Numerical investigation of the ethylbenzene dehydrogenation reaction in a fixed bed reactor with catalyst granules of various sizes

S A Solovev¹,², O V Soloveva¹, B Sh Gilmurahmanov² and A A Lamberov²

¹ Kazan State Power Engineering University, Krasnoselskaja st. 51, Kazan, 420066, Russia
² Kazan Federal University, Kremlevskaja st. 18, Kazan, 420008, Russia

E-mail: solovev.sa@kgeu.ru

Abstract. In this work, we get a numerical simulation analyzes the effect of catalyst granule size on the operation efficiency of the fixed bed reactor for the dehydrogenation of ethylbenzene to styrene. For the laboratory reactor, we built a detailed model of cylindrical catalyst granules with a length of 3 mm, 6 mm and 9 mm. We carried out an analysis of the granule size effect on the bed characteristics, such as porosity and the catalyst total surface area. We obtained results for a wide range of feed gas rates. The ranges and rates of the catalyst efficiency decrease for different feed gas rates are determined.

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 advanced reactors.

Researchers of [2] carried out a detailed numerical simulation of the gas flow in the granular layer including the chemical reaction. The calculation of a chemical reaction is a computationally expensive task. An additional complication is the presence of contact points when packing bodies in models of the granular layer. They lead not only to the presence of zero cells in the grid partition but also to an excessive number of grid elements. The smallest cell size determines the number of elements since the lack of a smooth transition to cell size can lead to significant computation errors. The authors of [3] use the bridge method to simulate a reaction on the surface of the granules in order to save computational resources. In many modern graphics editors and computational packages, when constructing geometry and grid partitioning, code optimizes the geometry by the fact that a more significant number of polygons lie in the same plane. The work [4] demonstrates such grid optimization.

Most researchers investigate chemical processes in the package of various shape granules. Authors of [5] consider heat transfer in the packaging of solid cylinders. In paper [6] was studied the flow in a layer of hollow cylinders. Authors of [7] calculate the velocity field, temperature fields, and the reaction rate in the
fixed bed reactor. As for the shape of granules, in [8] was considered the heat exchange in a reactor with spherical granules. Researchers of [9] made the hydrodynamic calculations in the region with stacked pellet shape.

Since most reactions in the chemical industry are exothermic, it is necessary to prevent overheating in the contact zones of the granules and on their surface. The solution to this problem can be the use of open cell foam material as a catalyst carrier. Authors of [10] investigate the flow in a bed composed of cubes of open cell foam material. In such a geometry, there is global and local porosity, which increases convection, reducing overheating in the reactor. The use of such structures in the reactor is promising.

In this work, we constructed a mathematical model of the ethylbenzene dehydrogenation reaction to styrene in a fixed bed catalyst, the granular bed. 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. Problem formulation and solution methods

2.1. Experimental setup

The process of ethylbenzene dehydrogenation to styrene in a fixed bed granular catalyst reactor is carried out on an iron-oxide catalyst in the gas phase. To shift the reaction equilibrium towards product formation, ethylbenzene is mixed with water vapor.

We based our studies on experimental results. Testing of the catalyst for the reaction of ethylbenzene dehydrogenation to styrene is carried out in an isothermal flow type reactor. The ethylbenzene dehydrogenation reaction is primary, and the following equation describes proceeds with the heat absorption and an increase in the volume of gaseous products

\[ C_8H_8C_6H_5CH_2CH_2 \leftrightarrow C_8H_8 + H_2 - 124.8 \text{kJ/mol.} \]

Activity indicators are styrene yield to missed ethylbenzene (activity - $A$), and decomposed ethylbenzene (selectivity - $S$) is calculated based on chromatographic analysis data. The formula (2) calculates the activity

$$ A = \frac{C_{\text{out}}^{\text{C8H8}}}{C_{\text{in}}^{\text{C8H10}}} \times 100, $$

where $C_{\text{out}}^{\text{C8H8}}$ is a mass fraction of styrene at the outlet (% mass.), $C_{\text{in}}^{\text{C8H10}}$ is mass fraction of ethylbenzene in raw materials (% mass.), $C_{\text{in}}^{\text{C8H8}}$ is a mass fraction of styrene in raw materials (% mass.).

The formula calculates the selectivity

$$ S = \frac{C_{\text{out}}^{\text{C8H8}}}{C_{\text{in}}^{\text{C8H10}}} \times 100, $$

where $C_{\text{out}}^{\text{C8H10}}$ is a mass fraction of ethylbenzene at the outlet (% mass.).

The experimental test result is taken as the average of 10 definitions. The discrepancy between the minimum and maximum values should not exceed 2.5% for the indicator yield of styrene on the missed ethylbenzene and 1.5% for an indicator of the yield of styrene on decomposed ethylbenzene. The obtained average values are $A = 69.1$, $S = 95.27$.

2.2. Numerical Simulation
The described problem was solved by the finite volume method with grid partitioning of the considered reactor domain. The flow is considered stationary. For a multicomponent gas phase, the conservation laws of mass, momentum, and energy are satisfied.

The mass conservation equation

\[ \nabla \cdot (\rho \vec{v}) = 0, \quad (4) \]

where \( \rho \) is the density, \( \vec{v} \) is the velocity.

The momentum conservation equation

\[ \nabla \cdot (\rho \vec{v} \vec{v}) = -\nabla p + \nabla \cdot \mathbb{T} + \rho \ddot{\vec{v}}, \quad (5) \]

where \( p \) is the pressure, \( \mathbb{T} \) is the stress tensor.

The mass conservation equation for the \( i \)-th component of the gas mixture

\[ \nabla \cdot (\rho_i \vec{v}_i) = -\nabla \cdot \vec{J}_i + R_i, \quad (6) \]

where \( Y_i \) is the mass fraction for the \( i \)-th component of gas mixture, \( R_i \) is the net rate of production of \( i \)-th species by chemical reaction, \( J_i \) is the diffusion flux of \( i \)-th species, which arises due to gradients of concentration and temperature.

\[ \vec{J}_i = -\rho D_{m,i} \nabla Y_i - D_{T,i} \frac{\nabla T}{T}, \quad (7) \]

where \( T \) is the temperature, \( D_{m,i} \) is the mass diffusion coefficient, \( D_{T,i} \) is the temperature diffusion coefficient.

The energy conservation equation

\[ \nabla \cdot (\rho_i h_i) + \nabla \cdot (\vec{J}_q) = \frac{\partial \vec{H}}{\partial t} + \mathbb{D} : \vec{v}, \quad (8) \]

where \( h = \sum_{i=1}^{N} Y_i h_i \) is the gas enthalpy, and

\[ \vec{J}_q = \lambda \nabla T + \sum_{i=1}^{N} h_i \vec{J}_i, \quad (9) \]

where \( \lambda \) is the thermal conductivity of mixture, \( N \) is a number of components in the mixture.

For chemical reactions, the term \( R_i \) in equation (6) is

\[ R_i = M_i \sum_{j=1}^{N_R} R_{i,j}, \quad (10) \]

where \( M_i \) is the molecular mass for \( i \)-th component, \( N_R \) is a number of reactions involving the \( i \)-th component of the mixture.

\[ R_{i,j} = \nu_k \prod_{j=1}^{N} [C_j]^n \prod_{j=1}^{N} [D_j]^m, \quad (11) \]
where \( r \) is the stoichiometric coefficient, \( C_j \) is the concentration of the \( j \)-th component of mixture, \( \eta_r \) is the rate exponent for reactant \( j \)-th species in reaction, \( k_r \) is the reaction rate constant.

\[
k_r = A_r e^{-E_r/RT},
\]

where \( A_r \) is the pre-exponential coefficient, \( E_r \) is the activation energy.

For the numerical solution of the problem, the entire area under consideration is divided into finite elements of a triangular shape, the dimensions of which are sufficient to determine the specific factors of the phenomenon under study. To numerically solve the problem of hydrodynamics and heat and mass transfer in the reactor of a fixed catalyst bed of ethylbenzene dehydrogenation to styrene, we need to specify conditions at the boundaries of the considered region (figure 1).

![Figure 1. The scheme of the calculated domain.](image)

The considered flow of the gas phase (at a temperature of 600°C) is considered to be a multicomponent ideal incompressible gas consisting of raw materials (ethylbenzene and water vapor) and reaction products (styrene and hydrogen). The physicochemical properties of the components are given according to the polynomial dependence on temperature.

3. Results

Consider a model of a laboratory reactor for a granulated catalyst bed for the dehydrogenation of ethylbenzene to styrene 4.5 cm in height and 2.8 cm in diameter. 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 of the order of 0.1 m/s. In this case, for example, in industrial radial-type reactors, the average gas velocity can be of the order of 5 m/s. Therefore, we will carry out calculations for a wide range of gas velocities. The verification of the mathematical model was carried out
for laboratory experiments with an average gas velocity of the order of 0.1 m/s. The yield of the product in the experimental setup for granules with a length of 3 mm averaged 69.1%.

Figure 2 shows the calculation results for a layer consisting of granules 3 mm, 6 mm and 9 mm long. Results are given for velocity of 1 m/s. It is evident, that when moving through a bed of short granules, the gas flow flows around all the granules without the formation of fast broad flows. When flowing through long granules, there is a large number of fast, full gas flows between the granules. In such flows, the gas is not in contact with the surface of the catalyst, which reduces the efficiency of the layer of granules.

Figure 3 presents the results of numerical calculations of the yield of the reaction product (styrene) for the entire investigated range of gas velocities and sizes of cylindrical catalyst granules.

Figure 2. The mass fraction of styrene in the reactor near the cylindrical catalyst granules with a length: a - 3 mm, b - 6 mm, c - 9 mm.

Figure 3. Calculated activity depending on gas velocity.
For granules with a length of 3 mm, it is evident that the yield of the product is maintained at a level of 66-70% in the gas velocity range up to 1 m/s. Further, there is a decline in values of up to 40%. At this, calculations for granules with a length of 6 mm show that maintaining a substantial yield of the product is possible only up to gas velocities of 0.5 m/s, then a decrease is observed. Calculations for granules with a length of 9 mm show a significant decrease in the yield of the product from a gas velocity of 0.1 m/s.

Let analyze the average surface bed area of the granules and the bed porosity. It is evident that the highest surface area of the catalyst and the smallest porosity should have granules of 3 mm in length since they are located in the bed more compactly. Table 1 shows the results of averaged calculations for 5 packs of a granules bed of each length.

The table shows that the differences in characteristics between the case of 3 mm and 6 mm granules are more significant than the differences in characteristics between the case of 6 mm and 9 mm granules. However, from figure 3 it can be seen that the differences in the product yield are more significant between the cases of 6 mm and 9 mm than between the cases of 3 mm and 6 mm; this suggests that not only the geometric parameters of the granules contribute to the efficiency of the catalyst bed. The volume of the empty zones formed between the granules and the hydrodynamics of the gas flow movement also have a significant effect, which together affects the contact time of the raw material molecules with the surface of the catalyst granules.

| Table 1. The dependence of the bed characteristics from the granule length. |
|-----------------------------------------------|
| Granule length, mm | 3 | 6 | 9 |
| Bed average surface area in the reactor, cm² | 19.2 | 15.3 | 12.2 |
| The average bed porosity in the reactor | 0.41 | 0.43 | 0.45 |

4. Conclusion
Thus, the granule size and the porosity of the catalyst bed can have a significant impact on the yield of the reaction product for an example of the process of dehydrogenating ethylbenzene to styrene using cylindrical catalyst granules. The granules show the best efficiency since they form a bed with the largest surface area and the lowest porosity. At the same time, in the package of such granules, the formed voids have small volumes and do not contribute to the formation of through gas flows without contact with the catalyst surface. The change in the efficiency of the catalyst when the size of the granules is evaluated. For the considered region and the reaction, the most significant differences are observed at gas velocities from 1 m/s to 2 m/s.

Acknowledgments
This work was supported by the Ministry of Science and Higher Education of the Russian Federation under the state contract No. 074-11-2018-030.

References
[1] Calis H P A, Nijenhuis J P B C, Paikert B C, Dautzenberg F M and Van Den Bleek C M 2001 Chem. Eng. Sci. 56 (4) 1713
[2] Wehinger G D, Eppinger T and Kraume M 2015 Chem. Eng. Sci. 122 197
[3] Rebudhini S, Cuoci A and Maestri M 2016 Chem. Eng. Sci. 141 240
[4] Partopour B and Dixon A G 2017 Powder Technol. 322 258
[5] Zhang M, Dong H and Geng Z 2018 Chem. Eng. Res. Des. 132 149
[6] Dong Y, Geske M, Korup O, Ellenfeld N, Rosowski F, Dobner C and Horn R 2018 Chem. Eng. J. 350 799
[7] Dong Y, Sosna B, Korup O, Rosowski F and Horn R 2017 Chem. Eng. J. 317 204
[8] Das S, Deen N G and Kuipers J A M 2017 Chem. Eng. Sci. 160 1
[9] Pavlišič A, Pohar A and Likozar B 2018 Powder Technol. 328 130
[10] Das S, Deen N G and Kuipers J A M 2018 Chem. Eng. J. 334 741