Power efficiency improvements of the industrial processes at application of thermochemical recuperation of heat of the leaving gases with use of microchannel reactors

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Abstract. The possibility of increasing the energy efficiency of production processes by converting the initial fuel – natural gas to synthesized fuel using the heat of the exhaust gases of plants involved in production is considered. Possible applications of this technology are given. A mathematical model of the processes of heat and mass transfer occurring in a thermochemical reactor is developed taking into account the nonequilibrium nature of the course of chemical reactions of fuel conversion. The possibility of using microchannel reaction elements and facilities for methane conversion in order to intensify the process and reduce the overall dimensions of plants is considered. The features of the course of heat and mass transfer processes under flow conditions in microchannel reaction elements are described. Additions have been made to the mathematical model, which makes it possible to use it for microchannel installations.

With the help of a mathematical model, distribution of the parameters of mixtures along the length of the reaction element of the reactor-temperature, the concentration of the reacting components, the velocity, and the values of the heat fluxes are obtained. The calculations take into account the change in the thermophysical properties of the mixture, the type of the catalytic element, the rate of the reactions, the heat exchange processes by radiation, and the longitudinal heat transfer along the flow of the reacting mixture.

The reliability of the results of the application of the mathematical model is confirmed by their comparison with the experimental data obtained by Grasso G., Schaefer G., Schuurman Y., Mirodatos C., Kuznetsov V.V., Vitovsky O.V. on similar installations.

1. Introduction

Now, natural gas is the most used fuel and energy resource in Russia and accounts for more than half in energy balance [1]. According to the global fuel and energy balance, natural gas is in third place, after oil and coal, in the total share of consumption in the oil equivalent. The constant growth of population gasification, the needs of industry, expansion of spheres of application and increase in export supplies requires an increase in the level of production, which, together with the increasing costs of developing fields, increases the cost of the resource. Increasing the energy efficiency of the energy potential of fuel using installations and reduction of consumption of natural gas has prime value for increase in power effectiveness of domestic economy, proceeds from export of a resource, energy security of the country and preserving the environment. The analysis of the dynamics of volume and structure of energy consumption shows a significant level of natural gas consumption and the growth of their share among other sources of primary energy. This circumstance, taking into
account the prospects of the cost of gaseous fuels, causes the increasing urgency of solving the problem of saving natural gas.

The internal structure of natural gas consumption mainly consists of electricity and heat generating sector, the supply to the population, municipal-household sector and industry. Industry consumes about a quarter of all natural gas used in the country [1]. Various sectors of Russian industry has considerable potential to increase the efficient use of fuels in general and natural gas in particular.

In technological process of the Russian industries, especially ferrous metallurgy, glass-making industry, building materials industry involved a large number of high-temperature installations. Their work is characterized by a large consumption of natural gas, substantial costs for heating fuel and oxidizer and high-temperature exhaust gases. The current practice of energy efficiency data of installations and the use of natural gas involves the use of heat recovery and utilization of sensible heat of exhaust gases at various stages of the process. Increasing the degree of utilization of the exhaust gases heat is one of the primary tasks on the way to to increase energy efficiency.

Thermochemical recuperation (TCR) is a method of increasing the efficiency of heat consuming installations by conversion of the original organic fuel (or its part) due to the absorption of the heat in part of the production process with the subsequent combustion of convertible fuel in installation [2, 3, 4, and 5].

The substance of a thermochemical recuperation is that high temperature combustion products and natural gas pass through the reaction system in the process which is carried out for the flow of the endothermic chemical reaction of steam conversion of methane. As a result, at the exit of the reactor composite fuel – the synthesized gas containing carbon monoxide and hydrogen which goes for immediate combustion in a heat consuming installation [4, 5] is formed.

This process allows to carry out more deep utilization of waste heat, because it increases not only physical, but also chemically-bound heat of the reacting fluids. The use of synthetic fuels in technological processes allows to obtain significant savings of the original fuel [2, 4].

The range of application of thermochemical recuperation is not limited to direct waste heat from high-temperature plants – in the presence of secondary combustible waste of primary production such as blast furnace, converter, coke, producer gas, and combustible liquid and solid waste – it perhaps to burn them to bring the temperature of thermal waste to the level required for the occurrence of reactions of conversion [4].

At the moment, there is a world and Russian practice of use of thermochemical recuperation in industrial processes. Developed variants of thermochemical reactors, data about the performance of the installations are available.

Taking into account the trends of the last decades directed to the common and the accompanying increase in efficiency of installations, particular interest represents a possibility of carrying out the process of thermochemical reaction of steam conversion of a methane in microchannel thermochemical reactors.

Theoretical and practical development of such units is conducted both abroad and in Russia [6-11]. In the transition from traditional thermochemical reactor to the installations using the microchannel reactionary elements, achieves a number of advantages, such as large heat flux that is passed to the reacting mixture in unit volume of the device, a high heat transfer coefficient, common reduction of the size of the unit with preservation of efficiency [12, 13].

However, at the moment, the processes proceeding in microchannel reactors are investigated insufficiently. In particular, there are no data that allow composing industrial installations – optimal type of reaction element, the characteristic dimensions of the elements, the layout of the reactor, the needing of additional hardware to operate the system. Also the answer to the question of what should be the degree of complexity for describing the kinetics of chemical reactions (2-stage, 3-stage process, or more) is unclear. The same question applies to the description of the hydrodynamics of the flow in the channel, for example, is it critical to use the full system of Navier-Stokes equations, either can be used with a sufficient degree of complexity one-, two-dimensional models in favor of which a simple geometry of the flow (annular channel with a longitudinal size substantially exceeding the cross).
2. Features of the processes occurring in microchannel reactors

The transition from traditional chemical reactors to microchannel requires taking into account several factors arising from the passage of fluid through channels with small cross-sectional dimension with a laminar mode of flow of reactants and heat transfer agent.

Environment flow in microchannels have high heat transfer coefficients associated with the small value of the equivalent diameter. Despite the laminar nature of the flow, heat transfer in such heat exchangers, can be similar to the turbulent flow or even a phase transition. However, small lateral dimensions of the channels result in high pressure drops requiring higher costs for pumping heat transfer agent. With increasing number of channels, the problem of non-uniformity of the costs of the individual channels caused by the different hydraulic resistances that occur over supplying coolant to reactionary elements [11].

Considering specifics of a range of application of these devices, the design of the reactionary elements exposed to high temperatures. This leads to the fact that the microchannel reactor operates in conditions of high thermal tension and a significant heat flow. Design of the reactionary elements also suggests the emergence of a significant longitudinal transfer of heat along the axis of the channel for the heat carrier and the wall-induced conductivity. This phenomenon reduces the efficiency of devices, and also reduces the strength of the structure due to the significant thermal stresses. Also, the problem represents the task of providing a uniform supply of thermal energy to the array of reactionary elements.

Due to the large longitudinal temperature gradients, it becomes evident the necessity to modify the thermophysical properties of the moving components of the reacting mixture along the reaction element.

3. Mathematical model of a thermochemical reactor

3.1. Process description and assumptions

To solve objectives one-dimensional mathematical model of a microchannel chemical reactor with the reaction elements, which is a hollow tube with embedded cylindrical catalysts was developed. Reactionary elements streamlined by flow of flue gases.

The distribution of the heat flow in the reactor volume and the single reaction element shown in figure 1.

At model building the following assumptions are accepted: the current is stationary; the gas mixture is an ideal gas; the surface of the walls, of the pipe and catalyst are gray; chemical reactions occur on the surface layer of the catalyst and proceed at the temperature the same throughout the thickness; transport of gases in the annular channel flows only along the longitudinal axis z, there is no diffusion along the z-axis; thermal resistance of tube wall and catalyst slightly in the radial direction;
the products of combustion are evenly distributed in the free volume of the reactor-heat exchanger and provide a uniform flux of radiation to the reactor. The annular channel is far superior to his gap; the conductivity along the walls of the reactor can be neglected. The changes of thermophysical properties in dependence on temperature was carried out according to [4].

At the description of the reactor the approximation of a continuous medium was used. The reason for this is the analysis of [5] where it is shown that in this region the temperature and pressure at the considered dimensions of the channel used by the system of equations does not lead to significant errors.

This model takes into account the processes of heat transfer by radiation and convection heat flows from high temperature incoming gas to the reactionary elements and the outer wall. Heat transfer condition at outer wall with the environment is adiabatic. From the wall of the reaction element heat moving inside him gas mixture and the catalyst surface, which proceeds endothermic reaction.

3.2. Mathematical modeling

According to the above, the basis for the mathematical model is represented by the following equations of energy balance:

The equation for the flow of flue gases:

\[
\rho_{d,g} \cdot W_{d,g} \cdot c_{p,d,g} \frac{\partial T_{d,g}}{\partial \tau} = -\rho_{d,g} \cdot W_{d,g} \cdot c_{p,d,g} \frac{\partial T_{d,g}}{\partial z} + \left[ -\alpha_{cm} \cdot \left( T_{d,g} - T_{cm} \right) \frac{n_{p,g} \cdot \Pi_{cm}}{F_{d,g}} - q_{u,cl,ct} \frac{n_{p,g} \cdot \Pi_{cm}}{F_{d,g}} \right] \left( T_{d,g} - T_{cm} \right) - \alpha_{sup} \frac{n_{p,g} \cdot \Pi_{cm}}{F_{d,g}} - q_{u,cl,ct} \frac{n_{p,g} \cdot \Pi_{cm}}{F_{d,g}} \right]
\]

The equation for flow of gas-vapor mixture:

\[
\rho_{e,g} \cdot W_{e,g} \cdot c_{p,e,g} \frac{\partial T_{e,g}}{\partial \tau} = -\rho_{e,g} \cdot W_{e,g} \cdot c_{p,e,g} \frac{\partial T_{e,g}}{\partial z} + \left[ \alpha_{ct,ct} \cdot \left( T_{e,g} - T_{ct} \right) \frac{\Pi_{cm,av}}{F_{e,g}} + q_{u,ct,ct} \frac{\Pi_{cm,av}}{F_{e,g}} \right] \left( T_{e,g} - T_{ct} \right) - \alpha_{sup} \frac{\Pi_{cm,av}}{F_{e,g}} - q_{u,ct,ct} \frac{\Pi_{cm,av}}{F_{e,g}} \right]
\]

The balance equation on the outer wall of a chemical reactor:

\[
\frac{\partial T_{sup}}{\partial \tau} = \alpha_{sup} \left( T_{d,g} - T_{sup} \right) + q_{u,cl,ct} - q_{u,cl,ct}
\]

The balance equation on the wall of the reaction element:

\[
\frac{\partial T_{cm}}{\partial \tau} = \left[ \alpha_{cm} \cdot \left( T_{d,g} - T_{cm} \right) \frac{d_{cm} + q_{u,cl,ct} \cdot d_{cm}}{n_{p,g}} \right] - \left[ \alpha_{cm,av} \cdot \left( T_{cm} - T_{cm} \right) \frac{d_{cm,av}}{n_{p,g}} + q_{u,ct,ct} \cdot d_{cm,av} \right]
\]

The balance equation on the surface of the catalyst:

\[
\frac{\partial T_{saw}}{\partial \tau} = \left[ \alpha_{saw} \cdot \left( T_{e,g} - T_{saw} \right) \cdot \frac{\Pi_{cm,av}}{F_{saw}} + q_{u,ct,ct} \cdot \frac{\Pi_{cm,av}}{F_{saw}} \right] - \alpha_{saw} \cdot \frac{\Pi_{cm,av}}{F_{saw}} \sum_{i=1}^{n} (-\Delta H_{i} \cdot \eta_{i} \cdot R_{i})
\]

Above equations was written with following symbols and indices:

Symbols: \( \rho \) – density, kg/m\(^3\); \( w \) – speed, m/s; \( C_{P} \) – specific heat, J/(kg·K); \( T \) – temperature, K; \( z \) is the longitudinal coordinate of the reactionary element, m; \( \alpha \) – heat transfer coefficient, W/(m\(^2\)·K); \( n_{r,e} \) – the number of reactionary elements; \( P \) – perimeter, m; \( F \) – cross-sectional area, m\(^2\); \( d \) – diameter, m;
q – heat flux, W/m²; ΔHᵢ is the heat effect of chemical reaction, j/mol; Nᵢ is the efficiency factor; Rᵢ – rate of i-th reaction, referred to 1 kg of catalyst, mol/(kg·s).

Index: g – gases; St – external wall of the reaction element; R.e – a reactionary element; I.D.St – the radiation from the flue gases to the outer wall of the reaction element; I.D. Nar – the inner surface of the outer wall of the reactor-heat exchanger; I. D. Nar – radiation from the flue gases to the outer wall of the reactor-heat exchanger; S. g – the synthesis gas; St. Vᵢ – the inner wall of the reaction element; I. St. SG – radiation from the inner wall of the reaction element to synthesis gas; cat – a catalyst; I. SG.kat – the radiation from the synthesis gas to a catalyst; I. Nar.St – radiation from the internal walls of the reactor-heat exchanger to the outer wall of the reaction element; I. senior cat – radiation from the inner wall of the reaction element for the catalyst; the indices 1, 2, 3 correspond to the numbers of chemical reactions of steam conversion of methane.

For calculation of heat transfer coefficient correlation was used for wrapping the cylindrical surface of tube flow is described in [14].

To calculate the heat transfer coefficient in laminar flow in the annular channel of the reactionary element that was used in the ratio described in [16].

The fluxes were determined using the electrothermal analogy [15].

A complete system of chemical equations describing the process of steam methane conversion, in accordance consists of 11 equations. However, only three of them are the most active:

\[ CH_4 + H_2O = CO + 3H_2 - 206,1 \text{ кДж / моль} \]  (6)

\[ CO + H_2O = CO_2 + H_2 + 41,15 \text{ кДж / моль} \]  (7)

\[ CH_4 + 2H_2O = CO_2 + 4H_2 - 165,05 \text{ кДж / моль} \]  (8)

Other reactions occur with negligibly small speed in comparison with the above speeds.

To calculate the concentrations of components of the gas mixture and converted synthesis gas is used the following equation of material balance:

\[ w_{i,z} \cdot \frac{\partial C_i}{\partial z} = \frac{F_{\text{am}}}{F_{i,z}} \cdot \rho_{\text{am}} \cdot r_i \]  (9)

– where z is the coordinate in the longitudinal direction of the reaction element, m; i is the component number of the mixture; ρₖₐₜ – density of catalyst, kg/m³; Cₗ – concentration of i-th component of the mixture, mol/m³; rᵢ – rate of formation of the i-th component gas mixture, referred to 1 kg of catalyst, mol/(kg·C); WC₉ – speed vapor flow, m/s, Fₖₐₜ, FC₉ – cross-sectional area of the gas channel of the reaction element and the catalytic inserts, m².

This equation is written for each component of the mixture at different time points of CH₄, H₂O, CO, CO₂, H₂. Included in its composition the rate of formation of the components is defined through the speed of a reaction. Equations of the kinetics obtained for three-stage reaction conversion of methane [4].

In the end, expressions for the velocities of the above reactions are follows:

\[ R_1 = \frac{k_1}{p_{H_2}^{2,5}} \left( p_{CH_4} \cdot p_{H_2,O} - \frac{p_{H_2}^4 \cdot p_{CO}}{K_{s1}} \right) \frac{1}{Q^2} \]  (10)

\[ R_2 = \frac{k_2}{p_{H_2}^{2,5}} \left( p_{CO} \cdot p_{H_2,O} - \frac{p_{H_2}^2 \cdot p_{CO}}{K_{s2}} \right) \frac{1}{Q^3} \]  (11)

\[ R_3 = \frac{k_3}{p_{H_2}^{2,5}} \left( p_{CH_4} \cdot p_{H_2,O}^2 - \frac{p_{H_2}^4 \cdot p_{CO}}{K_{s3}} \right) \frac{1}{Q^2} \]  (12)
\[ Q_t = 1 + K_{CO} \cdot P_{CO} + K_{H_2} \cdot P_{H_2} + K_{CH_4} \cdot P_{CH_4} + \frac{K_{H_2O} \cdot P_{H_2O}}{P_{H_2}} \]  

where \( R_j \) is the speed of the j-th reaction (j = 1..3), mol/(kg·C), pH2O, pH2, etc. respectively, the partial pressure of gas components, a bar, \( K_{\text{eq}} \) is the equilibrium constant of reaction [4].

To determine the partial pressures of the components according to the length of the reaction element, the hydraulic calculations was performed. The pressure drop in the inner tube and annular channel reactor was determined by the following equations [17]:

\[ \frac{dP_{\text{ct}}}{dz} = -\frac{f \cdot (\rho_{\text{ct}} \cdot w_{\text{ct}} \cdot F_{\text{kr}})^2}{2 \cdot \rho_{\text{ct}} \cdot d_{\text{eq}}} \]  

where \( f \) is the friction factor, Darcy; \( WC_\text{g} \) – the rate of flow of the synthesis gas, m/s; \( F_{\text{to/to}} \) – cross-sectional area of the annular channel, m²; \( d_{\text{eq}} \) – equivalent diameter of the annular channel, m.

The calculation of the partial pressures \( p_i \), Pa, was carried out according to the share of each component in the reacting mixture.

4. The results of numerical simulation

The adequacy of the proposed mathematical model is verified by comparison with experimental data [7]. Simulated chemical reactor is a hollow tube with a solid cylindrical catalyst element, similar to those presented in the experiment. Element length is 40 mm, outer diameter is 6 mm, and the annular gap is 1 mm. The temperature at which carried out the processes - 800°C. The ratio H2O : CH4 = 1.77. The used catalyst is Rh/Al2O3.

The results of the comparison of experimental data and numerical simulation results are presented in the figure below.

![Figure 2. Comparison with experimental data](image-url)
According to the Figure 2, there is a fairly high convergence of numerical simulation results with experimental data. For comparison and opportunity to further scale the performance of a microchannel reactionary elements to industrial processes, the simulation element with the above conditions at different volumetric capacity, the size of an annular gap are carried out.

![Figure 3. CH4 conversion at different volumetric capacity](image)

As the results show, reducing the annular gap leads to an increase in the degree of completion of reactions, that is, to a deeper degree of conversion of the original fuel. However, excessive increase of the volume flow supplied to the channel, decreases the degree of conversion, as not all of the original fuel has time to react for the time spent in the channel.

5. Conclusion
This paper presents the possibility of implementation of the process of thermochemical recuperation with the use of microchannel reactor. The proposed mathematical model in comparison with experimental data shows good agreement. By results of the conducted experiments, we can say that the use of microchannel reactionary elements allows to achieve a high degree of conversion of the initial fuel with significantly reduced dimensions. Moreover, at the outlet of the reaction element, it is possible to obtain a higher degree of conversion, due to the intensification of heat transfer processes and chemical transformations. To achieve the same performance necessary to solve the problem of layout many similar reactionary elements and a uniform supply of heat to them.

In summary, the microchannel reactor allows to carry out highly efficient process of steam methane conversion. Their use in the process of thermochemical recuperation will increase the efficiency of the production process and save the source fuel is natural gas.

6. References
[1] Gazprom 2016 Annual year report (Moscow) p 259
[2] Novoseltsev V N 1971 On the chemical heat recovery industrial gas-powered plants p 22
[3] Nosacg V G 1989 Energy fuel (Kiev) p 147
[4] Tararykov A V 2013 Research to improve methods for the assessment of energy saving and environmental effect of the application of thermochemical and integrated regeneration of heat of exhaust gas (Moscow)
[5] Mongi G A R 2011 Improving the efficiency of high-temperature plants by means of thermochemical recuperation of waste heat (Moscow)
[6] Murphy D M, Manerbino A, Parker M, Blasi J, Kee R J, Sullivan N P Methane steam reforming in a novel ceramic microchannel reactor 2013 International Journal of Hydrogen Energy.
[7] Kuznetsov V V, Vitovsky O V, Gasenko O A 2009 Methane Steam Reforming in an Annular Microchannel with Rh/Al2O3 Catalyst. Journal of Engineering Thermophysics.
[8] Grasso G, Schaefer G, Schuurman Y, Mirodatos C 2011 Methane Steam Reforming in Microchannel Reactors: Technical Challenges and Performances Benefits. Catalysis.
[9] Behroozsaranda A, Nakhaei A 2014 Pour Modeling of microreactor for methane dry reforming: Comparison of Langmuir–Hinshelwood kinetic and microkinetic models. Journal of Natural Gas Science and Engineering.
[10] Butcher H, Quenzel C J E, Breziner L, Mettes J, Wilhite B A, Bossard P 2014 Design of an annular microchannel reactor (AMR) for hydrogen and/or syngas production via methane steam reforming International Journal of Hydrogen Energy Volume 39
[11] Holladay J D, Wang Y 2015 A review of recent advances in numerical simulations of microscale fuel processor for hydrogen production Journal of Power Sources
[12] Donata M F 2008 Multiphase flow in microchannels: Hydrodynamics and implementation in process engineering. Diss., Eidgenössische Technische Hochschule ETH Zürich
[13] Zhai X, Din S, Cheng Y, Jin Y, Cheng Y 2010 CFD simulation with detailed chemistry of steam reforming of methane for hydrogen production in an integrated micro-reactor International Journal of Hydrogen Energy Volume 35
[14] Cvetkov F F, Grygoriev B A 2005 Heat and mass transfer (Moscow) p 548
[15] Kreith F, Black W Z 1983 Basic heat transfer p 512
[16] Baklastov A M (1986) Бакластов А.М. Industrial heat and mass exchange processes and installations (Moscow) p 326
[17] Klimenko A V 2001 Theoretical basis of heat engineering (Moscow) p 564