INVESTIGATION OF THE MECHANISM OF THE NEGATIVE TEMPERATURE DEPENDENCE OF THE REACTION RATE OF PARTIAL OXIDATION OF METHANE

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Abstract: Autoignition features of fuel-rich mixtures of methane with oxygen in a wide range of initial temperatures, pressures, and values of the equivalence ratio φ under the conditions of a plug flow reactor and a static reactor (constant volume bomb) were studied by computer simulation. The presence of a region of negative temperature coefficient (NTC) of the reaction rate for both types of reactors was shown in a wide range of equivalence ratios and pressures. This region was clearly visible both on the temperature dependence of the autoignition delay time and on the temperature dependence of the maximum heat release rate. The mechanism of the appearance of the NTC region during the oxidation of methane was reviewed. Since two mechanisms for the occurrence of this phenomenon are described in the literature for methane oxidation, one could expect the appearance of two NTC regions which was not observed. Apparently, both mechanisms operate in the same temperature range and, therefore, are not independent. So, when conditions change, there is a smooth transition from one mechanism to another. The yield of methane oxidation products and the effect of pressure on mixture autoignition were analyzed.

Keywords: methane oxidation; autoignition; fuel-rich mixtures; negative temperature coefficient of the reaction rate; flow reactor; static reactor

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Figure Captions

Figure 1 Temperature dependence of the autoignition delay time (*a*) and maximum heat release rate (*b*) in a flow reactor during autoignition of 96.774% CH_4 + 3.226% O_2 mixture, $P = 60$ atm

Figure 2 Temperature dependence of the autoignition delay time (*a*) and maximum heat release rate (*b*) in a static reactor during autoignition of 96.774% CH_4 + 3.226% O_2 mixture, $P = 60$ atm

Figure 3 Distribution of ethane concentration along the length of the flow reactor at $T_0 = 1000$ K: *1* — $\varphi = 60$ and $P = 60$ atm; *2* — $\varphi = 10$ and $P = 60$ atm; and *3* — $\varphi = 10$ and $P = 10$ atm

Figure 4 Distribution of ethane concentration along the length of the flow reactor at different temperatures, $\varphi = 60$, $P = 60$ atm: *1* — $T_0 = 900$ K; *2* — 1000; and *3* — $T_0 = 1100$ K

Figure 5 Dependence of the yield of the main products (*1* — CO; *2* — H_2O; *3* — H_2; and *4* — C_2H_4) on the initial temperature during the autoignition of 96.774% CH_4 + 3.226% O_2 mixture, $P = 60$ atm: (*a*) flow reactor; and (*b*) static reactor

Figure 6 Temperature dependence of the change in the concentration of carbon monoxide (*1*) and methanol (*2*) for flow-reactor conditions at low initial temperatures, $\varphi = 60$, $P = 60$ атм

Figure 7 Temperature dependence of the autoignition delay time in a flow reactor at pressures of 20 (*1*) and 60 atm (*2*), $\varphi = 60$

Figure 8 Dependence of the autoignition delay time on pressure in the flow reactor at $T_0 = 1000$ K, $\varphi = 60$

Figure 9 Temperature dependence of the autoignition delay time (*a*) and maximum heat release rate (*b*) in methane–oxygen mixture at $\varphi = 60$ and $P = 60$ atm. Calculations are based on mechanisms [18] (*1*) and [19] (*2*)

Figure 10 Distribution of carbon monoxide (*1*) and methanol (*2*) concentrations at low initial temperatures: solid lines — calculation according to the mechanism [18]; and dashed lines — calculation according to the mechanism [19]

Table Caption

Table 1 Product yield and methane residue (%(mol.)) at different initial temperatures for flow-reactor conditions

Table 2 Product yield and methane residue (%(mol.)) at different initial temperatures for static-reactor conditions

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