Comparative analysis of aerodynamic characteristics of catalysts for steam reforming methane

A N Mrakin¹, O V Afanaseva², I A Vdovenko¹, M A Ageev¹, A A Selivanov¹, P A Batrakov³
¹Yuri Gagarin State Technical University of Saratov, 77, Politechnicheskaya Str., Saratov, 410054, Russia
²Peter the Great St. Petersburg Polytechnic University, 29, Politechnicheskaya Str., St. Petersburg, 195251, Russia
³Omsk State Technical University, 11, Mira Pr., Omsk, 644050, Russia

Abstract. The main results of the aerodynamic resistance estimation of the catalyzing backfill of processes hydrocarbons steam reforming, and also units which implementing the process of thermochemical regeneration of the exhaust gases are considered. Empirical dependences of various authors are presented for determining the resistance coefficient. Expressions which is the most adequately describe the hydrodynamic picture of the ongoing process are determined. The calculated specific resistance is in the range of 25-26 kPa/m, and correlates with indicators of industrial units operated in similar hydrodynamic modes (resistance is 18-31 kPa/m).

Keywords: reforming, thermochemical regeneration, tubular furnace, catalyst, synthesis gas, aerodynamic resistance, temperature.

1. Introduction
The process of steam methane reforming is the principal for obtaining synthesis gas in production of hydrogen, ammonia, methanol and other highly liquid products [1]. It is carried out with reforming (conversion) using a nickel catalyst in tubular furnace. Since the steam reforming process is highly endothermic (requires a significant supply of thermal energy), the reaction tubes in which the catalyst is loaded are heated with flue gases at the temperature of 750-850 °C and the pressure of the initial vapor-gas mixture at the level of 25-30 bar. At the same time a similar process is used in equipment for thermochemical regeneration of waste gas. The essence of which consists in the beneficial use of the exhaust flue gases heat of heat power and heat technology equipment for the preliminary endothermic conversion of the original gaseous fuel [2-7]. In this case the flow of the original fuel receives a larger supply of chemically bound heat in the form of increased gross calorific value, which is released in the combustion chamber, leading to a decrease in the specific consumption of the primary fuel. The catalyst which used in such equipment should have a set of technological characteristics, the main of which are high activity, large specific surface area, low gas-dynamic resistance, mechanical strength and thermal resistance. For improvement the performance of steam reformers or thermochemical conversion reactors in the last time the catalysts of complex geometric shapes are being used. That catalysts provide the improved heat transfer from the pipe wall to the catalyst layer, the increase in catalytic activity due to an increase in the utilization of the inner surface, and the decrease in hydraulic resistance.
There are a lot of publications by domestic and foreign authors about modeling of the actual process of steam reforming natural gas (methane) as for the production of synthesis gas in tube furnaces, likewise, in the special equipment for thermochemical regeneration of exhaust flue gases [8-14]. Wherein, the hydrodynamic regimes and features of the choice of design ratios are not fully covered.

2. Problem statement
Hydromechanical processes occurring during thermochemical regeneration of the heat of exhaust gases or steam conversion of hydrocarbons are determine the intensity of heat and mass transfer and have their own characteristics. These features depend on properties of the catalytic backfill grains and, first of all, on the shape, size and grain-size distribution and density.

In the technical calculations of equipment the hydraulic resistance and the speed of movement of heat-transfer agent are usually calculated. These values are interrelated and, besides the effect on heat and mass transfer, determine the power consumption for the movement of heat-transfer agents and their residence time in the apparatus. It is obvious that the residence time of the reaction mixture in the apparatus should not be less than the time required for conclusion of processes.

3. Theory
For simplify of analysis the real catalyst grains of irregular shape are usually replaced by conventional spheroid particles [15] with an equivalent diameter (equal in volume to a real particle), which is determined from the condition of equality of the surface areas of real and spherical particles, m:

\[ d_p = \sqrt{F_p / \pi} = 0.564 \cdot F_p^{0.5}, \]  

where \( F_p \) is the surface area of a real particle, m².

The equivalent volumetric diameter is determined similarly, m:

\[ d_e = \sqrt[3]{6V_p / \pi} = 1.24 \cdot V_p^{0.333}, \]

where \( V_p \) is the volume of a real particle, m³.

The degree of deviation of the catalyst grain shape from the spherical one is characterized by the geometric shape factor, determined by the ratio:

\[ F = (F_p / F_S)V_p = V_S = dem, \]

where \( F_S, V_S \) are surface and volume of a spherical particle, m² and m³, respectively.

Taking into account (3), we can get, m:

\[ d_p = d_e \cdot F^{0.5}, \]

It also follows from (3) that:

\[ F = d_e \cdot f / 6, \]

where \( f \) is the particle surface area per unit of their volume, m²/m³.

For spherical particles, we can get, m²/m³:

\[ f = \pi d^2 /(\pi d^3 / 6) = 6 / d . \]

The share of free volume in the catalyst particle backfill determines the porosity of the layer. Porosity is an important layer characteristic. For a dense layer which composed of monodisperse particles, it does not depend on their size, but is determined only with the installation of particles in the layer. The value of the porosity and the specific surface area of the layer depend on the shape and size of the catalyst grains and the nature of their arrangement (chaotically or regularly).

The gas filtration through the dense layer of the catalyst particles can be considered as a movement along tortuous channels of variable cross-section formed with particles. The average transverse dimension of the channel is calculated as the equivalent diameter by the expression, m:

\[ D_e = 4\varepsilon / f_0, \]

where \( \varepsilon \) is the porosity backfill layer, \( f_0 = f (1 - \varepsilon) \) is the particle surface per unit layer volume, m²/m³.
Average gas velocity in channels, m/sec:

$$w_c = w/\varepsilon,$$  

(8)

where $w$ is the gas velocity related to the total layer section, m/sec.

The loss of the pressure (resistance) per 1 m of the height of the catalyst layer in the reaction element is determined by the well-known Darcy–Weisbach equation, Pa/m:

$$\Delta p = \xi \frac{\rho \cdot w^2}{D_c} = \xi \frac{\rho \cdot w^2 \cdot f_0}{2 \cdot \varepsilon^3},$$  

(9)

where $\xi$ is the hydraulic resistance coefficient of layer; $\rho$ is the gas density, kg/m$^3$.

The coefficient of hydraulic (aerodynamic) resistance is determined with empirical formulas. Moreover, various authors recommend different ratios. So in the works of V. Yurenev and P. Lebedev characteristic modes of gas phase filtration through a dense layer are distinguished:

- at $Re < 80$ $\xi = \frac{400}{Re^{0.85}},$
- at $80 < Re < 400$ $\xi = \frac{70}{Re^{0.45}},$
- at $Re > 400$ $\xi = \frac{16.5}{Re^{0.2}}.$  

(10)

Yu. Dytnersky gives another recommendation for determining the resistance coefficient for Raschig rings which randomly loaded:

- at $Re < 40$ $\xi = \frac{140}{Re},$
- at $Re > 40$ $\xi = \frac{16}{Re^{0.2}}.$  

(11)

Also in papers of Yu. Dytnersky have the data for catalyst particles in the form of granules, grains, spheroidal elements. However, the characteristic modes (laminar, transient and turbulent) are not distinguished, and the resistance coefficient is determined with the ratio:

$$\xi = \frac{133}{Re} + 2.34.$$  

(12)

Relations (11) or (12) will be chosen in the calculations depending on the presence of internal vents in the catalyst grain.

A similar equation for calculating the resistance coefficient is used in publication [16]:

$$\xi = \frac{36.3}{Re} + 0.4.$$  

(13)

For determination the resistance coefficient Z. Gorbis and V. Kalenderyan proposed to use a relation of the form:

$$\xi = \frac{8 \cdot k}{Re} + k_i,$$  

(14)

where $k$ is Kozeny-Karman constant; $k_i$ is the inertial component of the resistance coefficient.

The values $k$ and $k_i$ for cylindrical (tablets and granules) and saddle-shaped catalyst particles for the case of narrow channels (the ratio of the pipe diameter to the grain diameter is less than 10) are 6.9 and 0.68, respectively.

In the paper [15], and also in works of V. Yurenev and P. Lebedev was proposed to single out the characteristic modes of motion of the gas phase through the filling of particles, and the resistance coefficient to determine from the relations:

- at $Re < 45$ (laminar regime) $\xi = \frac{41}{Re},$
at 45<Re<5500 (turbulent regime) \[ \xi = \frac{35.5}{Re} + \frac{0.82}{Re^{0.08}}. \] (15)

The Reynolds number in expressions (10) – (15) is calculated with the formula:

\[ Re = \frac{w \cdot D}{\nu} = \frac{4 \cdot w}{f_0 \cdot \nu}, \] (16)

where \( \nu \) is the kinematic coefficient of gas viscosity, m²/sec.

The values \( w, \nu \) and \( \rho \) in the above ratios are calculated as average values for the layer (at average temperature), taking into account the change in the volume of flow rates of the reacting vapor-gas mixture. It should be noted that if we consider the movement of gas through the layer, then the hydraulic resistance coefficient of a particle in the layer is more than the corresponding coefficient of a single particle at the same velocities of the flow [15].

4. Experiments results

The initial data for the calculation were taken on the example of the M-750 methanol synthesis unit. According to the data [17], the gas composition, vol. %: CH₄=24.0; H₂O=73.0; CO=1.5; H₂=1.2; CO₂=0.02; N₂=0.28. The gas speed is 9.9 m/s; the pipe diameter is 100 mm; the inlet pressure is 25 atm; the length of the reaction tube is 12 m. The thermophysical properties were determined using the Aspen HYSYS Version 10 software package.

When performing variant calculations, the porosity of the layer and other structural characteristics of the catalyst layer were taken in accordance with the data of [18]. It's generally known that the structural parameters depend on the diameter of the equipment or the reaction tube. While the results [18] can be safely interpreted to the operating conditions of industrial converters, since the diameter of the apparatus which used in the publication is 100 mm.

The calculations were performed for catalysts, the characteristics of which are presented in Table 1, and the external appearance is shown in Fig. 1. Data on the ranking of catalysts in terms of specific aerodynamic resistance are presented in the form of histograms in Fig. 2.

Figure 1. Catalysts for the conversion of hydrocarbons:

a) cylindrical (for example, GIAP 3); b) circular (for example, GIAP 8).
### Table 1. Geometric and structural characteristics of industrial catalysts grains [1, 18]

| Indicator                               | Unit | GIAP3 | GIAP 16 | GIAP 5 | GIAP 16MT | GIAP 8 | GIAP-3-6-N | BASF |
|-----------------------------------------|------|-------|---------|--------|-----------|--------|------------|------|
| Grain diameter                          | mm   | 15.00 | 16.26   | 10.26  | 20.15     | 16.03  | 11.51      | 12.77|
| Grain length                            | mm   | 15.00 | 10.61   | 10.21  | 13.22     | 15.51  | 11.37      | 9.65 |
| Number of channels                      | pcs. | -     | 1       | 1      | 1         | 1      | -          | 1    |
| Channel diameter                        | mm   | -     | 7.22    | 3.87   | 8.80      | 4.00   | -          | 4.60 |
| Equivalent grain diameter               | mm   | 17.17 | 16.14   | 11.73  | 20.04     | 18.15  | 13.12      | 13.31|
| Form factor                             | -    | 1.144 | 1.069   | 1.089  | 1.072     | 1.120  | 1.144      | 1.095|
| Porousness of the layer taking into account the porosity of grains | -    | 0.445 | 0.550   | 0.502  | 0.561     | 0.483  | 0.426      | 0.501|

The analysis of Table 1 shows that the shape factor increases with decreasing particle size. With a decrease in size of the catalyst granules, the degree of utilization of the catalyst surface increases, as expected, and, at the same time, the aerodynamic resistance of the layer to the flow of passing gas increases.

![Graph showing the specific aerodynamic resistance of various industrial catalysts determined using different calculation formulas.](image)

**Figure 2.** The specific aerodynamic resistance of various industrial catalysts determined using with different calculation formulas: 1 – the expression (10); 2 – expressions (11) or (12); 3 – the expression (13); 4 – the expression (14); 5 – the expression (15).

Comparing the data received for the GIAP 16 catalyst \(d_{\text{ext}}=16.14 \text{ mm}\) with the calculated values which obtained in [1] for the NIAP-18 catalyst \(d_{\text{ext}}=15.32 \text{ mm}\), it can be noted that formulas (10) – (12) overestimate the specific resistance at the level of 5-6 kPa/m compared to the value indicated in
the paper at the level of 20 kPa/m for comparable gas-dynamic conditions of movement. At the same time the expressions (13) – (15) give unreasonably low absolute values at a level of 5-10 kPa/m, which gives doubts about their applicability in such calculations.

From the analysis of the calculation results for catalyst grains which made in the form of cylinders, it can be concluded that the increase in the equivalent diameter by 30.8% (when replacing the catalyst from GIAP-3-6N to GIAP 3) gives the decrease in aerodynamic resistance by only 1.64 times. Whereas, for ring-shaped catalyst grains (for example, for GIAP 5 and GIAP 16MT), the increase in diameter by 70.8% will lead to the decrease in resistance only by 3.16 times. Thus, for the considered grain shapes, there is no scale proportionality factor between the equivalent diameter and gas dynamic resistance.

5. Discussion of results

The developed innovative power plant scheme comprising the integrated waste disposal in oil and gas enterprises aimed at combining the processes of the thermal utilization of industrial wastes (combustible gases, effluents) with the processes of gasification and energy production (electricity, thermal energy, synthesis gas, water supply), reducing the specific consumption of the fuel gas for the energy resources production and waste disposal, improving the environmental safety and reliability of the facility was proposed. The dynamic head and the values of Reynolds numbers considered in the paper correspond to the real operating conditions of the tube furnace of reforming natural gas. The specific gas dynamic resistance, which depending on the loading mode of the converted product, is 14.4-59.1 kPa/m with using a reaction tube with d_{ext}=70-130 mm (corresponds to the fictitious speed of movement of the vapor-gas mixture at the level of 1.67- 10.83 m/sec).

In favor of correctness conclusions about the most applicable formulas for performing calculations evidence the practical data of the operation of the primary reformer. Thus, when using a reaction tube with d_{ext}=70-130 mm of the AM-76 methanol synthesis unit the specific resistance is in the range of 18-31 kPa/m.

In practice the reducing the aerodynamic resistance of the reaction tube which filled with catalyst backfill will make it possible to reduce the pressure drop (reducing the energy consumption for compression), or increase the unit load without increasing the pressure drop.

6. Conclusion

In this way according to the results of the performed comparative calculations, it is possible to recommend expressions (10) – (12) as the calculated dependences for determining the coefficients of the aerodynamic resistance of the catalyst layer.

The most preferred form of the considered catalysts in terms of the set of parameters can be considered circular with a tendency to transition to more complex geometric shapes. The obtained results of a comparative analysis and a set of calculation formulas can be used in engineering calculations not only for the steam conversion of hydrocarbons, but also for equipment for increasing the energy efficiency of high-temperature thermal engineering and heat-power processes based on the thermochemical transformation of the thermal energy of exhaust flue gases into chemically bound energy of a new synthetic fuel (synthesis gas).

7. References

This work is supported by the Russian Science Foundation under grant №19-19-00327.

8. References

[1] Afanasev S V, Roshchenko O S, Dulnev A V, Obysov A V 2011 [Science Vector of Togliatti State University] 4 (18) 25–27. Russian
[2] Pashchenko D I, Chastikova O I, Gorokhov V V. 2018 [Transactions of Academenergo] 1 7–17. Russian
[3] Pashchenko D 2019 [AIChE Journal] 65(5) e16558.
[4] Pashchenko D 2019 [Energy Conversion and Management] 185 465–472.
[5] Pashchenko D 2019 [Energy] 166 462–470.
[6] Pashchenko D 2019 [International Journal of Hydrogen Energy] 44(14) 7073–7082.
[7] Pashchenko D 2019 [Fuel] 236 686–694.
[8] Rostrup-Nielsen J R 2009 [Catalysis Today] 145(1-2) 72–75.
[9] Gallucci F, Paturzo L, Basile A A 2004 [International Journal of Hydrogen Energy] 29(6) 611–617.
[10] Froment G F 2000 [Journal of Molecular Catalysis. A: Chemical] 163(1-2) 147–156.
[11] Hoang D L, Chan S H, Ding O L 2005 [Chemical Engineering Journal] 112(1-3) 1–11.
[12] Verkhivker G, Kravchenko V 2004 [Energy] 29(3) 379–388.
[13] Chakravarthy V K, Conklin J C, Daw C S, Pihl A J 2010 [Energy Fuels] 24 1529–1537.
[14] Kurganov V A, Zeigarnik Yu A, Maslakova I V, Korabel’nikov A V 1996 [Thermal Engineering] 43(3) 198–210.
[15] Pechenegov Yu Ya, Mrakin A N, Kosova O Yu 2015 [Heat transfer and heat carriers in the processes of thermal treatment of crushed solid fuel] 164 Russian
[16] Sharifov A, Khamroev F B 2011 [The reports of the Academy of Sciences of the Republic of Tajikistan] 54(2) 129–135 Russian
[17] Kagyrmanova A P, Zolotarsky I A, Smirnov E I, Vernikovskaya N V 2005 [Chemical industry today] 11 18–30. Russian
[18] Ravichev I V, Bespalov A V 2007 [Khimicheskaya promyshlennost' segodnya] 1 4–8. Russian