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HEAT AND MASS TRANSFER IN DISPERSIVE AND POROUS MEDIA

METHANE-TO-HYDROGEN CONVERSION IN THE FILTRATION-COMBUSTION WAVE OF RICH METHANE–AIR MIXTURES

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The superadiabatic-effect-based process of noncatalytic conversion of methane to a hydrogenous synthesis gas in a cocurrent filtration-combustion wave has been considered. The influence of the composition and specific flow rate of the working mixture on the basic parameters of conversion — the maximum temperature in the filtration-combustion wave, the wave's propagation velocity, and the composition of the reaction products — has been investigated. Filtration-combustion regimes optimum from the viewpoint of the most efficient conversion of methane to a hydrogenous synthesis gas have been found from the experimental data obtained.

Introduction. The necessity of changing to alternative energy sources in connection with the protection of the environment has led to intense research in the field of production, transportation, and storage of hydrogen as one of the most promising energy carriers. Hydrocarbons, in particular, methane, are widely used as the primary hydrogen source in industry and transport. In commercial production of hydrogen or hydrogenous synthesis gas (syngas), one usually uses vapor conversion, incomplete oxidation [1], and thermocatalytic decomposition of methane [2]. The high efficiency of methane conversion in the above processes is ensured only under large-tonnage production or when catalysts are used. The inevitable deactivation of the catalyst requires its periodic replacement, which complicates the operation of catalytic converters and increases the total capital intensity of the production process. In this connection, a search for less capital-intensive noncatalytic processes is topical. One possible solution is carrying out the incomplete oxidation of methane in a tubular flow reactor according to the reaction

$$CH_4 + \frac{1}{2} O_2 = CO + 2H_2 \tag{1}$$

at elevated pressure (of the order 30 atm) and in heating of the reaction mixture to a temperature of about 350^{o}C [3]. The drawback of this process is the formation of soot in combustion, which leads to a degradation of the operating characteristics of the converter with time.

The process of conversion without a catalyst can also be organized by increasing the temperature in the reaction zone of incomplete oxidation to approximately 1500^{o}C. For this purpose one usually burns a certain additional amount of methane, since the intrinsic heat release of reaction (1) turns out to be insufficient to maintain the required temperature. Converters with the external heating of the reaction zone are successfully used under large-tonnage production, but they are insufficient in the case of small amd medium outputs. One alternative method for increasing the temperature of the conversion that is not subject to the above drawbacks is the use of the superadiabatic effect of the cocurrent filtration-combustion wave; this effect is observed in the case where a fuel mixture with a low adiabatic temperature is filtered through an inert porous medium of high heat capacity. The thermal combustion-product energy accumulated by the porous medium owing to the intense interphase heat exchange ensures the efficient heating of a fresh fuel mixture. As a result of the recuperation of heat in the porous skeleton, the maximum temperature in the reaction

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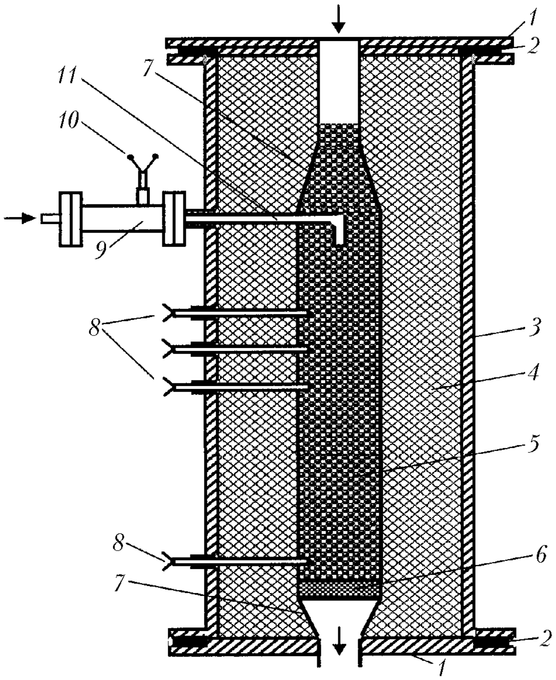


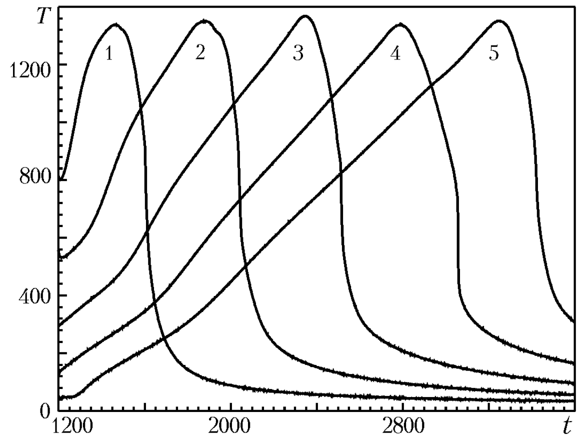
Fig. 1. Diagram of the experimental setup: 1) flanges; 2) sealer; 3) casing; 4) heat insulation; 5) ceramic fill; 6) porous ceramic disk; 7) quartz cone; 8) thermocouples; 9) heating unit; 10) spark plug; 11) quartz tube.

zone can be much higher than the adiabatic temperature of the starting fuel mixture [4]. Initially, the superadiabatic effect in filtration combustion was investigated for very lean fuel mixtures [5–9]. Subsequently, analogous investigations were carried out for fuel mixtures with a high content of the fuel [10–12]. The possibility, in principle, of noncatalytic conversion of hydrocarbons in filtration-combustion reactors was demonstrated in a number of investigations, including those performed by the authors of the present work [4, 13, 14]. The incomplete oxidation of methane in a superadiabatic regime was investigated in both cocurrent filtration-combustion waves [13, 14] and reversive reactors [4] where the periodic change in the direction of filtration of the fuel mixture enables one to make the process indefinite with time.

In this work, we have experimentally investigated the influence of the composition and specific flow rate of the starting methane-air mixture on the characteristics of the noncatalytic process of incomplete oxidation of methane in a filtration-combustion wave with the aim of determining the optimum regimes of conversion.

Experimental Equipment. The experimental setup incorporates a filtration-combustion reactor (see Fig. 1), a system of batching and mixing the starting reactants, a unit for heating the reactor's porous fill, a system for measuring the temperature field in the reactor, a refrigerator, a sump of liquid products, chromatographic equipment for analyzing the composition of gaseous reaction products, and an exhaust ventilation system for removing the reaction products from the room. The reactor represents a thick-walled flanged tube manufactured from stainless steel. Inside the reactor casing, there is a cylindrical layer of porous ceramic fill with an outside diameter of 40 mm and a length of 700 mm. Spherical aluminum-dioxide particles of diameter 5–6 mm are used as the fill. The porous fill is surrounded by a layer of high-temperature kaolin insulation.

To initiate a filtration-combustion wave we heat the upper layer of the fill to a temperature of 950 to 1000^{o}C by the methane-combustion products entering the reactor from the unit for heating the fill. In this device, the methane-air mixture burns in the regime of filtration combustion with a stabilized front. The mass flow rates of the mixture components are measured and maintained at a prescribed level by "Omega"-type electronic flowmeters and regulators. Before feeding to the reactor, air and methane are mixed in a small cylindrical chamber of volume about 0.3 liter. The temperature in the porous fill is measured by six S-type thermocouples with open junctions; the thermocouples are in-



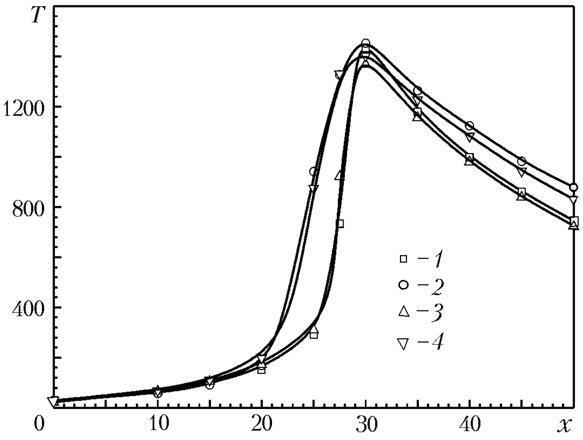


Fig. 2. Time variation in the temperature in the process of propagation of a filtration-combustion wave ((1–5) thermocouple Nos.) $g = 0.4$ kg/(m^2·sec) and $\gamma = 4.0$. T, ^{o}C; t, sec.

Fig. 3. Influence of the specific mass flow rate and the equivalent ratio on the longitudinal temperature distribution in the reactor: 1) $\gamma = 3.0$ and $g = 0.33$, 2) 3.0 and 0.7, 3) 3.6 and 0.3, 4) 3.6 and 0.7 kg/(m^2·sec). T, ^{o}C; x, cm.

troduced through the reactor lateral walls. The signals from the thermocouples are processed by a PC-based automated data acquisition and processing system.

Once the steam has been removed from the conversion products, their chemical composition is measured by a "CHROM 4" gas chromatograph. For analysis we use two three-meter columns of diameter 3 mm filled with CaA and Poropak Q molecular sieves. Argon is used as the carrier gas. The output signal of the chromatograph is digitized and processed on a PC. The chromatograph is calibrated using removable batching loops of different volume and standard gas mixtures. The concentrations of H_2, O_2, N_2, CH_4, and CO are measured in the experiments.

Experimental Results. The investigations have been performed for different values of the specific mass flow rate g and the composition of the reacting mixture, determined by the equivalent ratio γ. We investigated 20 regimes with different combinations of γ and g. Four experiments with different specific mass flow rates g (0.3, 0.4, 0.5, and 0.7 kg/(m^2·sec)) were carried out for each of the five fixed γ values (2.8, 3.0, 3.2, 3.6, and 4.0)). In all the experiments, we recorded the readings of the thermocouples arranged in the reactor's porous fill with a step of 100 mm and the composition of the conversion products. Figure 2 exemplifies the time variation in the temperature at different points of the porous fill in the process of propagation of the filtration-combustion wave for $\gamma = 4.0$ and $g = 0.4$ kg/(m^2·sec). As the wave develops, the maximum temperature is seen to change only slightly (within 10^{o}C) at different cross sections of the fill. The maximum temperature has a steady-state value when the combustion front reaches the level of the 5th thermocouple, i.e., is at a distance of about 500 mm from the initial cross section of the fill. The spatial temperature distributions along the fill axis are shown in Fig. 3. In the temperature profile, we recognize three characteristic portions: the portion of heating of the entering fuel mixture to the ignition temperature due to the intense heat exchange with the porous skeleton, the portion of intense rise in the temperature from the ignition point to a maximum due to the heat of chemical (predominantly exothermic) reactions, and finally the portion of decrease in the temperature, where endothermic reactions are dominant. It follows from a comparison of the temperature profiles obtained for different γ but for the same g that the influence of γ is appreciable only on the profile's portion near the temperature maximum and the portion of decrease in the temperature. On the portions of heating and rapid exothermic reactions, the temperature profiles are virtually coincident. The rate of rise in the temperature on the leading edge of the filtration-combustion wave is mainly dependent on the specific flow rate (or filtration rate) of the gas mixture: as g grows, the slope of the temperature profile decreases with simultaneous reduction in the rate of drop in the temperature on the trailing edge of the wave. Interestingly enough the maximum temperature in the porous fill changes as a function of the equivalent ratio γ only slightly compared to the adiabatic temperature of the reaction mixture.

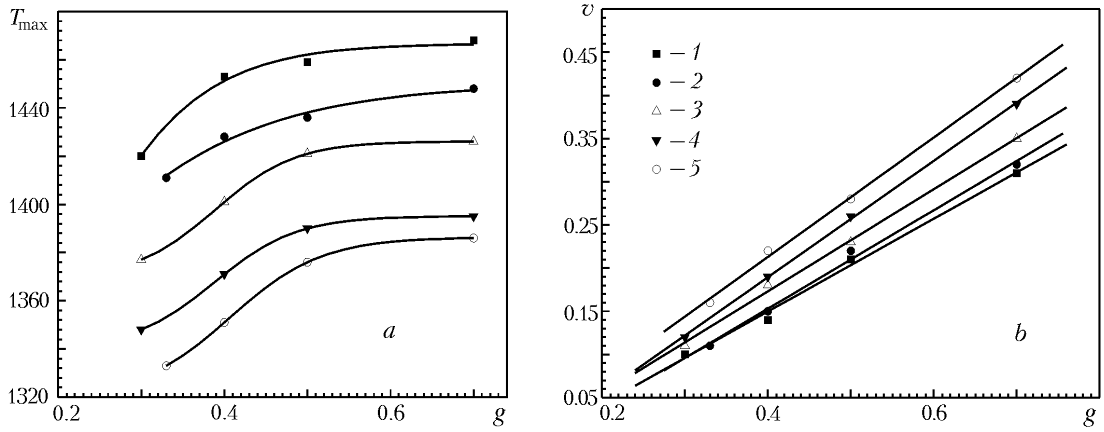


Fig. 4. Maximum temperature in the filtration combustion wave of a methane-air mixture (a) and velocity of its propagation (b) vs. specific mass flow rate with variation in the equivalent ratio: 1) $\gamma = 2.8$, 2) 3.0, 3) 3.2, 4) 3.6, and 5) 4.0. T, ^{o}C; v, mm/sec; g, kg/(m^2·sec).

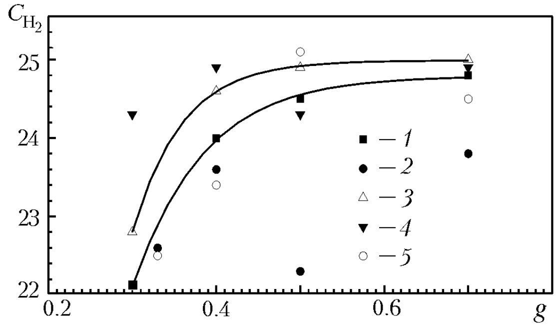


Fig. 5. Concentration of hydrogen in the methane-conversion products vs. specific mass flow rate for mixtures of different compositions. Notation 1–5 is the same as that in Fig. 4. C_{H_2}, %; g, kg/(m^2·sec).

The maximum temperature in the filtration-combustion wave and the velocity of its propagation as functions of the equivalent ratio γ and the specific mass flow rate of the fuel mixture g are given in Fig. 4. The maximum temperature monotonically grows with g. When g is fixed, it increases with decrease in γ, which is related to the increase in the adiabatic temperature of the fuel mixture. The highest value of the temperature in the reactor ($T_{max} = 1470^{o}$C) is observed for the minimum equivalent ratio $\gamma = 2.8$ and the maximum specific mass flow rate $g = 0.7$ kg/(m^2·sec).

The velocity of propagation of the filtration-combustion wave in the experiments was evaluated from the time of reaching the temperature maximum in the cross sections where the thermocouples were installed. For a fixed γ, the wave velocity increased nearly linearly with specific flow rate and with equivalent ratio (Fig. 4b).

An analysis of the composition of the gaseous conversion products enabled us to evaluate the three most important parameters characterizing the efficiency of the process under study: the concentration of hydrogen, the concentration of residual methane in the conversion products, and the degree of methane-to-hydrogen conversion. In the range of operating parameters investigated, the content of hydrogen in the conversion products varied only slightly — within 22–25% (in terms of dry gas). As is seen in Fig. 5, the concentration of hydrogen grows with decrease in the equivalent ratio and increase in the specific mass flow rate, which is determined by the corresponding increase in the maximum temperature in the reaction zone. The degree of methane-to-hydrogen conversion η, characterizing the fraction of hydrogen (converted to free hydrogen) contained in methane, was calculated from the concentrations measured:

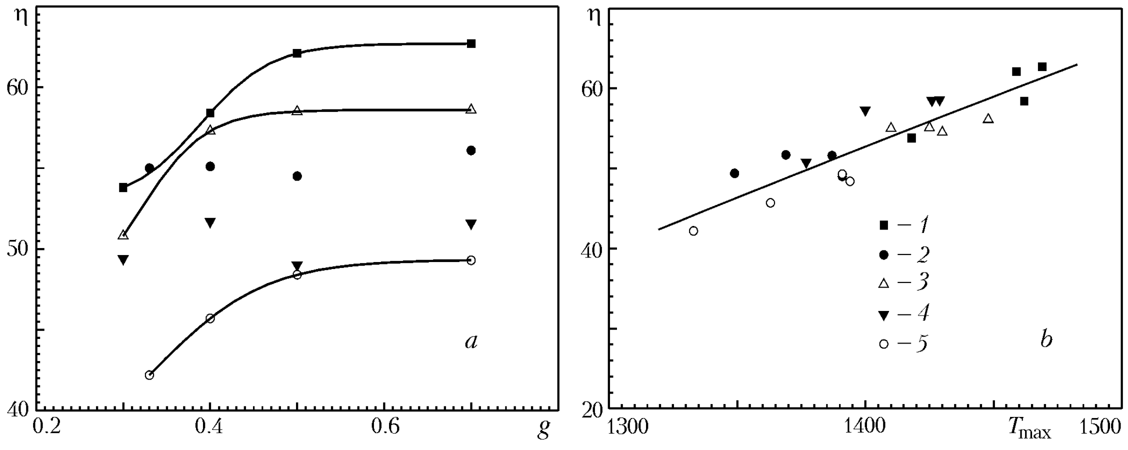


Fig. 6. Degree of methane-to-hydrogen conversion vs. specific mass flow rate (a) and maximum temperature in the reaction zone (b). Notation 1–5 is the same as that in Fig. 4. η, %; g, kg/(m^2·sec); T_{max}, °C.

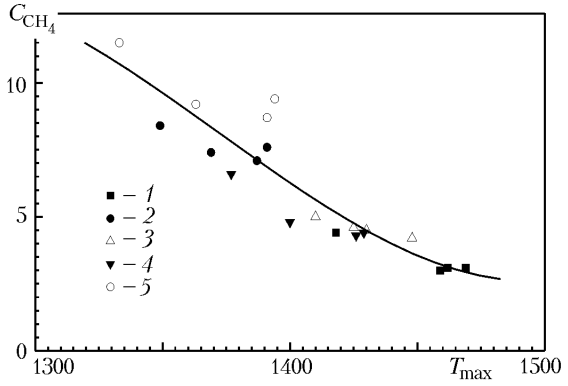


Fig. 7. Concentration of residual methane vs. maximum temperature in the zone. Notation 1–5 is the same as that in Fig. 4. C_{CH_4}, %; T_{max}, °C.

$$\eta = \frac{2C_{H_2}C_{N_2}^{in}}{C_{CH_4}C_{N_2}^{out}}, \tag{2}$$

where $C_{N_2}^{in}$ and C_{CH_4} are the concentrations of nitrogen and methane in the input mixture and C_{H_2} and $C_{N_2}^{out}$ are the concentrations of hydrogen and nitrogen at exit from the reactor.

The influence of the specific flow rate and the composition of the working mixture on the degree of conversion η for different operating regimes of the reactor is shown in Fig. 6a. A clear trend toward growing η with increase in the specific mass flow rate and decrease in the equivalent ratio is observed. The relatively low degree of methane-to-hydrogen conversion (40–65%) is attributable to both the difference of the actual maximum reaction temperature from that required theoretically and the short time of residence of the gas mixture in the reactor. The fact that it is precisely the temperature in the reaction zone that is the determining factor for efficient methane-to-hydrogen conversion is clearly confirmed by the plot in Fig. 6b. An analogous trend is observed for the concentration of residual (unreacted) methane in the reaction products. As is shown in Fig. 7, it is reduced with increase in the maximum temperature in the reaction zone.

Conclusions. Using the superadiabatic filtration-combustion effect we have realized a self-sustaining noncatalytic process of incomplete oxidation of methane with the resulting formation of a gas mixture (the mixture contained hydrogen and carbon monoxide (syngas)). The maximum values of the concentrations of hydrogen in the reaction products attained 25%, and those of carbon monoxide were 16%. The maximum value of the degree of methane-to-hydrogen conversion amounted to 63%, whereas the minimum concentration of residual methane in the reaction products amounted to 3% in the optimum conversion regimes.

The main factor determining the efficiency of the process of conversion of methane to a hydrogenous syngas is the maximum temperature in the reaction zone. Increase in the specific mass flow rate enables us to increase the temperature indicated and thereby to make the conversion all the more efficient. The most pronounced growth in the maximum temperature in the reaction zone is observed in a limited range of specific flow rates ($g < 0.6$ kg/(m^2·sec)) beyond which further increase in g does not lead to an appreciable increase in the temperature. The maximum temperature in the reaction zone can also be increased due to γ of the mixture; however, just as in the case with g, there is a certain limit ($\gamma = 2.8$) below which it becomes inexpedient to decrease γ, since the fraction of methane converted to water and carbon dioxide sharply increases. Thus, there is an optimum range of variation in the operating parameters within which the conversion of methane to a hydrogenous syngas is the most efficient.

It is significant that the results obtained are in good agreement with the results of [14] where a porous ceramic structure was used instead of the fill. The quantitative disagreements observed are attributable to the difference in the thermophysical properties and porosities of porous media with which the experiments were carried out.

NOTATION

T, temperature of the gas mixture, $^{\circ}$C; v, combustion-wave velocity, mm/sec; C, concentration of the component in the gas mixture; g, specific mass flow rate of the gas, kg/(m^2·sec); x, longitudinal coordinate, cm; t, time, sec; γ, equivalent ratio of the fuel mixture; η, degree of methane-to-hydrogen conversion. Subscripts: max, maximum; in, in the input gas mixture; out, exit from the reactor.

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