

Numerical simulation of the isoparaffins dehydrogenation in a bidisperse fluidized bed

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Abstract. We built a mathematical model and carried out a numerical simulation for the reaction of isoparaffins dehydrogenation in a fluidized-bed reactor using the example of dehydrogenating isobutane to isobutylene. Experimental data determine the parameters for the construction of the model. Numerical studies with the choice of the average diameter for the polydisperse catalyst were conducted. We performed the calculations for cases of the monodisperse and bidisperse composition of particles, carried out the analysis of the influence of the fine particles present on the reaction product yield in the numerical simulation.

1. Introduction

Fluidized bed reactors are used in the chemical and oil refining industry and the gasification of coal and biomass [1-3]. Reactors are widespread due to the high-efficiency properties of heat and mass transfer.

Mathematical modeling of fluidization generally bases on the Eulerian-Lagrangian and Eulerian-Eulerian approaches. Researchers consider the solid phase as discrete particles in the Eulerian-Lagrangian approach (for example, [4, 5]). In the Eulerian-Eulerian approach, the primary phase and the discrete phase are as continuous. To take into account the interaction of particles in the fluidized bed, by analogy with the kinetic theory of gases, an equation was added describing the change in the kinetic energy of the particles due to their collisions (for example, [6]). This approach is less demanding in terms of computational resources and requires discretization of particle characteristics. Discretization can be carried out using a multi-group approach, the essence of which is to divide the domain of definition into groups of diameters and assign them to correspond some value of the cumulative distribution function that characterizes the fraction of the group in the particle bed. The transport equations are solved for each group separately. The works [7-9] demonstrate a multi-group approach to simulate a fluidized bed. In [10], the method of taking into account polydispersity can affect the hydrodynamic characteristics of the flow obtained by numerical simulation.

We have considered the isoparaffins dehydrogenation on the example of the isobutane dehydrogenation process to isobutylene. Isobutylene is an essential monomer for petrochemical synthesis. On its basis, a wide range of products is obtained, such as synthetic rubbers, films, fibers,

high-octane components of automobile gasoline. The primary process for the production of isobutylene is the isobutane dehydrogenation in a catalyst fluidized bed.

2. Problem formulation and mathematical models

It is necessary to build a model for the isoparaffins dehydrogenation in a fluidized bed reactor. The model based on the example of the isobutane dehydrogenation to isobutylene reaction in the presence of a chromium-aluminum catalyst.

We verify mathematical models with experimental data. For the fluidized bed hydrodynamic models, the experimental setup is a glass tube with an internal diameter of 2.2 cm (fig. 1). The porous material is at the bottom of the tube, which ensures a uniform flow of air supplied from the compressor. We measured the volumetric flow at the outlet of the tube using a rotameter, filmed the process of fluidization on a high-speed camera, and estimated the bed height by frames.

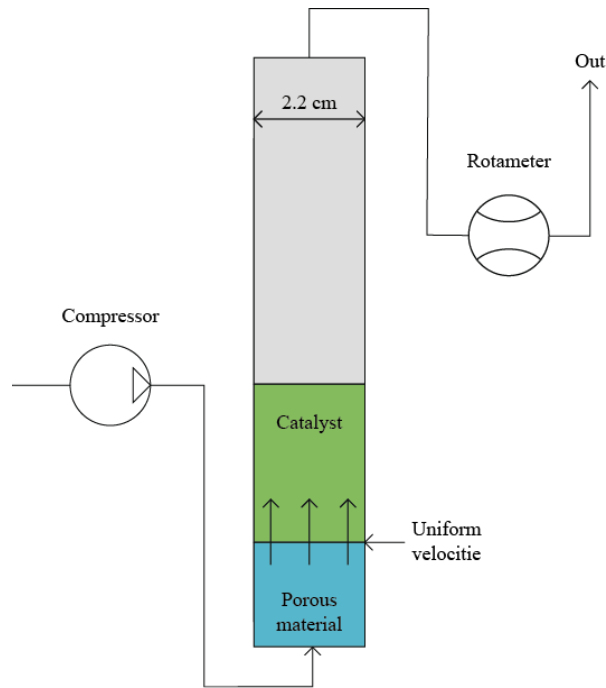


Figure 1. The scheme of the experimental setup

In order to verify the constructed mathematical model of the isobutane dehydrogenation to isobutylene in a fluidized bed reactor, we conducted experimental studies at a high-temperature reactor. The experimental setup is an insulated metal tube with an inner diameter of 3 cm. A 75-ml catalyst is poured into the tube. At the bottom of the tube is a porous material to ensure a uniform flow of raw gas (isobutane). Around the metal case are electric heaters that maintain the temperature of 570°C. We performed an analysis of contact gas at the tube outlet. For the experiment under consideration, the product yield is $45 \pm 2\%$.

2.1. Fluidized bed mathematical model

For the Eulerian-Eulerian approach, we write down the conservation laws for mass, momentum, and energy.

The mass conservation equation for gas or solid phase:

$$\frac{\partial \alpha_i \rho_i}{\partial t} + \nabla \cdot (\alpha_i \rho_i \vec{v}_i) = 0, \quad (1)$$

where α_i is volume fraction, ρ_i is density, \vec{v}_i is velocity.

The momentum conservation equation for gas phase:

$$\frac{\partial \alpha_g \rho_g \vec{v}_g}{\partial t} + \nabla \cdot (\alpha_g \rho_g \vec{v}_g \vec{v}_g) = -\alpha_g \nabla p + \nabla \cdot \bar{\bar{\tau}}_g + \alpha_g \rho_g \vec{g} + \sum_j K_{gj} (\vec{v}_g - \vec{v}_j), \quad (2)$$

where p is pressure, $\bar{\bar{\tau}}_g$ is stress tensor for the gas phase, K_{gj} is interfacial interaction coefficient between gas phase and j -th discrete solid phase. In equation (2), the stress tensor is

$$\bar{\bar{\tau}}_g = \alpha_g \mu_g (\nabla \vec{v}_g + \nabla \vec{v}_g^T) + \alpha_g \frac{2}{3} \mu_g \nabla \cdot \vec{v}_g \bar{\bar{I}}, \quad (3)$$

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

The momentum conservation equation for solid phase:

$$\frac{\partial \alpha_s \rho_s \vec{v}_s}{\partial t} + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \vec{v}_s) = -\alpha_s \nabla p - \nabla p_s + \nabla \cdot \bar{\bar{\tau}}_s + \alpha_s \rho_s \vec{g} + \sum_j K_{sj} (\vec{v}_s - \vec{v}_j), \quad (4)$$

where p_s is granule pressure in a solid phase, $\bar{\bar{\tau}}_s$ is stress tensor for solid phase, K_{sj} is interfacial interaction coefficient between the solid and j -th gas or solid phases. In equation (4), the stress tensor is:

$$\bar{\bar{\tau}}_s = \alpha_s \mu_s (\nabla \vec{v}_s + \nabla \vec{v}_s^T) + \alpha_s \left(\lambda_s - \frac{2}{3} \mu_s \right) \nabla \cdot \vec{v}_s \bar{\bar{I}}, \quad (5)$$

where μ_s, λ_s is shear and bulk viscosity.

The energy conservation equation for gas or solid phase:

$$\frac{\partial \alpha_i \rho_i h_i}{\partial t} + \nabla \cdot (\alpha_i \rho_i \vec{v}_i h_i) = \alpha_i \frac{\partial p_i}{\partial t} + \bar{\bar{\tau}}_i : \vec{v}_i + \sum_j Q_{ij}, \quad (6)$$

where h_i is enthalpy, Q_{ij} is heat transfer between the i -th and j -th phases.

The equation for the solid phase granule temperature [11]:

$$\frac{3}{2} \left[\frac{\partial}{\partial t} (\alpha_s \rho_s \Theta_s) + \nabla \cdot (\alpha_s \rho_s \vec{v}_s \Theta_s) \right] = \left(-p_s \bar{\bar{I}} + \bar{\bar{\tau}}_s \right) : \nabla \vec{v}_s + \nabla \cdot (k_{\Theta_s} \nabla \Theta_s) - \gamma_{\Theta_s} + \phi_{sg}, \quad (7)$$

where k_{Θ_s} is the granule energy diffusion coefficient; Θ_s is solid phase granule temperature; γ_{Θ_s} is energy dissipation from particle collisions; ϕ_{sg} is energy exchange between solid and gas phases.

The considered question's system is not closed. To close the system, use the models from [6, 13, 14]. For calculations, a dispersion turbulence $k - \varepsilon$ model was used. We solve the written system of differential equations in the ANSYS Fluent software package.

2.2. Average particle size mathematical model

We verified the mathematical model with experimental data. In the experiment, the catalyst is a polydisperse system of alumina microspherical particles belonging to the Geldart B group according to the classification. The curve of the particle size distribution function $f(D)$ is shown in fig. 2

Let us consider several ways of choosing the number and particle size for numerical simulation using the Eulerian-Eulerian approach. When conducting numerical calculations to save computational resources, as a rule, choose only one average particle diameter. One way to select the average diameter is to determine the mode on the particle size distribution curve $f(D)$

$$D_{\text{mod}} = \arg \max_D (f(D)). \quad (8)$$

To calculate the fluidized bed apparatus, it is also customary to use the mean Sauter diameter.

$$D_{32} = \frac{\int_0^{\infty} f(D) D^3 dD}{\int_0^{\infty} f(D) D^2 dD}. \quad (9)$$

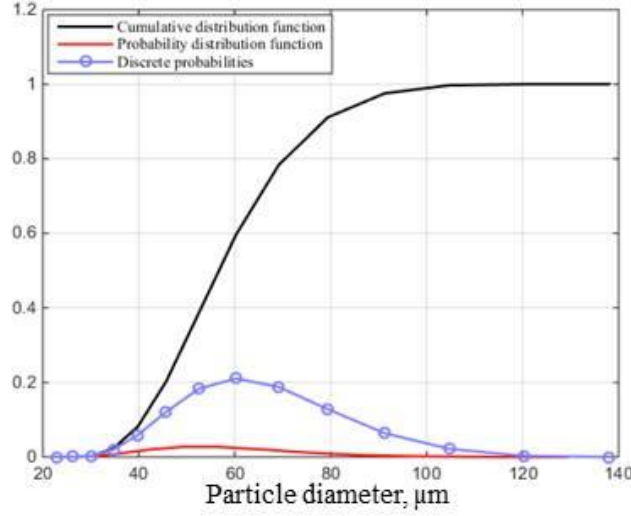


Figure 2. Particle characteristics

A detailed analysis of the effective diameter selection based on the balance of forces acting on a particle in a fluidized bed was carried out in [10]. Several fluidization regimes are considered, such as inertial, creeping, and intermediate. Resistance to gas flow for a single spherical particle [15]

$$F_D = \frac{1}{2} \rho_g v_{rel}^2 C_D A, \quad (10)$$

where $v_{rel} = v_s - v_g$ is relative gas velocity around the particle, A is relative area (area of body projection on the plane). In the case of spherical particle

$$A = \frac{1}{4} \pi D^2. \quad (11)$$

We introduce an additional effective diameter over the related area [16]. Let us consider the resistance force of a spherical particle in the form (10), taking into account the sectional area (11). Also, let us consider the expectation A_{av} for a particles mixture with a density distribution of particle diameter $f(D)$:

$$A_{av} = \frac{1}{4} \pi \int_0^{\infty} f(D) D^2 dD. \quad (12)$$

Equating (11) and (12) we find the effective particle diameter D_{eff} for the mixture:

$$D_{eff} = \left(\int_0^{\infty} f(D) D^2 dD \right)^{0.5}. \quad (13)$$

The choice of the fractions number and the particle size play an essential role in the behavior of the fluidized bed. In some cases, the addition of fine particles leads to bed expansion and an increase in the porosity of the dense phase [17-20]. However, in other cases, the addition of these particles leads to a decrease in solid-phase porosity [21, 22].

We select the fraction of coarse and fine particles for a bidisperse particles mixture. As a criterion for fine particles, we consider the terminal velocity

$$v_t = \left(\frac{4gD(\rho_p - \rho_f)}{3\rho_f C_D} \right)^{0.5}. \quad (14)$$

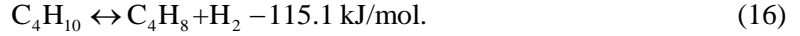
Let the diameter D_s of a particle under the action of gravity and resistance is in equilibrium. Then particles with a diameter less than D_s will be carried away by the flow, and particles with a larger diameter D_s will tend downwards.

For polydisperse particles, the following conditions we recommend for choosing effective diameters [16]:

$$D_{32} \leq D_{eff} \leq D_{mod} . \quad (15)$$

2.3. Chemical reaction mathematical model

The primary reaction of this process is the isobutane dehydrogenation. 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.



For the mathematical model, we define the chemical reaction rate constant. The Arrhenius equation gives the general dependence of the rate constant on temperature:

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2}, \quad (17)$$

where E_a is activation energy.

$$\ln k = -\frac{E_a}{RT} + const, \quad (18)$$

$$k = A \exp\left(\frac{-E_a}{RT}\right). \quad (19)$$

The parameters of the reaction rate constant and activation energy are obtained from experimental data carried out on high-temperature isobutane dehydrogenation reactors.

In the industrial process of isobutane dehydrogenation, along with the target reaction (16), a number of side reactions also take place, for the simulation was selected only one main reaction (16) taking place in the block.

The volume-mole concentration of the source substance, expressed in terms of the hydrodynamic characteristics of the flow, can be written as follows:

$$c = \frac{m_{C_4H_{10}}}{M_{C_4H_{10}} V_r} = \frac{\rho_{mixture} \cdot V_r \cdot Y_{C_4H_{10}}}{M_{C_4H_{10}} \cdot V_r} = \frac{\rho_{mixture} \cdot Y_{C_4H_{10}}}{M_{C_4H_{10}}}, \quad (20)$$

where $m_{C_4H_{10}}$ is isobutane mass, $M_{C_4H_{10}}$ is isobutane molar mass, V_r is the volume in which the reaction takes place, $Y_{C_4H_{10}}$ is isobutane mass concentration, $\rho_{mixture}$ is density for a mixture of isobutane, isobutylene, and hydrogen.

The model of an ideal incompressible gas determine the density of the mixture:

$$\rho_{mixture} = \frac{P}{RT \sum_i \frac{Y_i}{M_i}}, \quad (21)$$

where P is the pressure of a mixture, M_i is the molar mass of i -th component, R is universal gas constant, T is the temperature of a mixture, Y_i is the mass concentration of the i -th component.

Using the law of mass action and the Arrhenius equation, we obtain expressions characterizing the mass transfer from isobutane to isobutylene and hydrogen,

$$w_{C_4H_{10}} = k \cdot \rho_{mixture} \cdot Y_{C_4H_{10}} \cdot f(\alpha), \quad (22)$$

$$w_{C_4H_8} = \frac{M_{C_4H_8}}{M_{C_4H_{10}}} \rho_{mixture} \cdot Y_{C_4H_{10}} \cdot f(\alpha), \quad (23)$$

$$w_{H_2} = \frac{M_{H_2}}{M_{C_4H_{10}}} \rho_{mixture} \cdot Y_{C_4H_{10}} \cdot f(\alpha). \quad (24)$$

The function expresses the dependence of the reaction rate on the amount of catalyst:

$$f(\alpha) = \frac{\alpha}{\alpha_{max}}, \quad (25)$$

where α is catalyst volume fraction, α_{max} is maximum catalyst volume fraction.

3. Results

For numerical calculations, we used the fluidized bed model with a new effective diameter. We performed the calculations for the cases of a monodisperse and bidisperse catalyst. Fig. 3 shows pictures of the catalyst particles volume fraction in a reactor model. Gas velocity is 0.1 m/s.

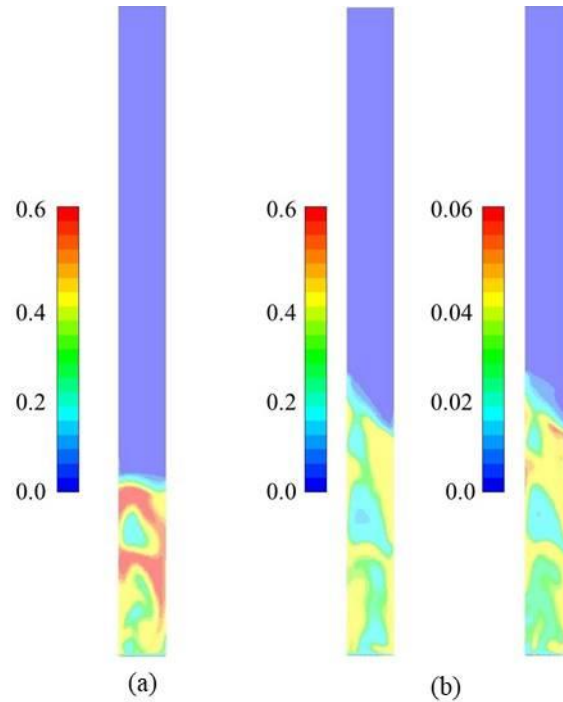


Figure 3. The catalyst particles volume fraction in the reactor tube: a - calculation of the monodisperse catalyst, b - calculation of the bidisperse catalyst.

For the case of the bidisperse catalyst, the particle bed is significantly higher, and the volume fraction is smaller. Also fig. 3b shows the field of the volume fraction of fine particles on a scale ten times smaller than the scale for coarse particles. Fine catalyst particles are not separated in the bed, and clots and rarefied zones correspond to the behavior of coarse catalyst particles.

Fig. 4a shows the gas temperature patterns in the reactor for the calculation of a monodisperse and bidisperse catalyst. The absorption of heat in the case of the bidisperse particles is more significant than of the monodisperse particles. It indicates a higher intensity of the chemical reaction that goes with the heat absorption.

Fig. 4b shows pictures of the mass fraction of the reaction product (isobutylene) in the reactor model for calculating the monodisperse and bidisperse catalysts. The reaction product is formed in the

zone where the catalyst circulates, and in the upper part of reactor model the mass fraction of isobutylene does not change.

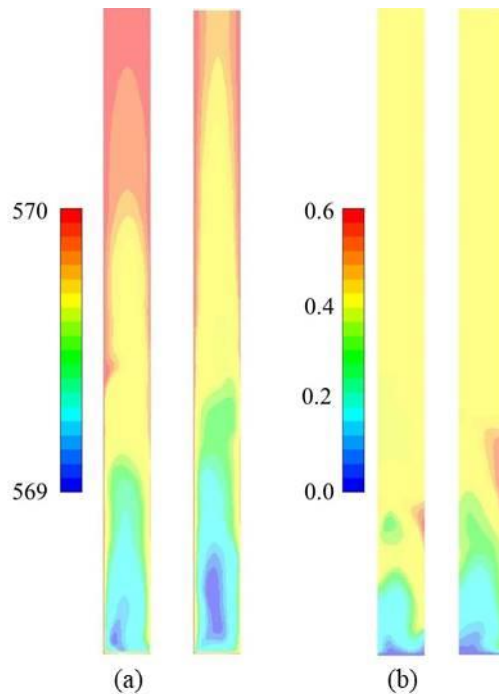


Figure 4. a - the gas temperature (°C), b - the mass fraction of the reaction product.

From the analysis of the calculations, we found that the product yield was: for the case of calculating the monodisperse catalyst - 45.43%, for the case of calculating the bidisperse catalyst - 43.69%. Thus, taking fine particles into account when modeling fluidized bed reactors can have a significant impact on the calculation results.

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