Modelling of the Methane Oxidation Process in Tubular Heating Elements

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Abstract

Catalytic heater model in the form of a tubular reactor, in the tube space of which heat is removed using a high-boiling heat carrier was elaborated. Kinetic parameters of methane oxidation rate constant on a manganese-alumina catalyst (pre-exponential factor and activation energy) that were used to calculate the observable reaction rates on grains of various shapes and sizes were determined. It was demonstrated that the maximum specific heat power of a catalytic heater was 19.25 kW/m^3; it can be obtained by applying the catalyst in the form of rings with dimensions of $5 \times 5 \times 2$ mm, under the following conditions: inlet methane concentration of 3 %, inlet temperature of 500 °C, heat carrier temperature of 400 °C, tube length of 1 m, tube diameter of 8 cm, linear rate of 0.05 m/s. With such parameters, the degree of methane conversion is greater than 98 %, and the maximum temperature does not exceed 770 °C, which meets accepted limitations.

Key words: mathematical modelling, catalytic oxidation, methane, tubular reactor, catalytic heater

INTRODUCTION

Currently, organic forms of fuel are the most common energy source. Over 70 % entire energy consumed in the world is produced due to hydrocarbon fuels combustion, therefore, improving the organization of the process of burning fuels in combustion chambers and furnace plants is relevant [1]. When flaring hydrocarbon fuels polluting and ozone-depleting substances are emitted to the atmosphere, which is considered to be one of the global environmental problems. In comparison with other fuel types, natural gas is more environmentally friendly, there are no ash and soot in its combustion products, however, such high-toxic substances as nitrogen oxides and carbon oxide may be present.

The use of catalysts ensures complete oxidation of hydrocarbons from natural gas at lower temperatures in the combustion zone, which leads to a decrease in the content of thermal nitrogen oxides in the reaction products. Based on flameless catalytic combustion of fuels one can create new environmentally friendly methods of heat generation at the lowest level of harmful emissions. Works [2–7] consider some examples of using catalytic burning in various heating plants that should be extended and to other application areas. In particular, natural

gas combustion is usually used in automatic gas distribution stations (AGDS) in the gas heating block, as a result of which flue gases that are emitted to the atmosphere are formed in boiler furnaces. Therefore, studying the possibility of applying heaters based on natural gas catalytic partial oxidation for heat generation at AGDS is relevant. The present work presents the study of the natural gas catalytic burning in a heater that represents a tube reactor, tubes of which are filled with a catalyst, and heat in the tube space is removed using a high-boiling heat carrier. The purpose of the present work was the determination of reactor optimum characteristics that may ensure the highest value of the removable thermal capacity.

MATHEMATICAL MODELLING OF A CATALYTIC HEATER

It is suggested that there are special mixing and distribution devices in the reactor that ensure equal conditions on the temperature, concentration, and gas flow rates at the entrance in all tubes with the catalyst, and the principle of evaporative cooling the tubes with a high-boiling heat carrier is used in the tube space for heat dissipation. This allows conducting calculations of modes for one tube only, since all the tubes are found under identical conditions. To calculate the removable thermal capacity from all the reactor tubes the calculated value of thermal capacity from one tube can be multiplied by the number of tubes in the reactor.

A stationary two-dimensional mathematical model of the processes of heat and mass transfer in catalyst layer is used. Stationarity of the model is determined by the fact that a catalytic heater operates in a stationary mode. The model describes a change in the concentration and substances concentrations also along the tube radius [8, 9]. The model takes into consideration that the reaction of complete methane oxidation with air oxygen occurs without a volume change.

The mathematical model in cylindrical coordinates has the following form:

$$\frac{u_0 P_0}{RT_0}\frac{\partial y_i}{\partial l} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{PD_r}{RT}\frac{\partial y_i}{\partial r}\right) = \gamma_i \omega,$$
$$i = CH_4, O_2, CO_2, H_2O \tag{1}$$

$$\frac{u_0 P_0}{RT_0}c_p\frac{\partial T}{\partial l} - \sum_i c_{pi}\left(\frac{\partial T}{\partial r}\right)\frac{PD_r}{RT}\frac{\partial y_i}{\partial r}$$
$$- \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_r\frac{\partial T}{\partial r}\right) = -\Delta H\omega \tag{2}$$

$$0 \le r \le R_t \quad l = 0 : T(0, r) = T_{in}, \ y_i(0, r) = y_{i\,in}$$

$$0 \le l \le L \qquad r = 0 : \frac{\partial T(l, 0)}{\partial r} = 0, \ \frac{\partial y_i(l, 0)}{\partial r} 0 \tag{3}$$

$$r = R_t : \lambda_r\frac{\partial T}{\partial r} = \alpha_w(T_w - T), \ \frac{\partial y_i(l, R_t)}{\partial r} = 0,$$

$$i = CH_4, O_2, CO_2, H_2O$$

where P is pressure, bar; R is universal gas constant, $m^3 \cdot atm/(mol \cdot K)$; T is temperature, K; u is linear flow rate, m/s; v_i is concentration of the i-th substance, mole fraction; l, L are coordinate along the length of the layer and the layer length, m; r is coordinate along the tube radius, m; D_r is radial diffusion coefficient, m^2/s; γ_i is stoichiometric coefficient of the i-th substance in the reaction; ω is observed reaction rate on the granule of the catalyst, $mol/(m^3_{layer} \cdot s)$; c_p is heat capacity of the mixture, $J/(K \cdot mol)$; c_{pi} is specific heat of the i-th substances, $J/(K \cdot mol)$; λ_r is radial coefficient of thermal conductivity, $J/(m \cdot s \cdot K)$; ΔH is reaction enthalpy, J/mol; R_t is tube radius, m; α_w is heat transfer coefficient from the convert gas flow to the tube wall, $J/(m^2 \cdot s \cdot K)$. Indexes: in − input values; 0 − values under normal conditions; w − tube wall.

In the equation of material balance of the i-th substance (1) takes into account convective mass transfer along the length of the layer, mass transfer by diffusion along the radius of the tube and the change of mass due to the reaction.

Thermal balance equation (2) considers the convective energy transport along the layer length, heat transfer by diffusion due to the difference between the heat capacity of diffusing substances and the conductivity along the radius of the tube, heat production as a result of the chemical reaction.

The radial heat and mass transfer coefficients, heat transfer coefficient from the convertible gas flow to the tube wall and the pressure drop in the catalyst layer are calculated according to the dependencies that consider the fact that in the layer of particles with a complex shape with a random number and shape

of straight-through channels, the current moves both between particles and through openings in them [8−10].

Heat of an exothermic methane oxidation reaction is withdrawn through the side tube walls to the heat carrier and then used for heat generation in the secondary circuit. Heat capacity removable from one tube is calculated according to the formula derived by integrating the energy balance equation along the length and radius of the tube taking into account the boundary condition (3) for the temperature at $r = R_t$:

$$Q = 2\left(c_p^{av} u_0 \frac{P_0}{RT_0} \int_0^{R_t} (T_{out} - T_{in}) r \, dr \right)$$
$$+ 2\left(\int_0^{L_t} \int_0^{R_t} (-\Delta H) r \omega \, dr \, dl \right) \qquad (4)$$

where c_p^{av} is average specific heat of the mixture, J/(mol · K).

Differential equation system (1)−(2) with boundary conditions (3) was solved numerically. When constructing a discrete model the integro-interpolation method and the method of straight lines were used, derivatives on the length herewith were not approximated. The resulting system of nonlinear ordinary differential equations along the tube length was solved using a semi-implicit L stable the Rosenbrock-type method of the 2nd accuracy order. A detailed description of the solution algorithm is given in [9].

KINETICS OF METHANE OXIDATION

The reaction stoichiometry of complete methane oxidation by oxygen has the following form:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (-\Delta H = 800 \text{ kJ/mol})$
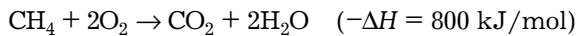
The kinetic order on methane in the oxidation reaction rate in a range of volume concentrations of methane up to 5 vol. % is equal to 1, and the orders on oxygen, CO_2 and H_2O are close to 0.1, 0.0 and 0.2 m, respectively [11], therefore, the reaction rate of methane oxidation can be represented by a first order kinetics equation relatively to methane concentration.

$\omega = \eta k_{kin} \rho_{cat} y_{CH_4} \qquad (5)$

where η is utilization degree of the inner surface of the catalyst grain; k_{kin} is the reaction rate constant in the kinetic region, mol/(g_cat · s); ρ_{cat} is bulk density of the catalyst, g_cat/m³_layer. The dependence of the reaction rate constant on temperature is determined by the Arrhenius equation: $k_{kin} = Ae^{-E/(RT)}$, where A is the pre-exponential factor, E is the activation energy.

Measuring the activity of an AOK-75-41 catalyst (Special Design and Engineering Office Katalizator JSC, Novosibirsk) in the form of balls with a diameter of 2−3 mm was carried out at the Boreskov Institute of Catalysis (BIC) SB RAS using a flow-circulation installation. This catalyst is made based on high-temperature forms of manganese and aluminum oxides, has a thermal stability up to 850 °C and high mechanical tensile strength and collapse resistance, bulk density is 1.03 g/mL. The initial mixture contained 1 vol. % methane, 20.7 vol. % oxygen, the rest is nitrogen. Cycle temperature was varied from 400 to 530 °C, the feed rate of the reaction medium was varied from 1000 to 100 mL/min, and the sample weight of the catalyst was 10 g, circulation rate − 800 L/h. When testing the catalyst, there was only unreacted methane among the reaction mixture components, CO_2 and H_2O, CO were not observed. The observable reaction rate values (W) at various temperatures and flow rates corresponding to the methane conversion degree (X) (50±5) % are given in Table 1.

When using a catalyst with another shape and/or size the observable value of the reaction rate may change because of pore-diffusion processes, therefore, the reaction rate parameters in the kinetic region we determined.

TABLE 1

Experimental values of the observable reaction rate (W)

T, K	V, mL/min	X, %	W, mL/(mL_cat · s)
678	150	47.06	0.001
703	180	55.49	0.002
728	330	55.22	0.004
753	500	54.83	0.005
778	700	53.45	0.007
803	1000	56.18	0.011

Represent the reaction rate by a first-order kinetic equation with respect to methane concentration: $W = k_{obs} y_{CH_4} = k_{kin} \eta y_{CH_4}$. Then

$$k_{kin} = W / (y_{CH_4} \eta) \qquad (6)$$

By setting the initial approximation for the utilization degree (η) from a range from 0 to 1 calculate k_{kin}, according to formula (6) using the data in Table 1. Then calculate the Thiele criterion, according to the formula

$$\varphi = R_{cat} \sqrt{k_{kin} / D_{ef}} \qquad (7)$$

where R_{cat} is radius of the catalyst particle, D_{ef} is effective methane diffusion coefficient in the catalyst grain. Further, calculate the use degree for the spherical grain, according to formula [12]

$$\eta = \frac{3}{\varphi} \left(\frac{1}{th(\varphi)} - \frac{1}{\varphi} \right) \qquad (8)$$

Take this value of the use degree as the second approximation. Further, the iterative process is repeated until the difference between the last two values of the use degree are lower than a given value ε [13] (ε is the iteration convergence accuracy). A similar procedure was performed at the remaining temperatures. The found values k_{kin} and η are given in Table 2.

According to Table 2 data, the activation energy value was $E_a = 90.75$ kJ/mol, pre-exponential factor $A = 2.16 \cdot 10^6 \, s^{-1}$, which corresponds to a value of $A = 93.75 \cdot 10^6 \, mol/(g_{cat} \cdot s)$ in the dimensionality adopted for the model.

To calculate the effective methane diffusion coefficient in the catalyst grain obtained when studying the porous structure using a Micromeritics AutoPore IV 9500 mercury porosimeter. The average pore diameter was 0.0254 μm.

The use degree of the catalyst in the form of a ring was calculated, according to the dependence for the catalyst grain in the form of a plate [12], in which when calculating the Thiele criterion the plate half-thickness equal to the ratio of the volume of the ring to its surface is used. The limiting size for the determination of the diffusion resistance to mass transfer in the ring is the ring thickness. Since the plate in the first approximation can be viewed as a ring with a large radius, the formula of the utilization degree was taken to evaluate for the catalyst particle in the form of plates.

MODELLING RESULTS OF THE METHANE OXIDATION PROCESS

During calculations, parameters were varied in the following limits:
– tube diameter (D_t) – from 3 to 10 cm;
– tube length (L) – from 0.5 to 3 m;
– heating medium temperature (T_x) – 400 °C;
– inlet temperature (T_{in}) – 500 °C;
– input methane concentration (C_{in}) – from 2 to 4 %;
– linear rate (u_0) – from 0.025 to 0.25 m/s;
– shape and size of the catalyst – sphere with a diameter (d_{sp}) of 3 and 5 mm;
– ring with a height (h) of 5 mm, an outer diameter (d_{out}) of 5 mm and an inner diameter (d_{inn}) of 2 mm.

The oxygen concentration in a methane-air mixture is assumed to be equal to 20.95 %.

Adopted restrictions. Methane catalytic combustion modes were selected in such a way for the methane conversion degree at a given temperature to be no lower than 98–99 %, the maximum temperature inside the catalyst layer (temperature in the hot spot) did not exceed 810 °C, herewith, the removable thermal capacity should be maximum.

Limitations on the maximum process temperature are determined by the catalyst thermal stability considering some reserve; limitations on the minimum methane conversion degree are explained by the necessity of complete using fuels to avoid the formation of methane explosive concentrations in air.

Calculations when using the spherical catalyst grain in the entire region of varying parameters demonstrated that it is impossible to obtain modes satisfying adopted restrictions because of insufficiently effective radial heat

TABLE 2

Values of kinetic constants and degrees of use (η)

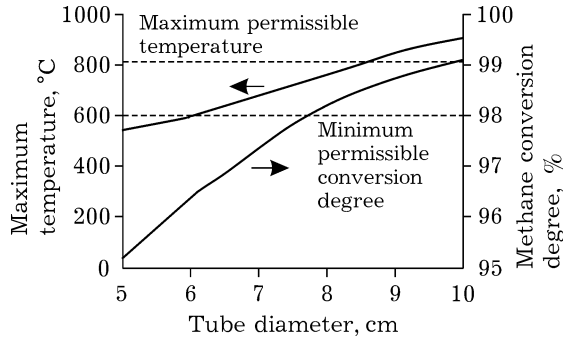| T, K	V, mL/min	X, %	k_{kin}, s^{-1}	η
678	150	47.06	0.22	0.98
703	180	55.49	0.41	0.97
728	330	55.22	0.77	0.94
753	500	54.83	1.09	0.92
778	700	53.45	1.64	0.89
803	1000	56.18	2.70	0.84

Fig. 1. Effect of tube diameter on the methane conversion degree. $T_{in} = 500$ °C; $C_{in} = 3$ %; $L = 1$ m; $u_0 = 0.05$ m/s; catalyst form − ring, $d_{out} = 5$ mm, $d_{in} = 2$ mm.
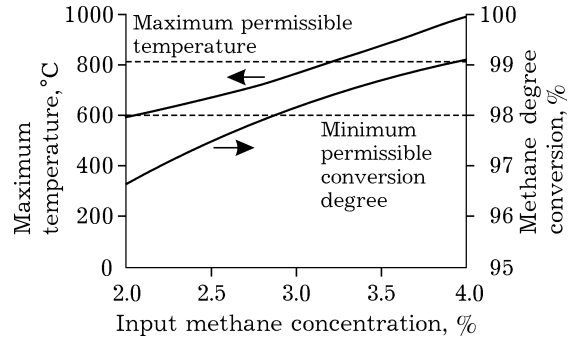
Fig. 2. Effect of the input methane concentration on the conversion degree. $T_{in} = 500$ °C; $D_t = 8$ cm; $L = 1$ m; $u_0 = 0.05$ m/s; catalyst form − ring, $d_{out} = 5$, $d_{in} = 2$ mm.

transmission in the layer, therefore, further calculations were performed for the catalyst in the form of rings.

ANALYSIS OF THE EFFECT OF PARAMETERS ON THE PROCESS INDICATORS

Effect of tube diameter

Dependencies of the methane conversion degree and the maximum temperature on tube diameter at $C_{in} = 3$ %, $L = 1$ m and $u_0 = 0.05$ m/s are given in Fig. 1. It can be seen that with increasing tube diameter, the maximum temperature increases and the conversion degree grows. However, the maximum temperature at a diameter of over 8.5 cm exceeds the permissible value, and one does not manage to reach the required conversion degree at a diameter of less than 8 cm. The removable heat capacity in a value range D_t equal to 8 and 8.5 cm is 0.097 and 0.11 kW. At $D_t = 8.5$ cm, the heat capacity is higher, however, the maximum temperature lies on the boundary region with the permissible temperature, which is undesirable from the viewpoint of the safe conduct of the process. Therefore, it is advisable to select a tube with a diameter of 8 cm for further studies of the effect of parameters.

Effect of the input methane concentration

The study results of the effect of the input methane concentration on the conversion degree and maximum temperature at a diameter of the tube of 8 cm are given in Fig. 2. With increasing the input concentration, the maximum temperature and methane conversion degree are increased. However, only the mode at the input methane conversion of less than 3 % corresponds to accepted temperature and conversion limitations. The removable heat capacity increases with increasing the methane concentration at the tube entrance, it reaches 0.097 kW at 3 % methane.

Effect of the linear rate at fixed contact time

Calculations of a tubular reactor with a tube diameter of 8 cm were carried out at a change in linear rate from 0.025 to 0.15 m/s. Herewith, the length of the catalyst layer commensurately increased in order for the contact time did not change. An increase in linear rate at the constant contact time leads to an increase in heat and mass transfer coefficients and heat exchange with the wall. Therefore, the removable heat capacity increases with increasing lin-

TABLE 3

Effect of the linear rate on the conversion degree and maximum temperature

L, m	u_0, m/s	Conversion degree, %	T_{max}, °C	Q, kW
0.5	0.025	98.27	781.5	0.048
1.0	0.05	98.19	762.8	0.097
1.5	0.075	98.08	744.64	0.145
2.0	0.10	97.95	727.07	0.193
2.5	0.125	97.81	710.1	0.241
3.0	0.15	97.65	693.73	0.289

ear rate, and the conversion degree and maximum temperature is decreased which is demonstrated in Table 3. The maximum temperature at all values of linear rate meet the adopted limitation of 810 °C, however, the specified conversion degree is reached only at $u_0 \leq 0.075$. The removed capacity is maximum at a rate of 0.075 m/s and amounts to 0.145 kW. However, when recalculating on the catalyst volume, the maximum removable capacity is reached at a tube length of 1 m and $u_0 = 0.05$ m/s and amounts to 19.25 kW/m³. The pressure drop does not exceed 0.001 atm.

CONCLUSION

Catalytic heater model representing a tubular reactor, tubes of which are filled with a catalyst and heat of the flowing exothermic reaction is taken away through side tube walls into the tube space, where removed using a high-boiling heat carrier was elaborated.

The kinetic parameters of the methane oxidation rate in a low-percentage methane-air mixture on a manganese-alumina catalyst (pre-exponential factor and activation energy) that were used to calculate the observable reaction rates on grains of various shapes and sizes were determined from experiments using a flow set-up n a temperature range of 400−530 °C.

The parameters of a kinetic heater, at which the maximum specific heat capacity is 19.25 kW/m³ were determined. Herewith, the resulting maximum specific removable heat capacity is 19.25 kW/m³. Herewith, the resulting methane conversion degree is over 98 %, and the maximum temperature does not exceed 770 °C, which meets accepted limitations. Such a capacity can be obtained by applying a catalyst in the form of rings with the sizes of $5 \times 5 \times 2$ mm at the following conditions: the input methane concentration is less than 3 %, inlet temperature of 500 °C, heating medium temperature of 400 °C, tube length of 1 m, tube diameter of 8 cm, linear rate of 0.05 m/s.

Acknowledgments

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