styrene in the reactor near the cylindrical catalyst granules.

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