PAPER • OPEN ACCESS

Mathematical modeling of isoparaffins dehydrogenation in fluidized bed reactor

To cite this article: S A Solovev and O V Soloveva 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **537** 062073

View the article online for updates and enhancements.

Mathematical modeling of isoparaffins dehydrogenation in fluidized bed reactor

S A Solovev[1] and O V Soloveva[2]

[1]Institute of Digital Technologies and Economics, Kazan State Power Engineering University, Krasnoselskaya st. 51, Kazan, 420066, Russian Federation
[2]Institute of Heat Power Engineering, Kazan State Power Engineering University, Krasnoselskaya st. 51, Kazan, 420066, Russian Federation

E-mail: solovev.sa@kgeu.ru

Abstract. A mathematical model has been built and a simulation has been carried out for the isoparaffins dehydrogenation reaction in a fluidized bed reactor using the example of isobutane dehydrogenation to isobutylene. The parameters for the model construction are determined on the basis of experimental data. Conducted numerical studies with the selection of the average diameter for the polydisperse catalyst. The calculations were performed for cases of monodisperse and bidisperse composition of particles. The analysis of the influence of the fine particle presence on the yield of the reaction product in the numerical simulation has been carried out.

1. Introduction
Fluidized bed reactors are used in the chemical and petrochemical 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 is based on the Eulerian-Lagrangian and Eulerian-Eulerian approaches. The solid phase is considered as discrete particles in the Eulerian-Lagrangian approach (for example, [4, 5]). In the Eulerian-Eulerian approach, the carrier (gas, liquid) and the discrete (solid) phase are considered continuous. To take into account the particles interaction in the fluidized bed, by analogy with the gases kinetic theory, an equation was added describing the change in the particle kinetic energy 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, and the transport equations are solved for each group in separately. A multi-group approach to simulate a fluidized bed was used in [7–9]. In [10], it was shown that the method of taking into account polydispersity can affect the hydrodynamic characteristics of the flow obtained by numerical simulation.

Dehydrogenation of isoparaffins is considered on the example of the isobutane dehydrogenation process to isobutylene. Isobutylene is an important monomer for petrochemical synthesis. On its basis, a wide range of products is obtained: synthetic rubbers, films and fibers, high-octane components of

automobile gasolines. The main process for the isobutylene production is the dehydrogenation of isobutane in a catalyst fluidized bed.

2. Mathematical model of isoparaffins dehydrogenation

We construct a mathematical model using the example of isobutane dehydrogenation process in a fluidized bed reactor. Let us consider a models of fluidized bed hydrodynamics and heat and mass transfer and a model of the chemical reaction kinetics of the process under study.

2.1. Fluidized bed model

We write down the laws of mass conservation, momentum conservation and energy conservation for the Eulerian-Eulerian approach.

The mass conservation equation for the gas or solid phase:

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

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

The momentum conservation equation for the gas phase:

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

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

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

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

The momentum conservation equation for the solid phase:

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

where p_s is granule pressure, $\bar{\bar{\tau}}_s$ is stress tensor in 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:

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

where μ_s, λ_s is shear and bulk viscosity.

The energy conservation equation for the gas or solid phase:

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

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]:

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

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

The questions system is unclosed. To close the system, use the models [6, 13, 14]. For calculations, a $k - \varepsilon$ dispersion model of turbulence was used. The written system of differential equations is solved in the software package ANSYS Fluent.

2.2. Average particle size selecting model

The mathematical model is verified with experimental data. In the experiment, the catalyst is a polydisperse system of microspherical particles, belonging to the Geldart B group.

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

$$D_{\mathrm{mod}} = \arg\max_{D}\left(f(D)\right). \tag{8}$$

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

$$D_{32} = \int_{0}^{\infty} f(D)D^3 dD \bigg/ \int_{0}^{\infty} f(D)D^2 dD. \tag{9}$$

A detailed analysis of the effective diameter choice 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] is

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

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

$$A = \frac{1}{4}\pi D^2. \tag{11}$$

We introduce an additional effective diameter over relative area [16]. Consider the resistance force of a spherical particle in the form of (10), taking into account the sectional area (11). Consider the mathematical expectation A_{cp} for a particle mixture with a diameter's density distribution $f(D)$:

$$A_{cp} = \frac{1}{4}\pi\int_{0}^{\infty} f(D)D^2 dD. \tag{12}$$

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

$$D_{eff} = \left(\int_{0}^{\infty} f(D)D^2 dD\right)^{0.5}. \tag{13}$$

The choice of the fractions number and the particle size play an important role in the behavior of the fluidized bed. In some cases, the addition of fine particles leads to the 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].

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

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

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

For polydisperse particles, the following conditions can be recommended for choosing effective diameters [16]:

$$D_{32} \le D_{eff} \le D_{mod}. \tag{15}$$

2.3. Isobutane dehydrogenation model

The main 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, sequential, strongly endothermic, occurring with an increase in volume due to hydrogen evolution.

$$C_4H_{10} \leftrightarrow C_4H_8 + H_2 - 115.1 \text{ kJ/mol}. \tag{16}$$

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

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

where E_a is activation energy.

$$\ln k = -\frac{E_a}{RT} + const, \tag{18}$$

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

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 through the hydrodynamic characteristics of the flow, can be written as follows

$$c = \frac{m_{C4H10}}{M_{C4H10}V_r} = \frac{\rho_{mixture} \cdot V_r \cdot Y_{C4H10}}{M_{C4H10} \cdot V_r} = \frac{\rho_{mixture} \cdot Y_{C4H10}}{M_{C4H10}}, \tag{20}$$

where m_{C4H10} is isobutane mass, M_{C4H10} is isobutane molar mass, V_r is reaction volume, Y_{C4H10} is isobutane mass concentration, $\rho_{mixture}$ is density of a mixture (isobutane, isobutylene and hydrogen).

The mixture density is determined in accordance with the model of an ideal incompressible gas:

$$\rho_{mixture} = \frac{P}{RT \sum\limits_i \frac{Y_i}{M_i}}, \tag{21}$$

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

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

$$w_{\text{C4H10}} = k \cdot \rho_{mixture} \cdot Y_{\text{C4H10}} \cdot f(\alpha), \tag{22}$$

$$w_{\text{C4H8}} = \frac{M_{\text{C4H8}}}{M_{\text{C4H10}}} \rho_{mixture} \cdot Y_{\text{C4H10}} \cdot f(\alpha), \tag{23}$$

$$w_{\text{H2}} = \frac{M_{\text{H2}}}{M_{\text{C4H10}}} \rho_{mixture} \cdot Y_{\text{C4H10}} \cdot f(\alpha). \tag{24}$$

The dependence of the reaction rate on the amount of catalyst is expressed by the function:

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

where α is catalyst volume fraction, $\alpha_{\max}$ is maximum catalyst volume fraction.

3. Results

To verify the constructed mathematical model of the isobutane dehydrogenation to isobutylene in a fluidized bed reactor, experimental studies and numerical calculations were carried out. 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. Contact gas analysis is performed at the outlet of the tube. For the experiment under consideration, the product yield is $45 \pm 2\%$.

For numerical calculations, we used the fluidized bed model with a new effective diameter. The calculations were performed for the cases of monodisperse and bidisperse catalyst. In figure 1 shows pictures of the catalyst particles volume fraction in a reactor model.
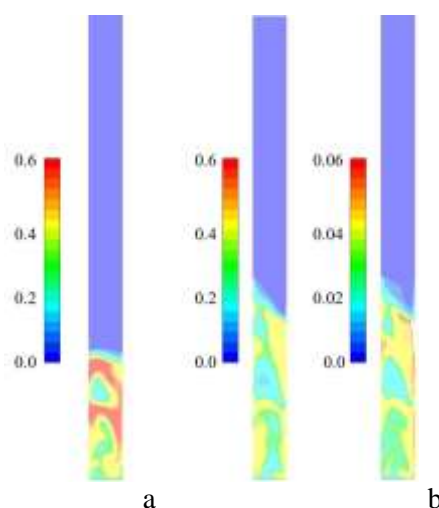
Figure 1. The catalyst particles volume fraction in the reactor tube: (a) for calculation of the monodisperse catalyst bed, (b) for calculation of the bidisperse catalyst bed.
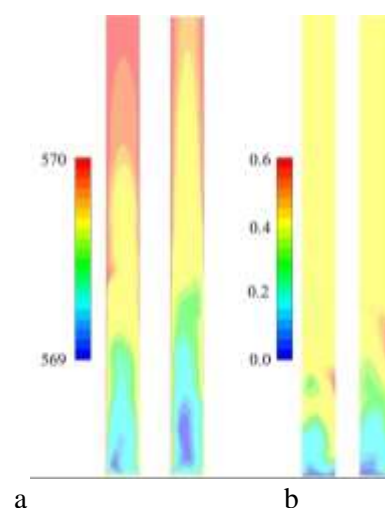
Figure 2. Gas temperature (a) and isobutylene mass fraction (b).

It is seen that for the case of the bidisperse catalyst model, the particle's bed is significantly higher, and the volume fraction is smaller. Also in figure 1b shows the field of fine particles volume fraction 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.

In figure 2a presents pictures of the gas temperature in the reactor model for calculating the monodisperse and bidisperse catalyst. The heat absorption in the case of the bidisperse particles composition is more significant. This may indicate a greater intensity of the chemical reaction that goes with the absorption of heat.

In figure 2b shows pictures of the mass fraction of the reaction product (isobutylene) in the reactor model for calculating the monodisperse and bidisperse catalysts. It can be seen that the reaction product is formed in the zone where the catalyst circulates, and in the upper part of the reactor model the mass content of isobutylene does not change.

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

Acknowledgements

References
[1] Yang W C 2003 *Handbook of Fluidization and Fluid-Particle System* (New-York: Marcel Dekker)
[2] Basu P 2006 *Combustion and Gasification in Fluidized Beds* (Boca Raton: CRC/Taylor & Francis)
[3] Sadeghbeigi R 2012 *Fluid Catalytic Cracking Handbook* (Elsevier Butterworth-Heinemann)
[4] Chen X and Wang J 2014 *Powder Technol.* **254** 94
[5] Zhou Q, Wang C, Wang H and Wang J 2016 *Int. J. Miner. Process.* **151** 40
[6] Gidaspow D 1994 *Multiphase Flow and Fluidization* (Boston: Academic Press)
[7] Shah S, Myöhänen K, Kallio S, Ritvanen J and Hyppänen T 2015 *Powder Technol.* **274** 239
[8] Solov'ev S A, Egorov A G, Lamberov A A, Egorova S R and Kataev A N 2016 *Catal. Ind.* **8(1)** 48
[9] Soloveva O V and Solovyev S A 2016 *IOP Conf. Ser.: Materials Sci. Eng.* **158(1)** 012086
[10] Loth E, O'Brien T, Syamlal M and Cantero M 2004 *Powder Technol.* **142** 209
[11] Ding J and Gidaspow D 1990 *AIChE J.* **36** 523
[12] Syamlal M 1987 *The Particle-Particle Drag Term in a Multiparticle Model of Fluidization* (Morgantown WV: EG & G Washington Analytical Service Center)
[13] Lun C K K, Savage S B and Jeffrey D J 1984 *J. Fluid Mech.* **140** 223
[14] Gunn D J 1978 *Int. J. Heat Mass Transfer*. **21** 467
[15] White F M 1991 *Viscous Fluid Flow* (New York: McGraw-Hill)
[16] Solovev S A, Solovev O V and Antipin A V 2019 *J. Phys.: Conf. Series.* **1158(4)** 042022
[17] Beetstra R, Nijenhuis J, Ellis N and van Ommen J R 2009 *AIChE J.* **55** 2013
[18] Brouwer G C, Wagner E C, van Ommen J R and Mudde R F 2012 *Chem. Eng. J.* **207-208** 711
[19] Gu Y, Ozel A and Sundaresan S 2016 *AIChE J.* **62(7)** 2271
[20] Soloveva O V, Solovev S A, Egorova S R, Lamberov A A, Antipin A V and Shamsutdinov E V 2018 *Chem. Eng. Res. Des.* **138** 212
[21] Khoe G K, Ip T L and Grace J R 1991 *Powder Technol.* **66** 127
[22] Saayman J, Ellis N and Nicol W 2013 *Powder Technol.* **245** 48