
COMBUSTION, EXPLOSION,
AND SHOCK WAVES

Kinetic Nature of Blue Flames in the Autoignition of Methane

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Abstract—Kinetic calculations within the framework of detailed reaction mechanisms showed that the blue flames observed during autoignition of methane in an internal combustion engine are combined cool–blue flames. In the course of methane oxidation, methyl hydroperoxide $\text{CH}_3\text{O}_2\text{H}$ and hydrogen peroxide H_2O_2 appear and accumulate almost simultaneously. The partial decomposition of these species yields a hydroxyl OH concentration peak, thereby giving rise to a local acceleration of the oxidation reaction, accompanied by luminescence. Kinetic curves for the main products were obtained and the boundaries of cool–blue flames were determined, which turned out to be in satisfactory agreement with the experimental data.

Keywords: methane, compression-induced ignition, blue flames

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INTRODUCTION

The spontaneous ignition of methane, isooctane, and other hydrocarbons during compression in an internal combustion engine (ICE) was investigated in a number of works [1–3] as long ago as the early 1950s. It was found that, under these conditions, the autoignition area (in the mixture composition–compression temperature coordinates) adjoins a blue-luminescence preflame zone, where a partial reaction occurs: the concentrations of fuel and oxygen decrease, while a number of intermediates and final reaction products appear. This reaction with blue luminescence due to the Vaidya spectrum of the electronically excited formyl HCO^* is known as a “blue” flame.

Around the same time, conditions were found in which the reaction of methane–oxygen mixtures in static reactors showed the same two-stage pattern as that inherent to higher hydrocarbons–oxygen mixtures [4, 5]. For higher hydrocarbons, the first (preflame) stage was and is called the “cool” flame, and apparently for this reason, the preflame stage for methane in these experiments was also referred to as the cool flame. Note that the same term was in [6], published much later (in 1995).

In the monograph [7], the author, based on a survey of a vast body of experimental data, introduced the concept of a multistage self-ignition of hydrocarbons, with individual stages of cool, blue, and hot flames. Simulations of the self-ignition of hydrocarbons using a detailed kinetic mechanisms have shown that cool flames are initiated by the decomposition of alkyl hydroperoxides, which produces OH, a highly reactive radical, whereas blue flames are initiated by the

decomposition of hydrogen peroxide H_2O_2 , which also yields hydroxyls [8]. For hydrocarbons, starting from ethane, these stages are separated. It was concluded [9] that, for the oxidation of methane in laboratory conditions similar to those described in [4–6], cool and blue are actually inseparable, appearing as combined cool–blue flames.

The aim of the present work is to elucidate the kinetic nature of blue flames observed in the aforementioned works on self-ignition of methane and engine at compression.

RESEARCH METHOD

The characteristics of the kinetic processes occurring during the compression of the gas by the moving piston in an ICE were simulated using the computer code described in [10]. This code makes it possible to calculate the characteristic of the self-ignition and combustion of (1) a homogeneous air–fuel mixture in the operation of an engine with a homogeneous charge and compression-induced ignition, of (2) drops in a diesel engine and (3) in a mixed gas–diesel cycle, where the gas mixture is ignited by liquid fuel droplets. In this paper, we consider a situation where a homogeneous air–fuel enters mixture enters the engine cylinder during the suction stroke.

First, we performed test calculations of the self-ignition of a methane–air mixture during compression in an engine cylinder by using a detailed kinetic mechanism of methane oxidation [11]. We assumed that the initial conditions, at $t_0 = 0$, correspond to the bottom dead center (BDC), at the crank angle of $\varphi = 0$. With

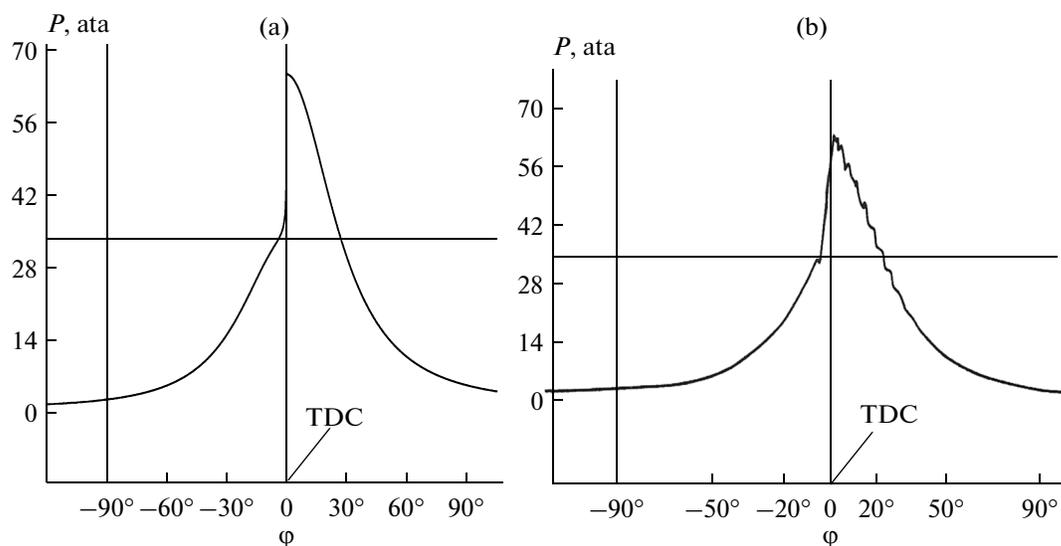


Fig. 1. (a) Calculated and (b) measured indicator diagrams [3] for the compression-induced self-ignition of a methane–air mixture on the compression ratio in an ICE. The initial temperature, $T_0 = 516$ K; initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; rotational speed, $n = 1000$ rpm.

this time reckoning, the top dead center (TDC) corresponds to $\varphi = 180^\circ$. Figures 1a and b compare the calculated and experimental indicator diagrams; the pressure in the cylinder as a function of the crank angle φ for the self-ignition and combustion of methane (in [3], the initial time corresponds to the TDC, i.e., $\varphi = 0$). As can be seen, the calculated indicator diagram is in satisfactory agreement with the experimental results.

Figure 2 shows the boundaries of the blue- and hot-flames [3] for the compression-induced ignition of methane–air mixtures (for ease of comparison, the temperature of the compressed gas T_c is given in Celsius degrees, as in the original). In the blue-flame area, at different values of T_c , a partial reaction occurs: chemical analysis showed [3] that unreacted methane (curve 1 in Fig. 3) intermediates (CO , curve 3 and H_2CO , curve 4) and end products (CO_2 , curve 2) were present. Our kinetic calculations for the conditions corresponding to this region demonstrated a similar pattern for the concentrations of the products (Fig. 4); i.e., simulations reproduced the characteristics of blue flames given in [1–3].

SIMULATION RESULTS

To obtain a more complete picture of the self-ignition process, characterize its kinetic nature of existence, and identify the areas of existence of blue flames, we performed a series of calculations. It was shown that the self-ignition of methane has a stage with incomplete heat release and with some rise in temperature (Fig. 5). Figure 5 shows that only a partial reaction occurs at this stage: the concentrations of fuel and oxygen decrease but remain finite, while the entire set of intermediate and final combustion products arises.

Note that, in Fig. 5 (and in Figs. 8 and 9), the concentrations of the products and CH_4 (Y) are given not in volume percent, as previously, but in mass fractions referred to a preset mass of certain defined. Note that, in this process, methyl hydroperoxide and hydrogen peroxide appear and accumulate almost simultaneously, a partial decay of which gives rise to a hydroxyl concentration peak. This leads to an unambiguous conclusion that blue flames in [1–3] are combined cool–blue flames.

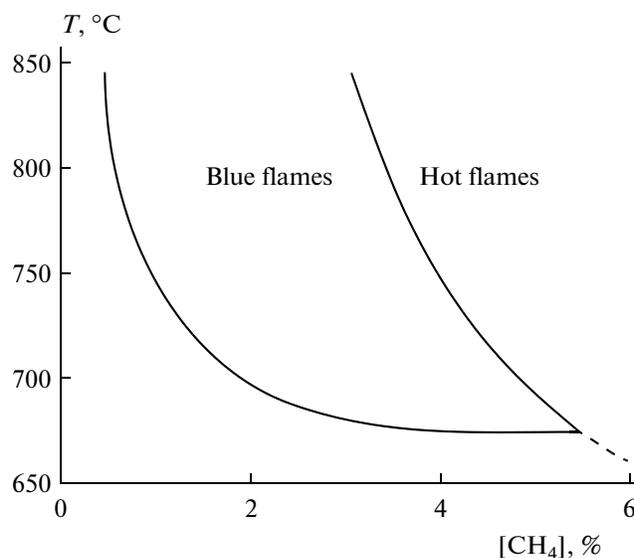


Fig. 2. Boundaries of the blue- and hot-flame regions for the compression-induced ignition of methane–air mixtures [3].

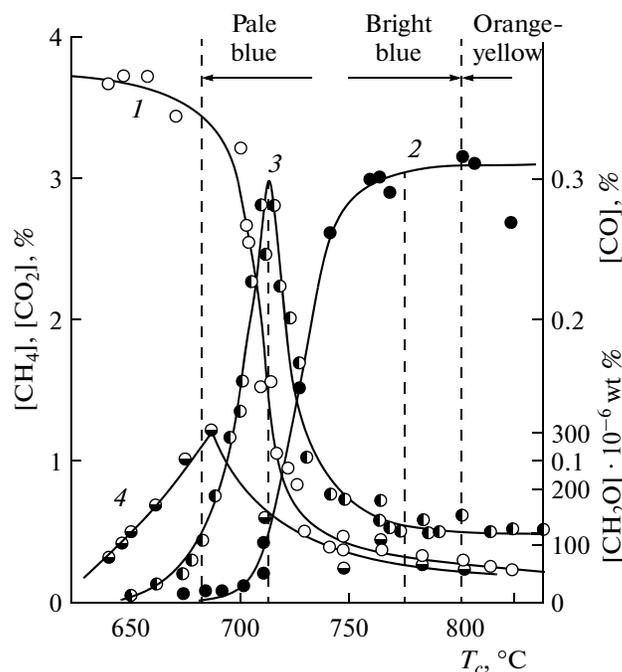


Fig. 3. Time profiles of the concentrations of (1) methane and oxidation products ((2) carbon dioxide, (3) carbon oxide, and (4) formaldehyde) in the blue-flame region [3]. The initial concentration $[\text{CH}_4]_0 = 3.7\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm. The compressed-gas temperature T_c changes with the initial temperature T_0 .

Cool-flame glow originates from excited H_2CO^* . In [7], its formation is ascribed to the reaction $\text{CH}_3\text{O} + \text{OH} = \text{H}_2\text{CO}^* + \text{H}_2\text{O}$. Figure 6 shows the

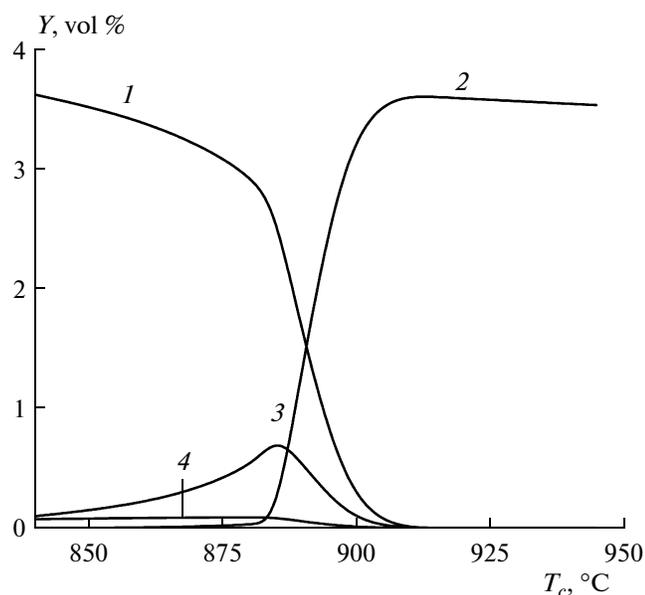


Fig. 4. Calculated concentrations of (1) methane and oxidation products ((2) carbon dioxide, (3) carbon oxide, and (4) formaldehyde) in the blue-flame region [3]. The initial concentration, $[\text{CH}_4]_0 = 3.7\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm. The compressed-gas temperature T_c changes with the initial temperature T_0 .

calculated time dependences of the products of mass fractions $X_1 = [\text{CH}_3\text{O}][\text{OH}]$ and $X_2 = [\text{H}_2\text{CO}][\text{OH}]$ for the compression-induced ignition of methane–air mixtures. It is seen that the concentration profiles and CH_3O and OH overlap partially; i.e., this reaction can occur in a cool flame, giving rise to H_2CO^* luminescence, the intensity of which in the simplest case is proportional to the product $[\text{CH}_3\text{O}][\text{OH}]$.

According to [7], blue-flame luminescence is produced by the H_2CO^* radical. It is assumed that this radical is formed by the reaction $\text{H}_2\text{CO} + \text{OH} = \text{HCO}^* + \text{H}_2\text{O}$. Figure 6 shows that the concentration profiles of H_2CO^* and OH also overlap in the reaction zone. This means that this reaction can occur with a certain probability, with its intensity being proportional to the concentration product $[\text{H}_2\text{CO}][\text{OH}]$. Note that, the detailed methane oxidation kinetic mechanism used herein does not include the indicated reactions involving electronically excited species, since the formation of these species and their luminescences do not affect the main chemical process of oxidation and heat release. In principle, H_2CO^* glow can be masked by a more intense HCO^* glow. Blue glow, which gave the name to flames under consideration, is nothing more than an outward manifestation of the multistage process of methane oxidation. An important manifestation of this reaction is the emergence of combined cool–blue flames because of the decomposition of $\text{CH}_3\text{O}_2\text{H}$ and H_2O_2 .

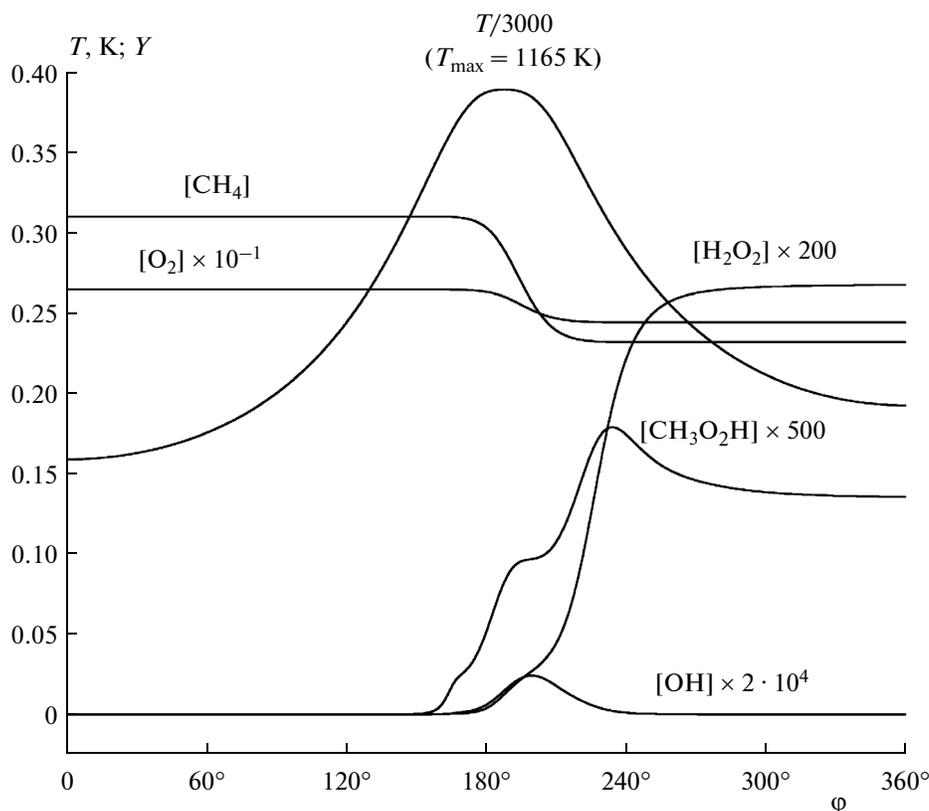


Fig. 5. Calculated time dependences of the temperature $T(t)$ and relative mass concentrations $Y(t)$ for the compression-induced ignition of methane–air mixtures. The initial temperature, $T_0 = 475$ K; initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm.

The boundary between hot and cool–blue flames can be determined with a sufficient accuracy. This is evident from the behavior of the temperature versus time curves $T(t)$ at different initial temperatures (Fig. 7). The temperature–time curves for the initial temperatures of $T_0 = 500$ and 481 K represent hot flames, with an almost complete burnout of methane (Fig. 8), whereas the curves for $T_0 = 475$ and 450 K refer to cool–blue flames. Consequently, the boundary between hot and cool–blue flames lies between the initial temperatures of $T_0 = 481$ and 475 K, which corresponds, as can be seen from Fig. 8, to the compressed-gas temperatures of $T_c = 1171$ and 1159 K (898 and 886°C), or $T_c = (892 \pm 6)^\circ\text{C}$. Thus, it is possible to determine the position of the boundary between the hot and cool–blue flames in the T_c – $[\text{CH}_4]_0$ coordinates.

Unlike the boundary between hot and cool–blue flames, the boundary between the cool–blue flame region and no-glow region is more difficult to determine. Although the respective temperature–time curves show no pronounced distinctions, this boundary can be approximately set using methane concentration curves (Fig. 9). For example, it can be assumed that this boundary corresponds to a definite value of methane consumption:

$$\eta = (Y_0 - Y_1)/Y_0,$$

where Y_0 and Y_1 are the concentration of methane at the beginning and end of the reaction, respectively.

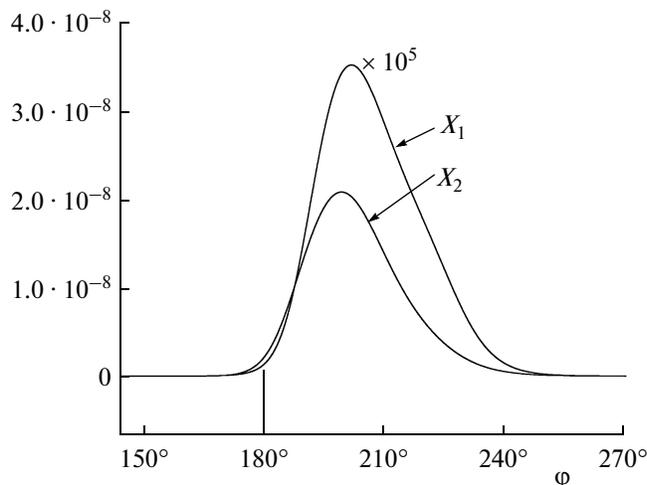


Fig. 6. Calculated time dependences of the mass fractions $X_1 = [\text{CH}_3\text{O}][\text{OH}]$ and $X_2 = [\text{H}_2\text{CO}][\text{OH}]$ for the compression-induced ignition of methane–air mixtures. The initial temperature, $T_0 = 475$ K; initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm.

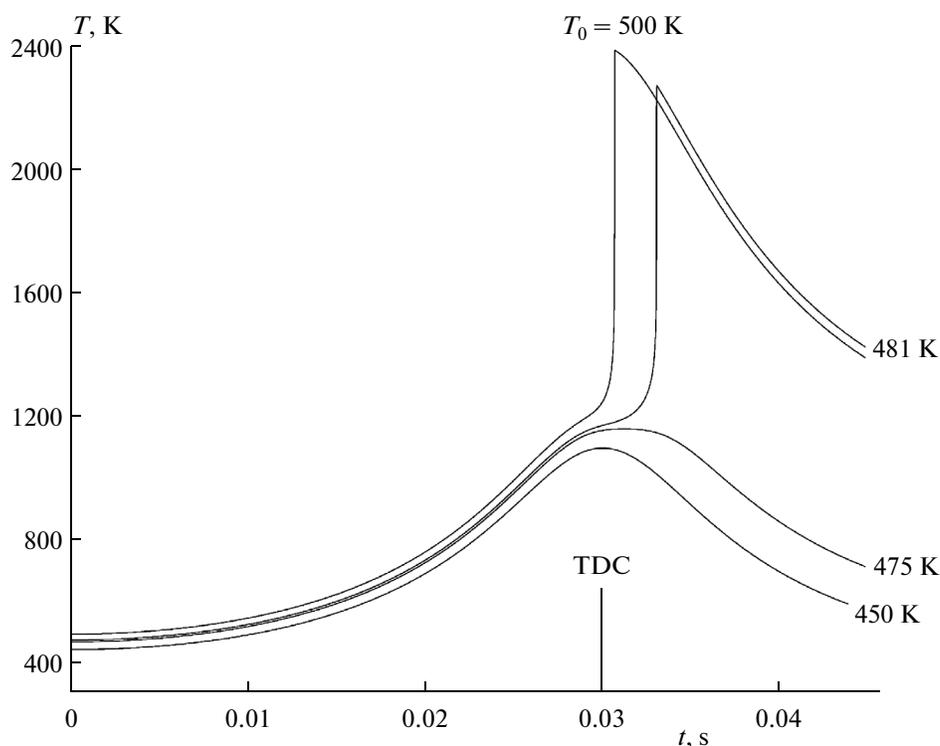


Fig. 7. Calculated time dependences of the temperature $T(t)$ for the compression-induced ignition of methane–air mixtures at various initial temperatures. The initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm.

Setting η equal, for example, to 1%, we can be obtained in the same coordinates (T_c – $[\text{CH}_4]_0$), the position of the lower boundary of cool–blue flames.

Figure 10 shows the calculated upper and lower boundaries of cool–blue flames. The calculated boundaries can be compared with the experimentally

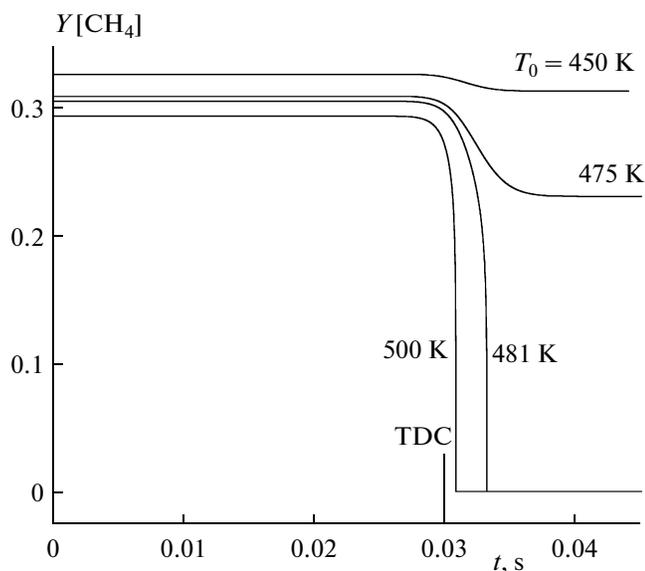


Fig. 8. Calculated time dependences of the methane concentration $Y(\text{CH}_4)$ for the compression-induced ignition of methane–air mixtures at various initial temperatures. The initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm.

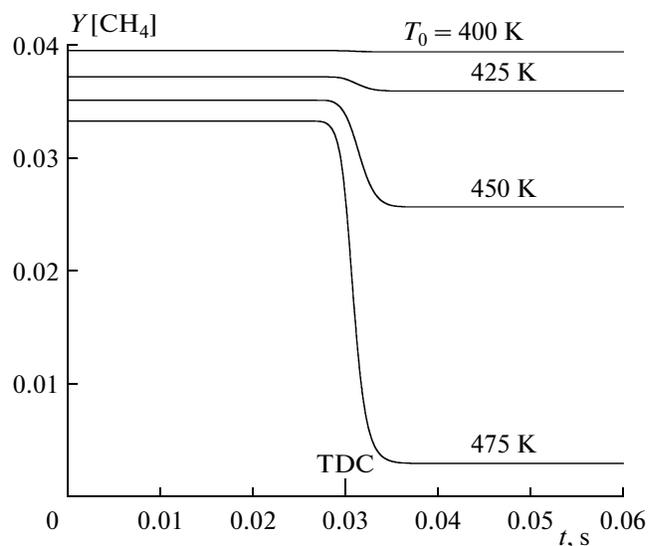


Fig. 9. Calculated time dependences of the methane concentration $Y(\text{CH}_4)$ for the compression-induced ignition of methane–air mixtures at various initial temperatures. The initial pressure, $P_0 = 1$ ata; $[\text{CH}_4]_0 = 4.67\%$; compression ratio, $\varepsilon = 14.7$; and rotational speed, $n = 1000$ rpm.

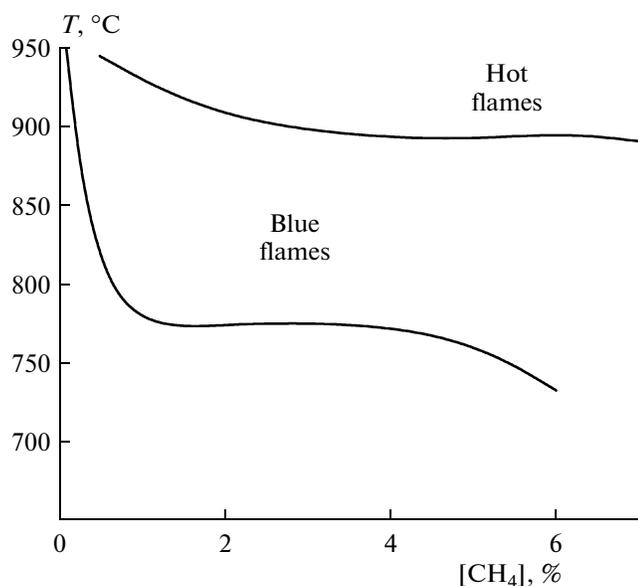


Fig. 10. Calculated boundaries of cool–blue and hot flames for the compression-induced ignition of methane–air mixtures.

determined boundaries (Fig. 3). As can be seen, the calculated area of cool–blue flames is shifted to higher temperatures by 100–200 K: $T_c = 1000–1200$ K ($\sim 700–950^\circ\text{C}$); however, in general, it qualitatively reproduces the experimentally observed area.

CONCLUSIONS

The main conclusion of the present paper is that blue flames observed in the spontaneous ignition of methane–air mixture under compression in the ICE are in fact neither cool nor blue, but combined cool–blue flames. During methane oxidation, methyl hydroperoxide $\text{CH}_3\text{O}_2\text{H}$ and H_2O_2 appear and accumulate almost simultaneously, with their partial decomposition producing a hydroxyl concentration peak and a local acceleration of the oxidation reaction is accompanied by luminescence.

These kinetic features of methane oxidation are typical of not only the conditions in the engine, but also of the conditions realized during the deflagration-to-det-

onation transition in methane–air mixtures. Under these conditions, the methane–air mixture is compressed in the shock waves generated by the accelerating flame. In this case, knowledge of the kinetic characteristics of the pre-ignition reactions can help in solving some practical problems, in particular problems of preventing explosions in coal mines and the development of a new generation of energy-saving pulse-detonation burners operating on natural gas [12].

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