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Theoretical Optimization of the Shape and Size of Adsorbent Grains for Associated Petroleum Gas Drying

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Abstract—The shape of adsorbent grains used for drying hydrocarbon gas flows at a reduced hydraulic resistance of their beds are theoretically optimized. A two-velocity model of gas flow in fixed beds consisting of differently shaped holed particles is used for calculations at typical parameters of the associated petroleum gas drying process. It is shown that the optimum shape of a grain is a four-spoke ring. At an equivalent diameter of 3 mm, such a grain is 6.154 × 6.154 mm in size, and its walls and baffles are 1.026 mm thick.

Keywords: associated petroleum gas drying, adsorbent grain shape, reduced bed hydraulic resistance

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INTRODUCTION

The adsorption drying of hydrocarbon gases and liquids is usually performed in fixed granular adsorbent beds. The adsorbent grains used in industry are usually shaped as cylinders and spheres. This practice was also observed earlier for catalyst grains used in catalytic processes with fixed granular beds. However, catalysts with complicated shapes, including ones with multiple holes, have found increasingly wide application in recent years [1–4]. Examples of such catalysts are shown in Fig. 1.

The developed outer surfaces and increased bed void fraction of these catalysts greatly reduce the internal diffusion resistance in their grains and the hydraulic resistance of a fixed bed, and thus intensify processes due to the possibility of performing them at increased linear velocities of the reaction mixture.

The aim of this work was to determine the optimum shape of adsorbent grains by calculating the parameters of the technology according to which adsorbents are used for the drying of associated petroleum gas.

Over the last 15 years, we have studied the properties of fixed beds consisting of grains with complicated shapes and mathematically modeled the processes conducted with them. A two-velocity model of gas flow in fixed beds consisting of holed particles was developed in particular. This model assumes a gas flows in the space between grains at average axial velocity u_{out} and inside channels at average longitudinal velocity u_i. The total void volume of a granular bed is considered a disperse macrosystem consisting of two conjugated continua that do not intersect but have shared boundaries. One of these subsystems in confined within the space between the outer surfaces of particles, while the other is located inside channels. This model was used to find correlations for the heat and mass transfer processes in such beds [5–7]. A systematic experimental study of the hydraulic resistance of grains whose cross-section shape is illustrated in Fig. 2 was performed in [8], and some improvements were introduced into the hydraulic model. The mean-

Fig. 1. Examples of catalysts with complicated shapes.

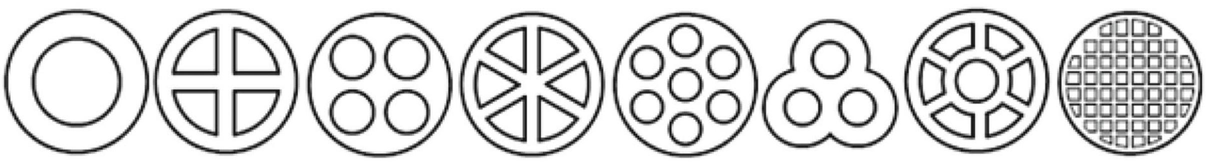


Fig. 2. Grain shapes used in hydraulic resistance measurement experiments.

square deviation between the calculations performed by the derived equations and the experimental data on pressure drops was 6.2%.

The void volume of a bed consisting of hollow particles without mutual intersection is composed of the volume between grains and the volume of all channels. As was shown in [9], this condition is ensured when the ratio between the channel and particle diameters is less than 0.5:

$$\varepsilon = \varepsilon_{out} + (1 - \varepsilon_{out})\varepsilon_i, \quad (1)$$

where ε is the total bed void fraction, ε_i is the inner grain void fraction (the ratio of the volume of channels to the total volume of a grain), and ε_{out} is the outer void fraction (the portion of the bed volume between grains).

COMPUTATIONAL SYSTEM FOR ESTIMATING THE PRESSURE DROP

In [8], our two-velocity hydraulic model of a fixed bed was used to derive a closed algebraic system for the analytical estimation of three independent parameters: pressure gradient dP/dx in a bed, axial gas velocity u_{out} between grains, and average longitudinal velocity u_i inside channels:

$$\begin{gathered} u_0 = \varepsilon_{out} u_{out} + 0.5(1 - \varepsilon_{out})\varepsilon_i u_i, \\ -\frac{dP}{dx} = 150\mu \frac{(1 - \varepsilon_{out})^2}{\varepsilon_{out}^2 d_p d_E} u_{out} + 1.75\rho \frac{(1 - \varepsilon_{out})}{\varepsilon_{out} d_E} u_{out}^2, \quad (2) \\ -\frac{dP}{dx} L_i + 3.7\rho u_{out}^2 \frac{F_w}{F_i} = 1.75\rho u_i^2 + C\mu \frac{L_i}{d_i^2} u_i, \end{gathered}$$

where u_0 is the velocity in an empty cross section, m/s; P is the hydrostatic pressure, Pa; μ is the gas viscosity, Pa s; ρ is the gas density, kg/m^3; L_i is the length of a grain channel, m; d_i is the equivalent diameter of an individual channel, m; $\pi d_i^2/4 = S_i$, where S_i is the surface area of the channel's cross section, $d_E = 6V_p/S_{out}$ is the effective diameter of a hollow particle, m, $d_p = 6V_p/S_p$ is the hydraulic dimension of a bulk particle, m, S_p is the surface area of a bulk grain, m^2, $S_{out} = S_p - 2(F_i + F_w)$ is the effective cross-section area of a hollow grain, m^2, F_i is the cross-section area of all grain channels, m^2, F_w is the cross-section area of partitions between grain channels, m^2, V_p is the volume of a bulk grain, m^3, $C = 64$ for a round channel, $C = 54$ for a square channel, and $C = 53$ for a circular sector and a triangle.

PARAMETRIC ANALYSIS OF THE MODEL

Calculating the bed void fraction for randomly packed grains is a non-trivial problem and is not con-

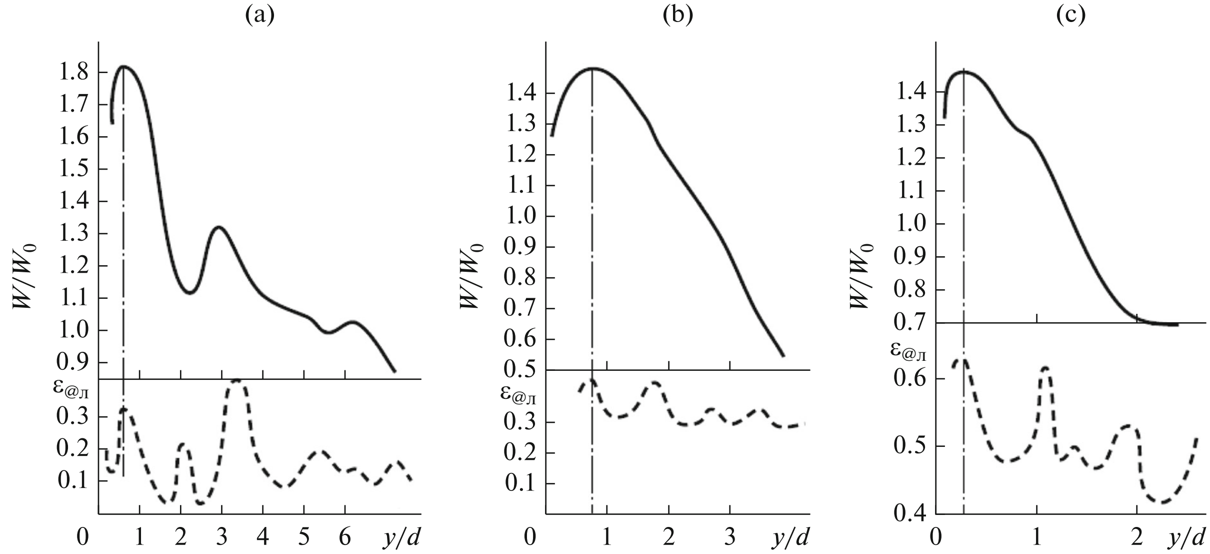


Fig. 3. Experimental data on the distribution of the void fraction (dashed line) and gas flow velocity ($U = u_{out}$) in an apparatus with a diameter of 94 mm at $u_0 = 2$ m/s: (a) balls with diameter $d = 6$ mm at bed height $H/d = 2$, (b) balls with diameter $d = 9.5$ mm at bed height $H/d = 3$, (c) balls with diameter $d = 14.5$ mm at bed height $H/d = 2$. y/d is a dimensionless radial coordinate.

sidered in this work. The model uses empirically obtained parameters that agree with the literature data [10–18]. It is useful to analyze this problem by means of a similarity theory, which allows us to limit our selection of the character of relationships between the parameters characterizing the phenomenon. The main parameter to be determined in this problem is the loss of pressure per unit bed length, which must depend on four physical parameters that characterize the properties of a flow and a granular bed:

(1) the flow velocity in the space between grains;

(2) the equivalent diameter of bed elements;

(3) the flow density; and

(4) the flow dynamic viscosity.

The resistance forces for any granular bed are generally described by a binomial interpolation function of the type

$$\frac{\Delta P}{\ell} = Au + Bu^2, \tag{3}$$

where A and B are coefficients of proportionality, u is the gas filtration velocity, m/s, and ℓ is the granular bed length (height) element. This function considers the contribution from both inertia and viscosity forces. It was first proposed by Dupuis and then by Forchheimer, and experimentally verified by Zhavoronkov, Aerov, Umnik, and Ergun [10, 15–17]. It was subsequently used in a number of studies and is now generally accepted. The classic Ergum equation has the form [19, 20]

$$\frac{\Delta P}{\ell} = 150\frac{(1-\varepsilon)^2}{\varepsilon^3}\frac{\mu}{d^2}u + 1.75\frac{1-\varepsilon}{\varepsilon^3}\frac{\rho}{d}u^2. \tag{4}$$

The proposed model describes the generalized properties of flows of any nature, so it can be used to describe the physical properties of a real system. Among the varied parameters of a medium are the dynamic viscosity and density of a flow and hydrodynamic parameter U_0. It is also worth noting that the local distribution of flow velocities over the cross section of an apparatus is of a nonuniform character. In [12–15], it was shown that the maximum specific gas flow rate corresponds to the area of the highest void fraction and is observed near the wall of an apparatus with a fixed granular bed. The flow velocity profile is much smoother than the local void fraction profile, due to the continuity of flow in a fixed granular bed and the ejection effect [18]. Profiles of a local gas flow velocity in a fixed granular bed are shown in Fig. 3 (experimental data from [10, 18, 23]).

Analysis of the hydrodynamic situation for the flow through a fixed granular bed shows that the pressure loss in it is generally determined by the structure of the bed and the friction between the flow and the surfaces of grains. The friction coefficients themselves depend on a wide range of parameters, e.g., the material of the grains; the composition, temperature, and pressure of the moving flow; and its viscosity, density, phase state, and so on. In the considered model, we shall confine ourselves to the effect produced by the flow viscosity and density and therefore use the modified Euler criterion

$$\mathrm{Eu_m} = \frac{\Delta P \varepsilon^2}{H S_d \rho u_0^2}. \tag{5}$$

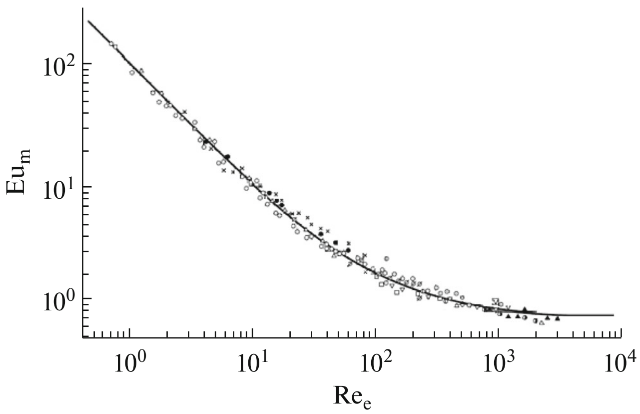


Fig. 4. Euler number (Eu_m) versus Reynolds number (Re_e), according to the experimental data of different authors. Zhavoronkov's data [17]: D_{tube} = 305 mm; pieces of coke of (▲) 28.6 and (◑) 24.4 mm in size; (□) pieces of ammonia synthesis catalyst of 6.1 mm in size; (▽) pellets of sulfuric acid catalyst of 11 × 6.5 mm in size; (⊙) pellets of CO conversion catalyst of 11 × 6 mm in size. Our data: (○) D_{tube} = 32 mm, glass balls with d = 2–3 mm; (△) silica gel with d = 3–4 mm; (●) D_{tube} = 52 mm, glass balls with d = 2–3 mm; (x) silica gel balls with d = 3–4 mm; (Ø) 4–5 mm metallic catalyst fraction; (Ø) 5–6 mm metallic catalyst fraction. Kel'tsev's data [22]: (⍜) D_{tube} = 25 mm; 2–3 mm fraction of coal grains.

The experimental dependence of the modified Euler criterion on the Reynolds number is plotted in Fig. 4.

The mathematical model proposed in this work assumes that the flow filtered through a granular bed is a single phase, and the grains are quiescent over time. The effect produced by the physical parameters of a flow (viscosity, density, and linear velocity per total cross section area of the apparatus) on the hydraulic resistance of a bed was studied within the framework of the considered model in [12–15] and some other works. According to Eq. (3), the pressure drop along a granular material bed has a quadratic functional dependence on the linear gas or liquid flow velocity in a fixed granular bed. Equation (4) gives the linear dependence between the pressure drop and the filtered medium density. These dependences allow us to estimate the effect of flow properties on the drop and determine the area of the technologically admissible application of this mathematical model: normally, the pressure drop along an apparatus must not exceed 150 kPa.

This model does not consider the effect of friction forces, which greatly complicate numerical calculations, but the question of the effect produced by the material of grains on the hydrostatic parameters of a bed may be considered in later studies. The flow viscosity, density, and linear velocity have a functional dependence on the temperature and pressure of a performed process. The above analysis allows qualitative estimates of the contribution from every parameter to the pressure drop along a bed.

RESULTS OBTAINED FOR TYPICAL ASSOCIATED PETROLEUM GAS DRYING PARAMETERS

Our theoretical basis allows us to estimate the prospects for using it in the drying of hydrocarbon gas flows for adsorbents with complicated grain shapes that ensure reduced hydraulic resistance of their bed. The calculations were performed at typical drying process parameters:

(1) pressure, 30 atm (3.04 MPa); temperature, 35°C; working velocity of the gas in the free bed cross section, 0.1 m/s;

(2) mixture composition (vol %): methane, 81.77; CO_2, 0.41; N_2, 0.1; O_2, 0.04; ethane, 6.54; propane. 5.93; *iso*-butane, 1.43; *n*-butane, 2.35; *iso*-pentane, 0.61; *n*-pentane, 0.61; *n*-hexane, 0.21.

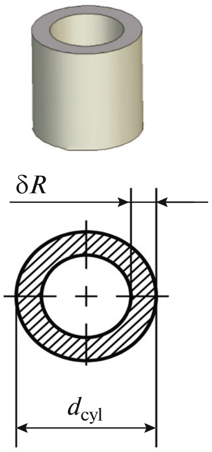
The physical properties of the mixture were determined using the HYSIS software: mixture density, 25.125 kg/m^3; viscosity, 1.21×10^{-5} Pa s.

The grain shapes presented in Table 1 were studied. The parameters that were varied in calculations were equivalent grain diameter $d_e = \frac{6V}{S}$ and internal grain void fraction $\varepsilon_i = \frac{V_p - V}{V_p}$, where V is the particle volume (without correction for channels), and S is the external grain surface area (with correction for channels). In these calculations, the height of all grains was assumed to be equal to the diameter, and all other geometrical dimensions were varied proportionally. For grains 2, 3, and 7 (see Table 1), the thickness of a hole–outer surface wall and that of an interhole partition were assumed to be the same. For grains 4, 5, and 6, the thicknesses of the outer walls and partitions were also assumed to be equal. At the same time, the ratio between the outer wall and interhole partition thicknesses for particles 8 and 9 was taken to be 0.95 : 0.45.

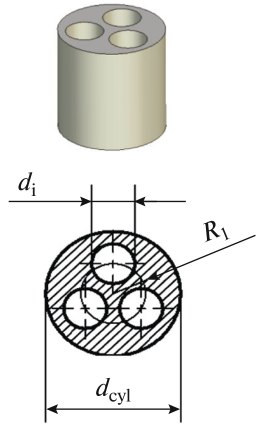
Intergrain bed void fraction ε_{out} for grains 1–6 was taken to be 0.4. Grains 7, 8, and 9 were more closely packed, especially grains 7. Therefore, ε_{out} = 0.38 for grains 7 on the basis of the available experience [9], while the intergrain void fraction for grains 8 and 9 was taken to be 0.38, plus the volume occupied by outer channels.

The calculated dependences of the pressure drop $\left(\frac{dP}{dx}\right)$ at a bed height of 1 m on the equivalent diameter for bulk cylinders and Raschig rings with inner void fraction ε_i = 0.1, 0.2, and 0.3 are plotted in Fig. 5. From these it follows that Raschig rings have much lower hydraulic resistance then bulk cylinders. It is

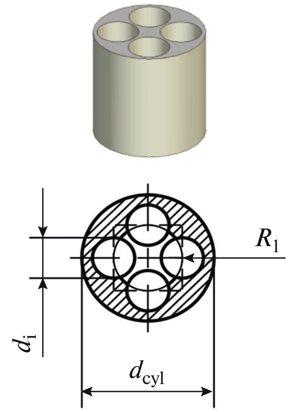
Table 1. Studied adsorbent grain shapes



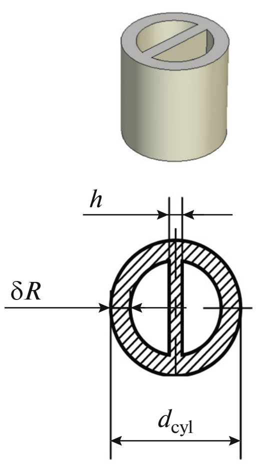
1. Raschig ring



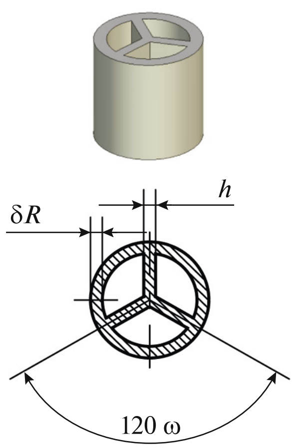
2. Three-hole cylinder



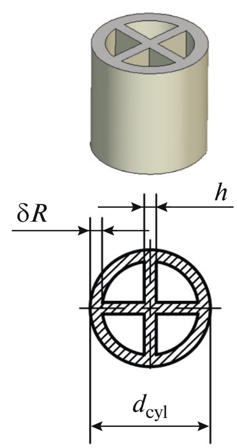
3. Four-hole cylinder



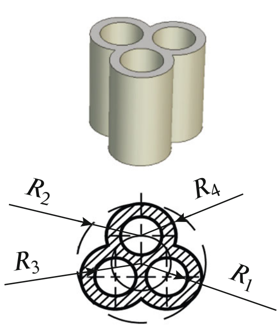
4. One-spoke ring



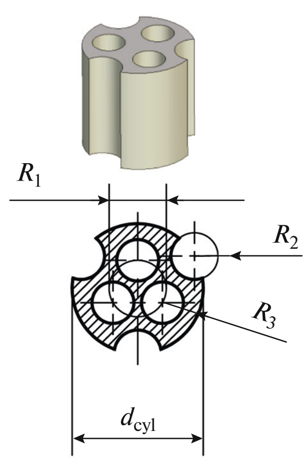
5. Three-spoke ring



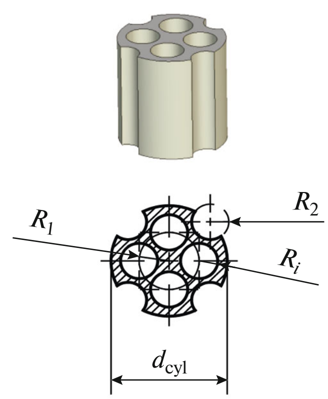
6. Four-spoke ring



7. Three-hole trefoil



8. Three-hole three-channel cylinder



9. Four-hole four-channel cylinder

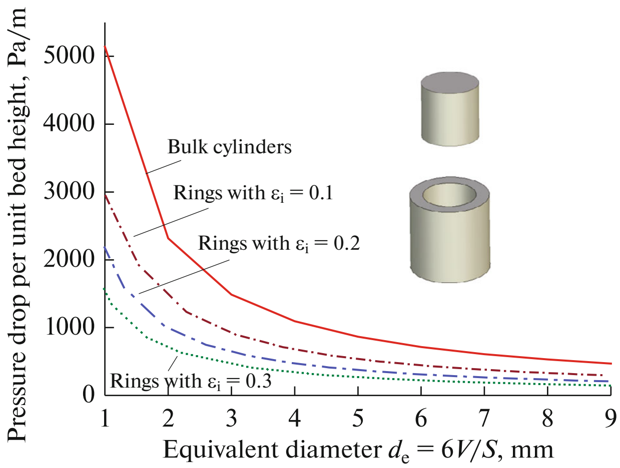


Fig. 5. Pressure drop for bulk cylinders and Raschig rings with different inner void fractions (hole sizes) at the same bed height of 1 m.

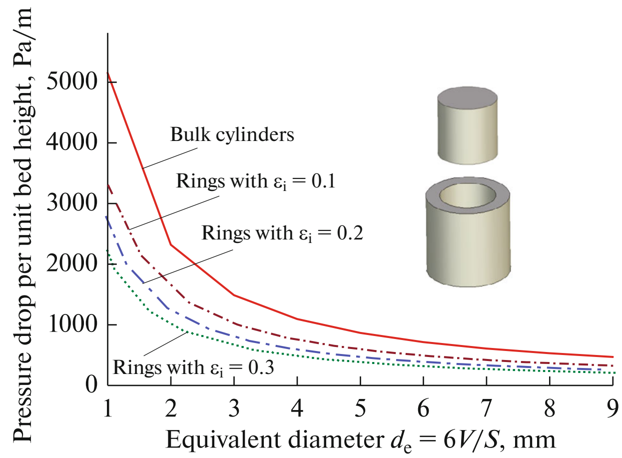


Fig. 6. Pressure drop for bulk cylinders and Raschig rings with different inner void fractions (hole sizes) at the same amount of the material corresponding to bulk cylinders at a bed height of 1 m.

known from the theory of the mathematical modeling of catalytic processes that catalyst grains with complicated shapes and through holes have nearly the same internal surface efficiency as bulk grains with the same effective diameter: $d_e = 6V/S$ [21]. We would expect that adsorbents in the shape of grains with through holes also have the same dynamic capacity per unit mass as bulk grains with the same equivalent diameter. For example, the equivalent diameter of bulk 3 × 3-mm cylinders is 3 mm. The geometrical dimensions of Raschig rings with the same equivalent diameter are given in Table 2.

The existence of though holes in Raschig rings results in increased bed void fraction, compared to bulk particles, for which this parameter is equal to 0.4. The static capacity per unit bed volume for Raschig rings is thus reduced in comparison to bulk particles, in proportion to the change in the amount of solid material per unit bed volume:

$$\frac{1-(\varepsilon_{out}+(1-\varepsilon_{out})\varepsilon_i)}{(1-\varepsilon_{out})} = (1-\varepsilon_i). \quad (6)$$

To retain the static bed capacity for adsorbent grains with through holes, we must increase the bed volume by $1/(1-\varepsilon_i)$ times. The dependences of the pressure drop on the equivalent diameter at the same amount of material corresponding to bulk cylinders at a bed height of 1 m, $\frac{dP}{dx}\frac{1}{(1-\varepsilon_i)}$, are plotted in Fig. 6 for more complete comparison of the costs of overcoming hydraulic resistance upon replacing bulk cylinders with Raschig rings. As can be seen from Fig. 6, much lower hydraulic resistance of the bed is in this case also observed for Raschig rings.

Similar dependences were obtained for grains in the shape of three-spoke rings and cylinders with four round holes. The dependences of the pressure drop on the equivalent diameter for grains with these shapes at the same amount of the material corresponding to bulk cylinders at a bed height of 1 m are shown in Figs. 7 and 8. The results from calculations and a comparison of the dependences plotted in these figures indicate that the use of such shapes additionally reduces the pressure drop in an adsorber, compared to Raschig rings.

Figure 9 allows us to compare the pressure drop in beds of the grains of all the shapes characterized in Table 1 with inner void fractions of 0.2. As follows from Fig. 9, the efficiency of grain shapes declines in the order four-spoke rings > three-spoke rings > one-spoke rings > four-hole cylinder > three-hole cylinder > three-hole trefoil > Raschig rings > four-hole four-

Table 2. Geometrical dimensions of Raschig rings with an equivalent diameter of 3 mm

Inner ring void fraction	Height, mm	Outer diameter, mm	Hole diameter, mm	Wall thickness, mm	Total bed void fraction
0.1	3.924	3.924	1.240	1.342	0.46
0.2	4.615	4.615	2.061	1.277	0.52
0.3	5.421	5.421	2.970	1.226	0.58

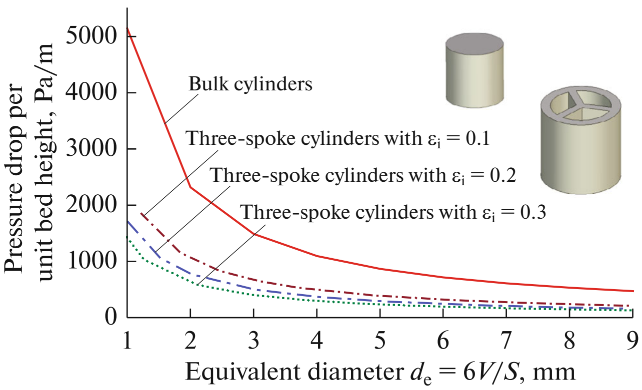


Fig. 7. Pressure drop for bulk cylinders and three-spoke rings with different inner void fractions (wall and baffle thicknesses) at the same amount of the material corresponding to bulk cylinders at a bed height of 1 m.

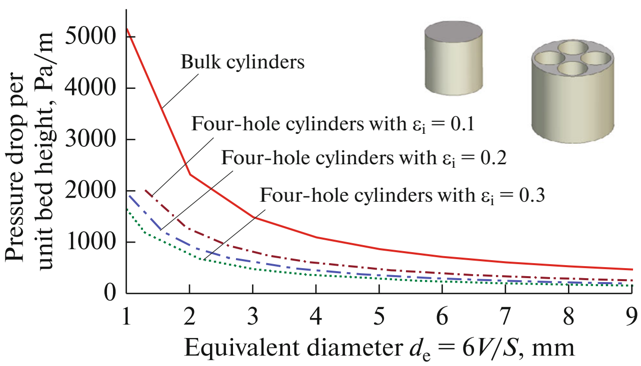


Fig. 8. Pressure drop for bulk cylinders and four-hole cylinders with different inner void fractions (hole sizes) at the same amount of the material corresponding to bulk cylinders at a bed height of 1 m.

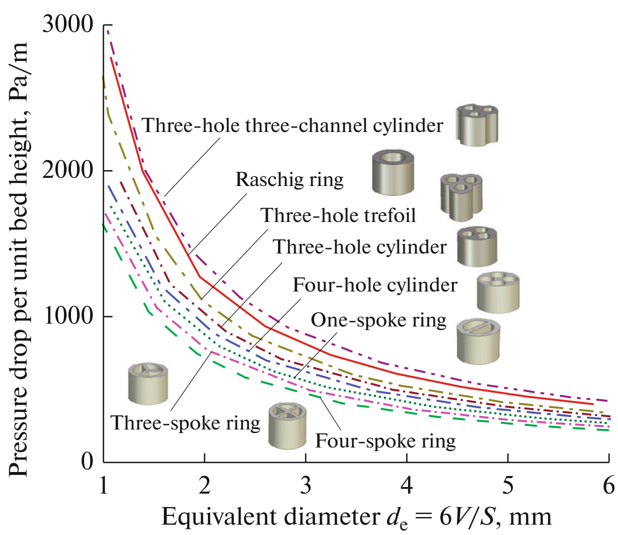


Fig. 9. Pressure drop in a bed of differently shaped particles (see Table 1) with void fraction $\varepsilon_i = 0.2$ at the same amount of the material corresponding to continuous cylinders at a bed height of 1 m.

channel cylinder > three-hole three-channel cylinder. The optimum grain shape is thus a four-spoke ring. At an equivalent diameter of 3 mm, such a grain is 6.154 × 6.154 mm in size, and the thickness of its walls and baffles is 1.026 mm.

CONCLUSIONS

The considered mathematical model can be used for a wide range of single-phase flows in a fixed granular bed. Our parametric analysis of this model allows quantitative and qualitative estimates of the contribution from each parameter to the pressure drop along a fixed granular bed. The dependences given in this work can be used to estimate the effect of flow properties on the hydrodynamic resistance of a granular bed and determine the technologically admissible ranges of apparatus loads, operational regimes of industrial reactors, and process conditions (as a rule, the pressure drop along an apparatus must not exceed 150 kPa). Our calculations for the drying parameters and the drying agent's grain shape allowed us to estimate the prospects for using adsorbents with optimized shapes that ensure reduced hydraulic resistance of their bed in the drying of hydrocarbon gas flows. It was shown that the optimum grain shape is a four-spoke ring. At an equivalent diameter of 3 mm, such a grain is 6.154 × 6.154 mm in size, and the thickness of its walls and baffles is 1.026 mm.

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REFERENCES

1. Beskov, V.S., *Khim. Prom-st',* 1990, no. 7, pp. 413–416.
2. Kagyrmanova, A.P., Zolotarskii, I.A., Smirnov, E.I., and Vernikovskaya, N.V., *Chem. Eng. J.,* 2007, vol. 134, nos. 1–3, pp. 228–234.
3. Hartmann, V.L., Obysov, A.V., Dulnev, A.V., and Afanas'ev, S.V., *Chem. Eng. J.,* 2011, vols. 176–177, pp. 102–105.
4. Afandizadeh, S. and Foumney, E.A., *Appl. Therm. Eng.,* 2001, vol. 21, no. 6, pp. 669–682.
5. Smirnov, E.I., Muzykantov, A.V., Kuzmin, V.A., Zolotarskii, I.A., and Kronberg, A.E., *Chem. Eng. J.,* 2003, vol. 91, nos. 2–3, pp. 243–248.
6. Smirnov, E.I., Muzykantov, A.V., Kuzmin, V.A., Zolotarskii, I.A., Koning, G.W., and Kronberg, A.E., *Chem. Sustainable Dev.,* 2003, vol. 11, no. 1, pp. 293–296.
7. Smirnov, E.I., Kuzmin, V.A., and Zolotarsky, I.A., *Chem. Eng. Res. Des.,* 2004, vol. 82, no. 2, pp. 293–296.
8. Voennov, L.I. and Zolotarskii, I.A., *Theor. Found. Chem. Eng.* (in press).

9. Dixon, A.G., *Can. J. Chem. Eng.,* 1988, vol. 66, no. 5, pp. 705–708.
10. Aerov, M.E. and Todes, O.M., *Gidravlicheskie i teplovye osnovy raboty apparatov so statsionarnym i kipyashchim zernistym sloem* (Hydraulic and Thermal Foundations of Fixed and Fluidized Granular Bed Apparatuses), Leningrad: Khimiya, 1968.
11. Schwartz, C.E. and Smith, J.M., *Ind. Eng. Chem.,* 1953, vol. 45, no. 6, pp. 1209–1218.
12. Roblee, L.H.S., Baird, R.M., and Tierney, J.W., *Am. Inst. Chem. Eng. J.,* 1958, vol. 4, no. 4, pp. 460–464.
13. Lerou, J.J. and Froment, G.F., *Chem. Eng. Sci.,* 1977, vol. 32, no. 8, pp. 853–861.
14. Sonntag, G., *Chem. Ing. Tech.,* 1960, vol. 32, no. 5, pp. 317–329.
15. Aerov, M.E., Zavelev, E.D., Semenov, V.P., and Vakk, E.G., *Azotn. Prom-st.,* 1978, no. 3, pp. 24–31.
16. Aerov, M.E. and Umnik, H.H., *Zh. Prikl. Khim.,* 1950, vol. 23, no. 10, pp. 1009–1017.
17. Zhavoronkov, N.M., *Teoreticheskie osnovy khimicheskoi tekhnologii* (Theoretical Foundations of Chemical Engineering), Moscow: Nauka, 2007.
18. Myasnikov, V.P. and Kotelkin, V.D., in *Aeromekhanika* (Aeromechanics), Moscow: Nauka, 1976, pp. 307–316.
19. Ergun, S., *Chem. Eng. Prog.,* 1952, vol. 48, no. 2, pp. 89–94.
20. Ergun, S. and Orning, A.A., *Ind. Eng. Chem.,* 1949, vol. 41, no. 6, pp. 1179–1184.
21. Rester, S., Jouven, J., and Aris, R., *Chem. Eng. Sci.,* 1969, vol. 24, no. 6, pp. 1019–1022.
22. Kel'tsev, N.V., *Osnovy adsorbtsionnoi tekhniki* (Adsorption Equipment Fundamentals), Moscow: Khimiya, 1984.
23. Pushnov, A., Baltrenas, P., and Kagan, A., *Aerodinamika vozdukhoochistnykh ustroistv s zernistym sloem* (Aerodynamics of Air Purification Granular-Bed Devices), Vilnyus: Tekhnika, 2010.

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