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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Choice of Mode Parameters of Partial Gas-Phase Oxidation of Methane by Atmospheric Oxygen To Obtain Synthesis Gas of Required Composition

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Abstract—Results of theoretical and experimental studies of the partial gas-phase oxidation of methane by atmospheric oxygen were used to determine the range of main technological parameters providing the maximum yield of synthesis gas suitable for use in further catalytic synthesis of methanol.

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The technology for manufacture of motor fuels from natural or associated petroleum gas is economically and ecologically efficient. The process of conversion of hydrocarbon gases to liquid commercial hydrocarbons (Gas-to-liquids, GTL, technology) includes three main stages: production of synthesis gas, synthesis of an intermediate, and manufacture of the final product [1]. The main difficulty in setting-up such industries consists, first, in developing a high-output capacity and sufficiently low-cost method for production of synthesis gas and, second, in creating high-efficiency catalysts necessary for obtaining the final product.

Each particular chemical technology of catalytic synthesis has its own requirements to the composition of the synthesis gas obtained (which differ both in the ratio of hydrogen and carbon monoxide and in the admissible admixtures of other substances).

The stage of production of synthesis gas by the conventional techniques requires more than 50% of the total investment, and, therefore, the problems of synthesis-gas production have been the subject of numerous researches and developments aimed to improve the existing technologies and create new ones [2].

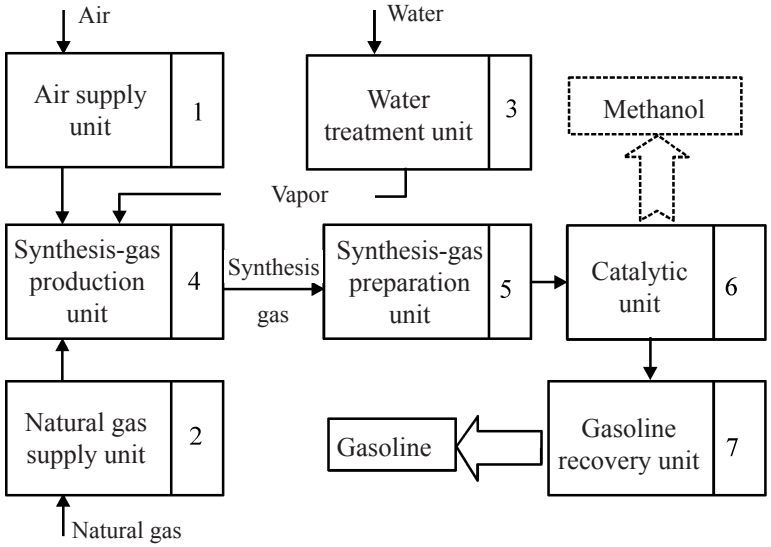
An important disadvantage of modern technologies for production of synthesis gas, based on conversion of liquid and gaseous hydrocarbons, is that they use catalysts or pure oxygen. As a result, the operating costs increase, the installations used become more sophisticated and expensive, their reliability is deteriorated, and their fire- and explosion hazard grows [3].

The technology suggested for processing hydrocarbon gases is based on direct partial gas-phase oxidation of a hydrocarbon gas by atmospheric oxygen: hydrocarbon gas → oxidation → synthesis gas → intermediate (methanol, dimethyl ether) → motor fuel [4]. Synthesis gas is produced in high-temperature reactors (HTRs) developed on the basis of achievements in the field of liquid-propellant engines [5]. The high-temperature reactor is a small-size, highly energetic design in which synthesis gases of various compositions can be produced by varying mode parameters. Use of HTRs can provide a high output capacity in conversion of the starting raw materials in a single run.

In this technology, synthesis gas can be produced both from methane and from natural and associated gases, i.e., the system is undemanding toward raw materials. In addition, the system requires no expensive catalysts and use of air instead of pure oxygen not only lowers the operation costs, but also substantially diminishes the fire and explosion hazard of the system upon a slight increase in its mass. The process suggested for processing of natural gas into gasoline, with methanol as intermediate product, can be represented by a block diagram.

The widely presently used Cu–Zn–Al oxide methanol

Block diagram of natural gas processing to gasoline



catalysts impose the following main requirements to synthesis-gas parameters: the maximum total concentration of H_2 and CO in the synthesis gas at a volume concentration ratio $H_2/CO \geq 1.8$, content of water ≤ 0.5 vol %, content of carbon black and solid admixtures ≤ 0.5 mg Nm^{-3}; content of $CO_2 < 2.0$ vol %, working temperature 220–250°C, working pressure 5.1–5.3 MPa.

The aim of our study was to find the range of main mode parameters of the gas-phase partial oxidation of methane by atmospheric oxygen, at which the maximum yield of synthesis gas can be achieved at its characteristics most appropriate for further stages of organic synthesis.

The process of the gas-phase partial oxidation of a hydrocarbon gas (methane, in the given case) by atmospheric oxygen can be represented by the reaction:

$$CH_4 + (O_2 + 3.76N_2) \rightarrow CO + H_2 + N_2 + CO_2 + H_2O + C. \quad (1)$$

The full theoretically possible conversion of methane to synthesis gas occurs by the reaction

$$CH_4 + 0.5(O_2 + 3.76N_2) \rightarrow CO + 2H_2 + 1.88N_2. \quad (2)$$

with the oxidant excess coefficient α = 0.25 and oxidant-to-fuel mass ratio $K_m \approx 4.3$.

The "ideal" specific yield of synthesis gas is 2 kg per 1 kg of methane [reaction (2)]. The real yield of synthesis gas will be lower [reaction (1)] and depends on thermodynamic conditions: temperature of methane and air, component ratio (K_m or α), pressure, and residence time of the components in the reactor, i.e., the extent to which equilibrium is attained.

Synthesis gas is produced in two stages: "fast" (primary reactions)

$$3CH_4 + 4O_2 \rightarrow CO_2 + CO + 5H_2O + H_2 + C. \quad (3)$$

and "slow" (secondary reactions)

$$CH_4 + H_2O \rightarrow CO + 3\,H_2, \quad (4)$$

$$C + CO_2 \rightarrow 2CO, \quad (5)$$

$$C + H_2O \rightarrow CO + H_2. \quad (6)$$

As can be seen from reaction (3), in the first stage, a considerable part of raw materials is converted to CO_2, H_2O, and C, rather than to synthesis gas ($CO + H_2$). For a more complete conversion of raw materials to synthesis gas, it is necessary to perform reactions (4)–(6) to a full extent, i.e., to reach the thermodynamic equilibrium.

At a given composition of raw materials (composition of a hydrocarbon gas depends on a particular gas field) and reactor pressure (determined by the catalyst operation mode), the following parameters can be varied to control the process: component ratio (K_m or α), reactor temperature (depends on α and temperature of the components), and reaction duration (residence time) determined by the flow

rate of the reaction products, i.e., by the total flow rate of the components and by the reactor volume.

The total mass flow rate of the reaction products is equal to the total flow rate of raw materials and air. At a prescribed mass flow rate of the raw materials to be processed, the residence time depends on the reactor volume and component ratio. Thus, the condition for obtaining the maximum specific yield of synthesis gas per 1 kg of raw materials is that the reactor volume should provide attainment of the thermodynamic equilibrium. Requirements to a reactor volume providing that the thermodynamic equilibrium is attained are similar to the requirements to the volume of a combustion chamber of a liquid-propellant engine.

If this requirement is satisfied, calculations can rather precisely determine the composition, temperature, and other parameters of synthesis gas produced in the reactor.

Thermodynamic calculations also enable evaluation of the effect of various additives on the parameters of the synthesis gas obtained.

The production of synthesis gas is affected by a large number of design and technological factors: composition of raw materials, oxidant excess coefficient, pressure in the reactor chamber, initial temperature of fuel components, temperature of the reaction mixture, residence time determining the extent to which the physicochemical reaction occurs, system for fuel component mixing (intrachamber or preliminary), and thermodynamic and thermal processes in the HTR volume.

The main important mode parameters to be provided by an installation for synthesis gas production are the following: oxidant (air) excess coefficient α, pressure P_C in the combustion chamber of the reactor, initial temperatures of the fuel components T_{in}, and residence time τ.

The composition of natural gas strongly depends on a particular gas field. To generalize all the possible variants of calculations, methane, which constitutes the largest volume fraction of natural hydrocarbon gases, was considered as a fuel.

The pressure at which synthesis gas is obtained is predetermined by the technological mode of the methanol catalyst. It was chosen to be 5.5 MPa.

To find conditions providing the necessary yield of a synthesis gas of required composition, we performed thermodynamic calculations by the procedure previously described in [6, 7].

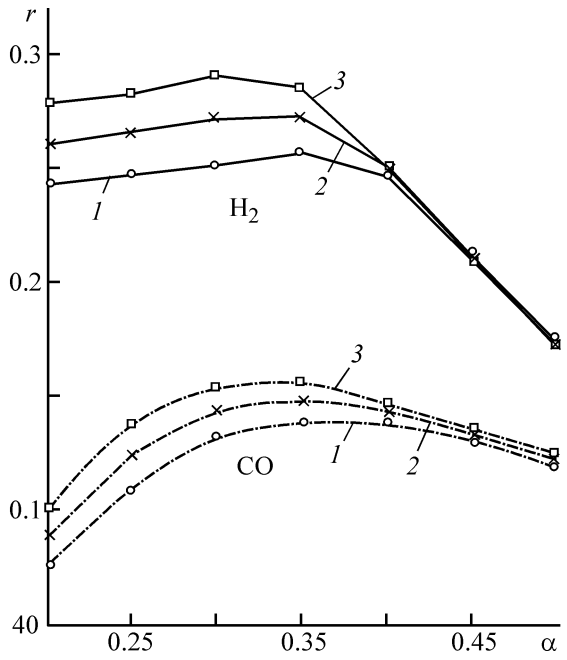


Fig. 1. Volume fraction *r* of hydrogen and carbon monoxide vs. the oxidant excess coefficient α. Initial component temperature T_{in}: (*1*) 300, (*2*) 500, and (*3*) 700 K; the same for Fig. 2.

The goal of a thermodynamic calculation is to find the equilibrium chemical composition of combustion products and determine thermodynamic and thermal properties of a mixture. The conditional formula and full enthalpy of the fuel, and also the pressure in the combustion chamber serve as input data.

At a prescribed intrachamber pressure, the temperature and equilibrium chemical composition of combustion products are uniquely determined by solving the following system of equations: equilibrium (dissociation equations), material balance equations (conservation of matter), Dalton equation, and energy conservation law.

Taking into account the aforesaid, we calculated the composition of the products of methane combustion with air, with the following input data: oxidant excess coefficient α = 0.2–0.5, intrachamber pressure P_c = 5.5 MPa, initial component temperatures 300, 500, and 700 K.

In the calculation, we assumed that the residence time is sufficiently close to the time in which thermodynamic equilibrium is attained.

Analysis of the results of the thermodynamic calculations suggests that various process conditions of methane + air combustion affect the yield of target and by-products.

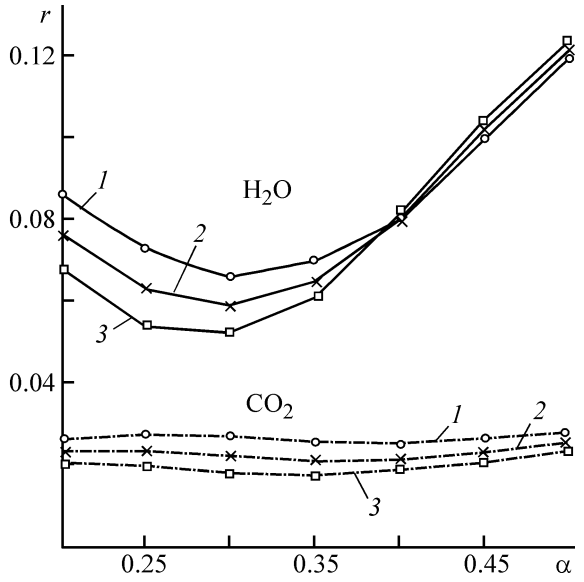


Fig. 2. Volume fraction *r* of water vapor and carbon dioxide vs. the oxidant excess coefficient α.

(1) The volume content of the main components of synthesis gas (H_2 and CO) increases as the initial temperature of the components is raised and the intrachamber pressure is lowered; as a function of the oxidant excess coefficient, it has a maximum at α = 0.3–0.35 (Fig. 1).

2. The water vapor concentration in the combustion products (Fig. 2) decreases as the pressure is lowered and the initial temperature of air and methane is raised and reaches the minimum value at α = 0.3.

3. The content of carbon dioxide does not exceed 3 vol % it decreases as the component temperature is raised, and is nearly independent of the intrachamber pressure and oxidant excess coefficient (Fig. 2).

According to the results of our thermodynamic calculations, the maximum specific yield of synthesis gas is obtained at an oxidant excess coefficient α = 0.4 and component heating to 700 K: 1.73 kg of synthesis gas from 1 kg of methane, or about 87% of the maximum theoretically possible value of 2 kg of synthesis gas per 1 kg of methane.

Analysis of the results of our thermodynamic calculations suggests that it is impossible to find working process parameters fully satisfying the requirements to the methanol catalyst. Obtaining the maximum sum concentrations of H_2 and CO requires a preliminary heating of air and methane (to no less than 700 K); however, this leads to a decrease in the CO_2 content of combustion products (to <2.0 vol %) and in the H_2/CO ratio. To obtain the required ratio between hydrogen and carbon monoxide, it is necessary to perform the process in which synthesis gas is formed at $\alpha \leq 0.35$, but the yield of condensed carbon increases at such low oxidant excess coefficients [8].

The process of partial gas-phase oxidation of methane by atmospheric oxygen to obtain synthesis gas is carried out at small oxidant excess coefficients at an oxidant-to-fuel mass flow ratio K_m = 5–9. With this ratio taken into account, it is appropriate to consider preliminary heating of only a single component of the fuel mixture, air.

To improve the characteristics of the synthesis gas obtained, we performed additional thermodynamic calculations in which the effect of water vapor addition to the reacting gas flow in amounts of 10, 30, and 50% relative to the fuel flow rate was used.

Addition of water vapor leads to a decrease both in the sum content of hydrogen and carbon monoxide and in the specific yield of synthesis gas, but, at the same time, this favors an increase in the content of CO_2 in products formed in methane + air combustion and in the H_2/CO ratio, which will yield a synthesis gas of the required composition at large oxidant excess coefficients.

Analysis of the results of our thermodynamic calculations makes it possible to suggest the real, achievable range of parameters for the production of synthesis gas with the most favorable characteristics for methanol catalysis: oxidant (air) excess coefficient $\alpha \approx 0.36$–0.38, combustion chamber pressure 5.5 MPa, initial air temperature ≥ 700 K, addition of water vapor in an amount of 20–30% relative to the fuel flow rate.

The calculated composition (vol %) for these parameters is given below, with the temperature of synthesis gas equal to 1380 K:

H_2	CO	H_2O	CO_2	N_2	Ar
26.5	13.2	11.6	2.8	45.4	0.5

It can be seen that synthesis gas satisfies the requirements of the methanol catalyst in the H_2/CO ratio and CO_2 content. According to the results of equilibrium thermodynamic calculations made at these input parameters, the content of condensed carbon and solid admixtures in synthesis gas will be lower than 10^{-8} mol. fraction. In addition, analysis of published data indicates that introduction of water vapor into the combustion zone of hydrocarbon fuels with air suppresses the process of carbon black formation [8].

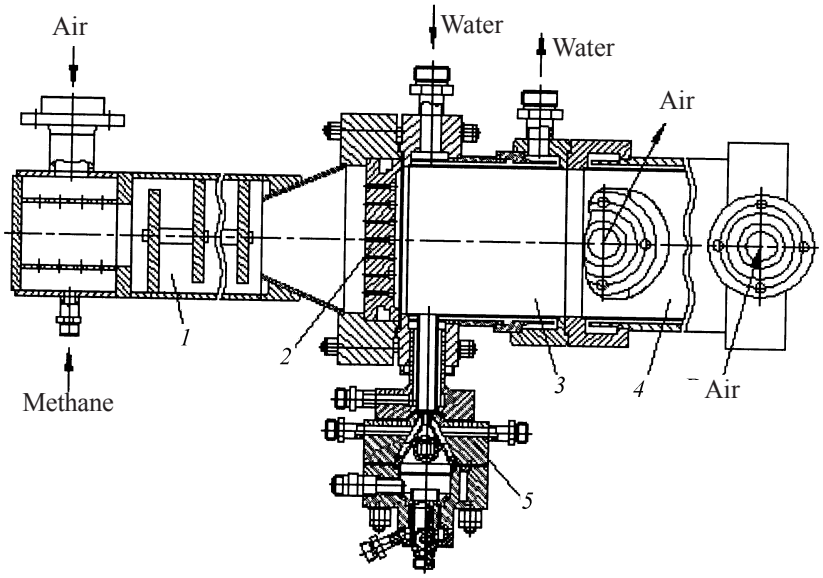


Fig. 3. High-temperature reactor with a labyrinth mixer. (*1*) Mixer, (*2*) jet grid, (*3*) combustion chamber, (*4*) cylindrical spacer ring (reactor chamber), and (*5*) igniting device.

It is impossible to obtain catalytically acceptable temperature and water content of combustion products by varying the technological parameters of synthesis gas production, and at a water content of synthesis gas exceeding 9.5 vol %, the yield of methanol decreases.

For dehumidifying and thermostating the synthesis gas and for guaranteeing that there is no solid carbon in the combustion products, a system for synthesis gas preparation should be installed before the unit for catalytic synthesis of methanol [9].

EXPERIMENTAL

For an experimental study of the production of synthesis gas in a high-temperature reactor by direct gas-phase oxidation of natural gas by atmospheric oxygen, with the aim of its further processing to methanol, and to confirm the possibility of using this technology in practice, we performed a full-scale experiment. The test was made on two installations with different output capacities.

In the first stage, the process of synthesis gas production was experimentally refined on a simplified processing line (SPL) with the minimum output capacity (~4 g s^{-1} methane) because the cost of fabrication and maintenance of such a low-capacity installation is comparatively low. The installation was intended for verification of theoretical calculations of the synthesis gas production in a high-temperature reactor, experimental refinement of separate apparatus in the technological process, determination of optimal design solutions for elements of the technological circuit, and development of recommendations for design of a pilot industrial installation.

The SPL was used to perform 39 fire runs. The yield of synthesis gas (10–11 vol %) was close to the theoretical yield (10–13 vol %) of the first stage (fast reactions), and the output of condensed carbon (up to 15% relative to the amount of carbon in raw materials) substantially exceeded the calculated equilibrium values. The data obtained can be accounted for by the fact that the process was performed at comparatively low temperatures in the HTR combustion chamber, about 1300 K (without preliminary heating of air), which made it only possible to perform the first stage of the physicochemical processes (3) during a time $\tau \approx 100$ ms. The second stage of reactions (4)–(6), in which carbon is for the most part converted to CO, had not enough time to occur. The results obtained confirmed that the technique suggested for production of synthesis gas is practicable.

In the second stage, fire tests were made on a pilot-industrial installation (PII) with an output capacity of up to 120 g s^{-1}.

The first part of PII tests was carried out in a high-temperature reactor with intrachamber mixing of components. The results of these experiments suggest that it is difficult to obtain gas-dynamic parameters and synthesis gas composition uniform over the combustion chamber cross-section when using an HTR with

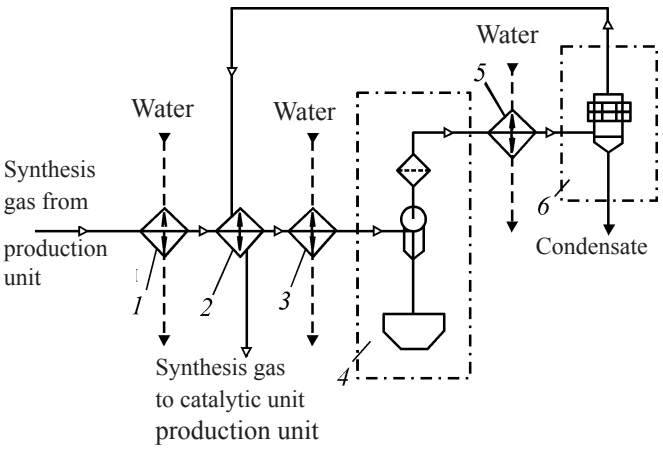


Fig. 4. Circuit diagram of synthesis gas preparation for the catalytic process. (*1–3, 5*) Heat-exchange apparatus, (*4*) carbon black separation unit, and (*6*) condensate separation installation.

Calculated and experimental composition of synthesis gas

Component	Composition, vol %		
	calcd.	Experimental (before preparation unit)	Experimental (after preparation unit)
H_2	24	16–20	19–22.5
CO	14	9–11.5	11–13.5
N_2	51	58–60	61–64.0
H_2O	8	8–12	0.2–0.4
CO_2	2	1–3	2–4

intrachamber mixing of components, which has smaller mass-dimension characteristics. This gives rise to regions with an oxidant excess coefficient in the gas flow substantially lower than the average value. As a result the yield of condensed carbon increases (up to 10% relative to the amount of carbon in raw materials).

The main fire tests of the PII involved refinement of various types of HTRs with preliminary mixing of fuel components.

Several kinds of mixers were studied: of centrifugal, jet, and labyrinth types. It was found that the best, as regards providing cross-sectionally uniform concentration, pressure, and velocity fields, is the labyrinth mixer, and, therefore, the main experiments were performed in an HTR with a labyrinth mixer (Fig. 3).

Various kinds of reactor cooling systems were studied in the PII: by water, air, and of mixed type.

The air cooling of HTRs is preferable for preliminary heating of air delivered to the combustion chamber, because it diminishes the time in which the thermodynamic equilibrium is attained and, at a given reactor chamber volume, raises the yield of synthesis gas. This reactor-cooling system reliably operates in the pressure range 2–10 atm. As pressure is raised (or the combustion chamber is made longer), the heat fluxes grow and it becomes appropriate to change the cooling system to that of the water type. If, however, water is used as a cooling agent, the amount of condensed carbon deposit on the reactor walls strongly increases, because, as is known, carbon black is deposited on cooled surfaces [8]. As a result of the experiments performed, we suggest a combined cooling system: cooling the combustion chamber *3* and igniting device *5* with water, and spacer rings *4* of the reactor chamber, with air (Fig. 3).

The pilot-industrial installation enabled a study of the synthesis gas production at the following input parameters: oxidant excess coefficient 0.35–0.55; intrachamber pressure 35–60 atm; initial air temperature 0–700°C; residence time 50 ms to 2 s; intrachamber or preliminary component mixing; cooling system of the air, water, or combined types.

The final part of experiments on the PII was performed using a synthesis gas preparation unit intended for removing water and condensed carbon from the synthesis gas and obtaining gases with a temperature necessary for catalytic synthesis of methanol (Fig. 4).

Synthesis gas with a temperature of about 1400 K is delivered to the preparation unit. It is preliminarily cooled in a water heat exchanger *1* and then is delivered to a system of gas-gas heat exchangers *2*, which simultaneously lower the temperature before carbon black and water removal and raise the synthesis gas temperature to a level necessary for methanol catalysis. Water heat exchanger *3* serves to cool synthesis gas before its being delivered into the carbon black removing system.

A two-stage system *4* was developed to remove carbon black from the gas flow. In the first stage, a preliminary purification is performed in a cyclone apparatus, with particles having effective diameters exceeding 10 μm separated and coagulation of fine carbon black particles achieved. In the second stage, the gas flow is filtered through a metal-screen filter.

The gas purified to remove condensed carbon is additionally cooled in a heat-exchanger–condenser *5* to a temperature $T \approx 310$ K. In the process, water vapor

condenses to give a liquid, coarse drops, and fog. The resulting gas-liquid flow is delivered into the condensate-separating installation.

The condensate-separating installation *6* comprises two in parallel-connected batteries of demistors, in which water flows down into the condensate receiver in the form of a liquid and coarse drops and the fog passes through three packages of a metallic demistor screen, its drops become coarser and are captured by the screen, and also flow down into the condensate receiver. During the condensation of water, the gas is additionally purified to remove carbon black because of the effective capture of carbon particles by the water drops being formed.

A total of 140 runs were performed in the PII. The main results concerning the composition of the synthesis gas obtained are listed in the table.

As can be seen from these data, the parameters of the synthesis gas after the preparation unit fully satisfy the requirements imposed by methanol catalysts.

The experiments performed made it possible to choose the range of main mode parameters of the process of partial gas-phase oxidation of methane by atmospheric oxygen to obtain a synthesis gas with characteristics that are the most favorable for catalytic synthesis of methanol: oxidant excess coefficient 0.35–0.40, combustion chamber pressure ~5.5 MPa, air temperature at the reactor inlet 700–900 K, residence time 500–2000 ms, preliminary mixing of fuel components, reactor wall temperature ≥600 K, additional water vapor supply at a rate of 30% relative to the amount of carbon in raw materials.

Thus, we can consider confirmed the possibility of using the technique for production of synthesis gas in a high-temperature reactor by direct gas-phase oxidation of methane by atmospheric oxygen, with the parameters of the synthesis gas satisfying the requirements of further stages of organic synthesis, and recommend its industrial application.

CONCLUSIONS

(1) The main technological parameters affecting the yield of synthesis gas in partial gas-phase oxidation of methane by atmospheric oxygen were found.

(2) It was determined that the main technological characteristics at which synthesis gas is obtained in maximum yield with parameters that are the most favorable for the further stage of catalytic synthesis of methanol are the following: oxidant excess coefficient 0.35–0.40, combustion chamber pressure ~5.5 MPa, air temperature at the reactor inlet 700–900 K, residence time 500–2000 ms, preliminary mixing of fuel components, reactor wall temperature ≥600 K, additional water vapor supply at a rate of 20–30% relative to the amount of carbon in raw materials.

(3) It was demonstrated that synthesis gas of varied composition can be obtained by varying the mode parameters of a high-temperature reactor within the range acceptable for given working conditions.

(4) The possibility of obtaining synthesis gas with parameters required for further organic synthesis by direct gas-phase oxidation of methane with atmospheric oxygen in a high-temperature reactor was experimentally confirmed.

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