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COMBUSTION, EXPLOSION,  
AND SHOCK WAVES

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# Autoignition and Combustion of Hydrocarbon–Hydrogen–Air Homogeneous and Heterogeneous Ternary Mixtures

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**Abstract**—A numerical simulation of the ignition and combustion of hydrocarbon–hydrogen–air homogeneous and heterogeneous (gas–drop) ternary mixtures for three hydrocarbon fuels (*n*-heptane, *n*-decane, and *n*-dodecane) is for the first time performed. The simulation is carried out based on a fully validated detailed kinetic mechanism of the oxidation of *n*-dodecane, which includes the mechanisms of the oxidation of *n*-decane, *n*-heptane, and hydrogen as constituent parts. It is demonstrated that the addition of hydrogen to a homogeneous or heterogeneous hydrocarbon–air mixture increases the total ignition delay time at temperatures below 1050 K, i.e., hydrogen acts as an ignition inhibitor. At low temperatures, even ternary mixtures with a very high hydrogen concentration show multistage ignition, with the temperature dependence of the ignition delay time exhibiting a negative temperature coefficient region. Conversely, the addition of hydrogen to homogeneous and heterogeneous hydrocarbon–air mixtures at temperatures above 1050 K reduces the total ignition delay time, i.e., hydrogen acts as an autoignition promoter. These effects should be kept in mind when discussing the prospects for the practical use of hydrogen-containing fuel mixtures, as well as in solving the problems of fire and explosion safety.

**Keywords:** hydrocarbon–hydrogen–air homogeneous and heterogeneous (gas–drop) ternary mixtures, autoignition, laminar flame, numerical modeling

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## INTRODUCTION

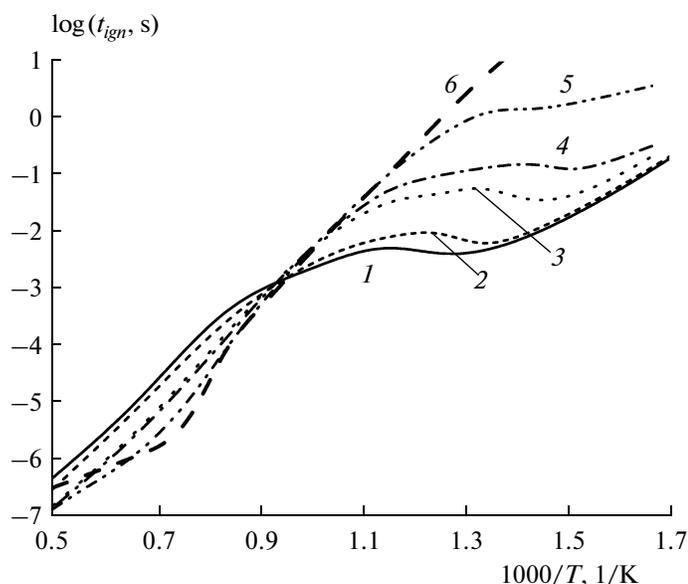
The idea of switching from classic hydrocarbon fuels to a partial or full use of hydrogen as a fuel is currently actively discussed in the engine and power industries [1]. This is mainly due to the unique properties of hydrogen, such as a low density (0.08 kg/m<sup>3</sup> at 300 K and 1 atm), wide flammability limits (from 4 to 75 vol % in air under normal conditions (NC)), high laminar flame speed (2.3 m/s in air under NC), wide detonability limits (from 18.3 to 58.9 vol % in air under NC), and a very low ignition energy (0.02 mJ). It is known that the only pollutants formed during the combustion of hydrogen–air mixtures are nitrogen oxides, which are virtually absent at fuel equivalence ratio of  $\varphi < 0.5$ . The combustion of hydrocarbon fuels additionally produces carbon oxides and soot. However, substituting hydrogen for part of hydrocarbon fuel and making the mixture leaner may lead to a dramatic decrease in the emission of pollutants. This feature of mixed compositions attracts the attention of specialists due to increasingly stringent requirements for the emission performance of vehicle engines and stationary power plants. In addition, replacing part of hydrocarbon fuel by hydrogen can provide a rapid autoignition, sustained combustion, and controlled detonation of

mixed compositions, a feature important for aerospace propulsion systems.

While the ignition and combustion characteristics of hydrogen and motor fuels very well studied, data on mixed compositions are limited. Most of them concern the combustion of methane–hydrogen [2], propane–hydrogen [3], and hydrogen–kerosene [4, 5] mixtures and the autoignition of mixtures of light hydrocarbons with hydrogen, such as hydrogen–methane [6].

For example, the paper [7] reports the results of experimental studies on the processes of ignition and combustion in a diesel engine running on diesel fuel with additives of secondary gaseous fuels (hydrogen, methane, ethanol or propane) and on the emissions of unreacted hydrocarbons, nitrogen oxides, and CO. The author concluded that, with proper workflow settings of an engine running on mixed fuel, it is possible to reduce the ignition delay, avoid “knock” and significantly decrease the emission of pollutants.

In [8], in order to find out whether the emission of nitrogen oxides can be reduced by adding hydrogen to the fuel, experimental and mathematical modeling studies of the operation of a reciprocating spark-ignition engine were performed. The fuel used was *n*-hep-



**Fig. 1.** Dependence of the ignition delay time on the initial temperature for  $n\text{-C}_7\text{H}_{16}\text{-H}_2\text{-air}$  mixture with various hydrogen concentrations (vol %): (1) 0, (2) 50, (3) 90, (4) 95, (5) 99, and (6) 100; pressure,  $P_0 = 15$  atm.

tane. It was shown that the addition of hydrogen to the fuel reduces the yield of  $\text{NO}$  but increases that of  $\text{NO}_2$ , with the total  $\text{NO}_x$  emission being higher. The mathematical model used in [8] failed to adequately describe the emission of  $\text{NO}_x$ , so the authors suggested that the increase in  $\text{NO}_2$  is due to a high concentration of  $\text{HO}_2$  radicals, capable of oxidizing  $\text{NO}$ . It should be noted that the addition of hydrogen led to a decrease in the yields of soot,  $\text{CO}$ ,  $\text{CO}_2$ , and unreacted hydrocarbons.

Surprising as it is, but discussions of the prospects of using mixed compositions have so far disregarded that fact that the reactivity of hydrogen in air is not always higher than the reactivity of hydrocarbons, especially at relatively low temperatures. The aim of the present work is to theoretically study the influence of hydrogen additives on the autoignition and combustion of homogeneous and heterogeneous (hybrid gas-drop) mixtures of heavy hydrocarbon fuels with air. The hydrocarbon fuels considered were  $n$ -heptane,  $n$ -decane, and  $n$ -dodecane. The calculations were performed using a detailed kinetic mechanism (DCM) of the oxidation and combustion of  $n$ -dodecane, including the mechanisms of the oxidation of  $n$ -decane,  $n$ -heptane, and hydrogen as constituent parts [9]. The characteristics of the ignition of homogeneous hydrocarbon–hydrogen–air ternary mixtures were calculated by the kinetic code from [10], whereas those of hydrocarbon liquid drop–hydrogen–air, by the code from [11]. The characteristics of the combustion of homogeneous ternary mixtures of hydrocarbon, hydrogen, and air were carried out using the code described in [12].

## AUTOIGNITION OF HOMOGENEOUS HYDROCARBON–HYDROGEN–AIR MIXTURES

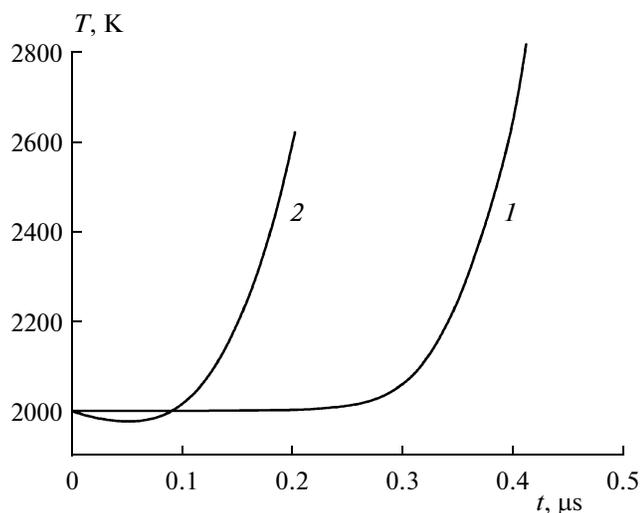
Figure 1 shows the calculated temperature dependences of the ignition delay time for stoichiometric homogeneous ternary mixtures of  $n$ -heptane, hydrogen, and air at  $P_0 = 15$  atm. As can be seen, at  $T_0 \approx 1050$  K, the ignition delay times for a stoichiometric  $n$ -heptane–air binary mixture (without hydrogen) and hydrogen–air (without hydrocarbon) are identical. At lower initial temperatures, adding hydrogen to a homogeneous  $n$ -heptane–air mixture increases the ignition delay time. An analysis shows that hydrogen is involved in chain termination reactions with the active atoms and radicals formed by the rapid oxidation of the hydrocarbon; i.e., hydrogen acts as an autoignition inhibitor. Note that, even in ternary mixture with very high concentrations of hydrogen, e.g. about 99 vol % (curve 5 in Fig. 1), low-temperature numerical experiments demonstrate multi-stage ignition (hot explosion preceded by “cool” and “blue” flames [13]), with the temperature dependence of the ignition delay time showing a region with a negative temperature coefficient (NTC).

By contrast, at  $T_0 \approx 1050$  K, hydrogen addition to homogeneous  $n$ -heptane–air mixtures reduces the ignition delay time. In this temperature range, the roles of hydrogen and hydrocarbon are interchanged: the rapid oxidation of hydrogen is inhibited by chain termination reactions between the hydrocarbon and active atoms and radicals formed during hydrogen oxidation, i.e., the role of autoignition inhibitor is now played by the hydrocarbon.

For homogeneous  $n$ -heptane–hydrogen–air ternary mixtures with low concentrations of hydrocarbon at very high temperatures ( $T_0 \sim 2000$  K), the ignition delay time again becomes shorter than that for the respective hydrogen–air binary mixture (without hydrocarbon): under these conditions, the reaction is accelerated due to the rapid thermal decomposition of hydrocarbon molecules to form a large amount of active species (Fig. 2). In the presence of the hydrocarbon, despite a small initial drop in temperature due to the endothermic decomposition of  $n\text{-C}_7\text{H}_{16}$ , the ignition delay time of a  $(0.01\text{C}_7\text{H}_{16} + 0.99\text{H}_2)\text{-air}$  ternary mixture turned out to be lower than that of the hydrogen–air, all other things being equal. This behavior of ternary mixtures at high temperatures can affect, for example, the characteristics of detonation waves.

## AUTOIGNITION OF HYDROCARBONS DROP–HYDROGEN–AIR HYBRID MIXTURES

The stoichiometric composition of ternary hybrid (gas-drop) mixtures of  $n$ -heptane and  $n$ -decane with air and hydrogen were determined as follows. First, the volume of air required for a complete combustion of the droplets was determined. Then, a certain amount

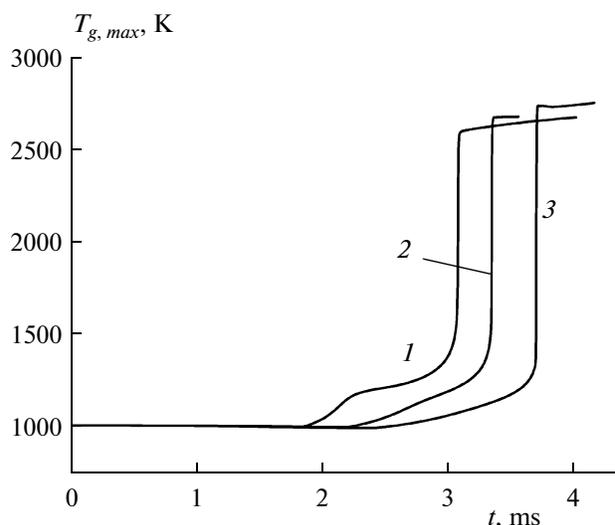


**Fig. 2.** Calculated time histories of the mixture temperature for the autoignition of (1)  $\text{H}_2$ –air binary and (2) stoichiometric  $(0.01\text{C}_7\text{H}_{16}-0.99\text{H}_2)$ –air homogeneous ternary mixtures at the same initial conditions:  $T_0 = 2000\text{ K}$  and  $P_0 = 15\text{ atm}$ .

of hydrogen was added to this air, and lastly, the volume of air required to completely oxidize the hydrogen was added to the homogeneous hydrogen–air mixture. The volume fraction of hydrogen in the gas phase was calculated according to this procedure.

Figure 3 shows the calculated time dependence of the maximum temperature  $T_{g, \max}$  in the gas phase on the time  $t$  for stoichiometric  $n$ -heptane (drops)–hydrogen–air ternary hybrid mixtures with different hydrogen contents: 0, 7.5, and 14.75 vol %. Calculations were performed for an initial droplet diameter of  $d_0 = 60\ \mu\text{m}$  at an initial temperature of 1000 K and a pressure of 20 atm. Analysis of the spatial distribution of the intermediate reaction products showed that the stepwise change in the maximum gas temperature in Fig. 3 is due to the appearance of a local blue flame associated with the decomposition of the accumulated hydrogen peroxide. With increasing hydrogen content in the ternary hybrid mixture, the blue flame zone degenerates, and the total ignition delay time increases.

Given the results presented in Fig. 1, this effect might seem trivial. Indeed, at an initial temperature of 1000 K, the ignition delay time for the homogeneous  $n$ -heptane–air mixture is about 2 times shorter than that for the homogeneous hydrogen–air mixture (Fig. 1). However, it should be kept in mind that the plots shown in Fig. 3 relate to the autoignition of a hybrid (gas–drop) rather than a homogeneous mixture. During the autoignition of drops, the temperature and concentration of fuel vapor are distributed unevenly around the drops, with vapor autoignition occurring in an area where gas temperature is lower than at a large distance from the droplet and the gas–vapor mixture

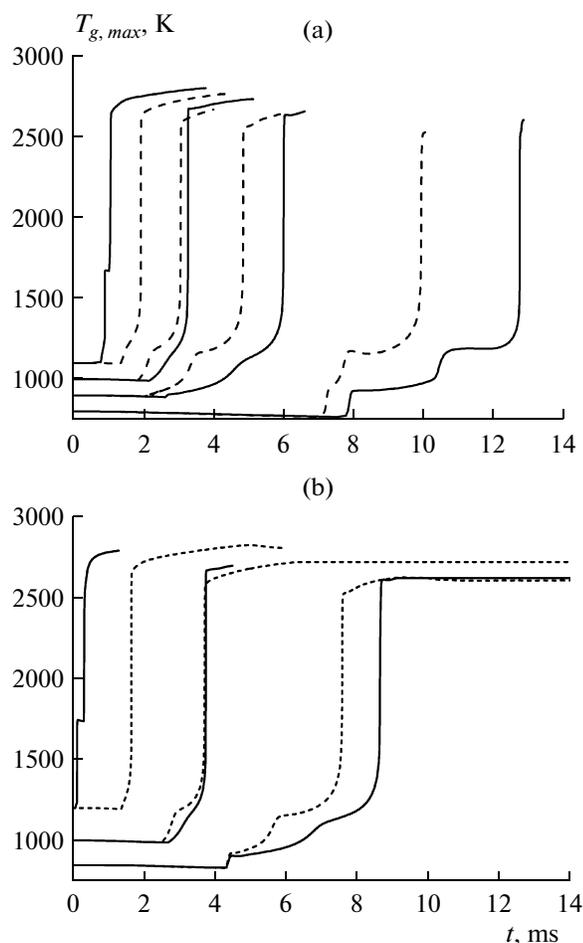


**Fig. 3.** Calculated time histories of the maximum temperature  $T_{g, \max}$  in the gas phase for stoichiometric  $n$ -heptane (drops)–hydrogen–air hybrid ternary mixtures at various hydrogen concentrations (vol %): (1) 0, (2) 7.5, and (3) 14.5;  $d_0 = 60\ \mu\text{m}$ ,  $P_0 = 20\text{ atm}$ , and  $T_{g0} = 1000\text{ K}$ .

composition is substantially depleted in fuel [14]. Therefore, the results presented in Fig. 3 are nontrivial.

It should be emphasized that the ignition characteristics of the ternary hybrid mixtures were performed using a DCM including the hydrogen oxidation mechanism as an integral part. This means that the active radicals produced in the oxidation of  $n$ -heptane can react with hydrogen and intermediate oxidation products. As a result of such interactions, less active species (e.g.,  $\text{HO}_2$ ) are formed, which leads to the inhibition of the reaction. In particular, this manifests itself through the degeneration of the blue flame stage with increasing hydrogen content in the ternary mixture. In other words, hydrogen and the products formed via the oxidation of hydrogen affect the processes of accumulation and decomposition of hydrogen peroxide, which determine the development of the stage of the blue flame in  $n$ -heptane-containing mixtures.

The above considerations are confirmed by the calculation results shown in Fig. 4. The figure compares the time histories of the maximum gas temperature for hybrid ternary mixtures of  $n$ -heptane (Fig. 4a) and  $n$ -decane (Fig. 4b) without (dashed curves) and with (7.5 vol %) hydrogen at different initial temperatures. It is clearly seen that the addition of hydrogen not only affects the total ignition delay time, but also the duration of the intermediate stages of the multistage ignition of drops. At relatively low initial temperatures (e.g.,  $T_0 = 800\text{ K}$ ), a significant increase in the duration of the cool and a blue flame zones is observed. This is indicative of reactions of hydrogen with intermediate active radicals involved in the respective steps of chain initiation and branching. Nevertheless, as in the homogeneous mixture, at  $T_0 < 1050\text{ K}$ , the ignition



**Fig. 4.** Calculated time histories of the maximum temperature  $T_{g,max}$  in the gas phase for stoichiometric hybrid ternary mixtures of (a) *n*-heptane (drops) and (b) *n*-decane (drops) with hydrogen and air at various initial temperatures and hydrogen concentrations: solid line, 7.5 vol %; dashed line, 0 vol %;  $d_0 = 60 \mu\text{m}$ ,  $P_0 = 20 \text{ atm}$ .

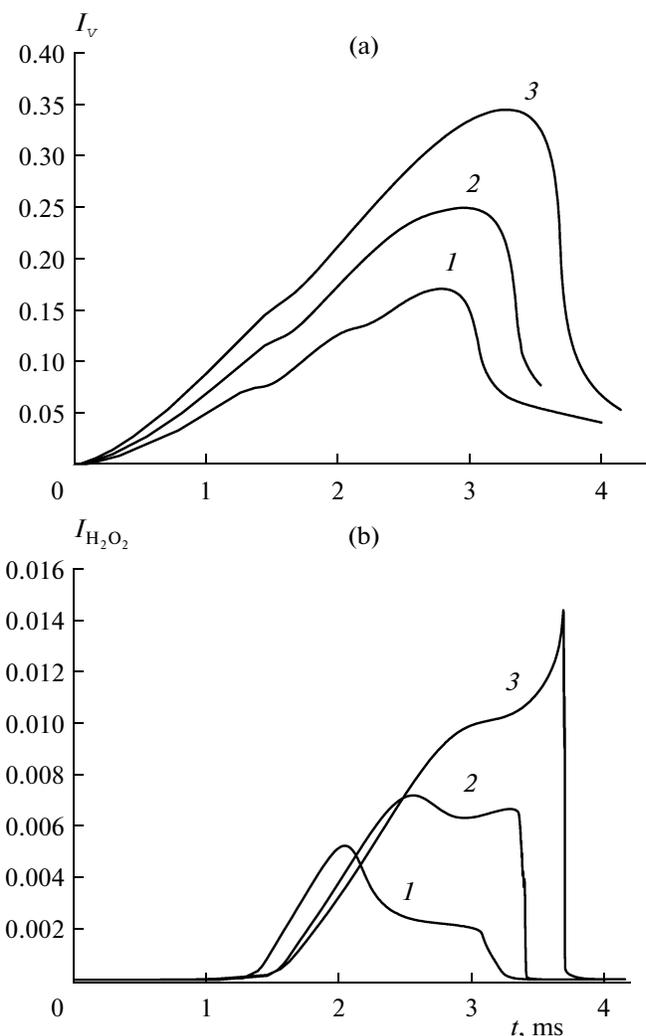
delay time for ternary gas–drop mixtures increases upon hydrogen addition, decreasing at  $T_0 > 1050 \text{ K}$ .

A detailed analysis of the physicochemical processes near the surface of the droplets enabled to find out some interesting features of the autoignition of hydrocarbon (drop)–hydrogen–air ternary hybrid mixtures. Figure 5 shows the time histories of the reduced (referred to the initial mass of the drop) mass contents of vaporized hydrocarbon  $I_v$  (Fig. 5a) and hydrogen peroxide  $I_{\text{H}_2\text{O}_2}$  (Fig. 5b) in a spherical volume around the droplet the radius  $R$  of which is equal to the effective half distance between drops in the gas–drop suspension [15]. The reduced mass contents of the  $i$ th species in the gas phase is determined by the formula [16]

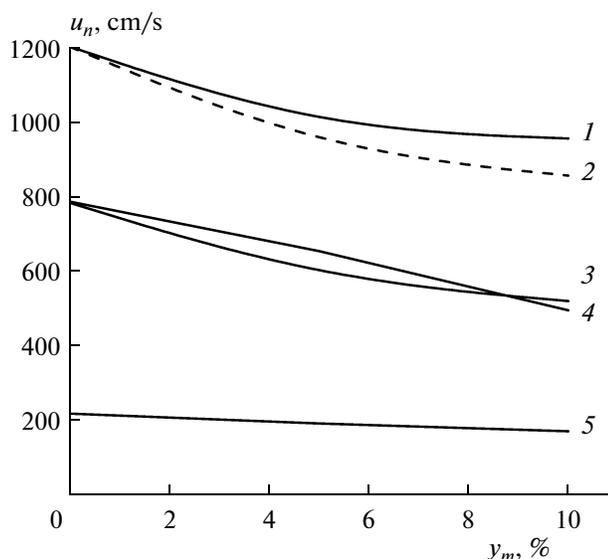
$$I_i(t) = m_0^{-1} \int_{r_s(t)}^R 4\pi\xi^2 Y_i(\xi, t) d\xi,$$

where  $m_0$  is the initial weight of the drop,  $Y_i$  is the mass concentration of the  $i$ th species,  $\xi$  is the spatial coordinate,  $r_s$  is the radius of the drop, and  $t$  is the time.

According to Fig. 5, the beginning of the ignition is accompanied by a sharp decrease in the parameters  $I_v$  (Fig. 5a) and  $I_{\text{H}_2\text{O}_2}$  (Fig. 5b). It can be seen that, with increasing hydrogen content in the hydrocarbon (drops)–hydrogen–air ternary hybrid mixture, the total autoignition delay time increases. Interestingly, the rate of evaporation of hydrocarbon droplets increases with the hydrogen concentration: it is seen from the change of the initial slope of the curves in Fig. 5a.



**Fig. 5.** Calculated time histories of the (a) reduced mass content of hydrocarbon fuel vapor and (b) hydrogen peroxide around drops for stoichiometric *n*-heptane (drops)–hydrogen–air hybrid ternary mixtures at various hydrogen concentrations in the gas phase (vol %): (1) 0, (2) 7.5, and (3) 14.5;  $d_0 = 60 \mu\text{m}$ ,  $P_0 = 20 \text{ atm}$ .



**Fig. 6.** Calculated dependences of the laminar flame speed on the mass concentration of hydrocarbon in stoichiometric *n*-heptane (drops)–hydrogen–air hybrid ternary mixtures at various initial conditions (solid lines, *n*-heptane; dashed line, *n*-dodecane): (1, 2)  $\varepsilon = 10$ ,  $P_0 = 20$  atm, and  $T_0 = 585$  K; (3)  $\varepsilon = 7$ ,  $P_0 = 12.5$  atm, and  $T_0 = 525$  K; (4)  $\varepsilon = 7$ ,  $P_0 = 15$  atm, and  $T_0 = 500$  K; and (5)  $\varepsilon = 1$ ,  $P_0 = 1$  atm, and  $T_0 = 293$  K.

Apparently, this effect is associated with the high thermal conductivity and diffusion coefficients of hydrogen. Furthermore, increasing the hydrogen concentration in the initial ternary hybrid mixture leads to an increase in the mass of the fuel vapor and hydrogen peroxide accumulated by the time of ignition, which is evident from a comparison of the maxima of the curves in Figs. 5a and 5b.

#### LAMINAR FLAME PROPAGATION IN HYDROCARBON–HYDROGEN–AIR TERNARY HOMOGENEOUS MIXTURES

It was of interest to see how the effects revealed in the autoignition of hydrocarbon–hydrogen–air homogeneous ternary mixtures manifest themselves during the propagation of a laminar flame in such mixtures: as is known, the reaction zone of a laminar flame is characterized by a wide range of temperatures.

The calculations were performed at (1)  $P_0 = 1$  atm and  $T_0 = 293$  K and (2)  $P_0 = 15$  atm and  $T_0 = 500$  K. In addition, simulations were carried out under the conditions realized in the internal combustion engine (ICE). Since the conditions in the engine are determined by the compression ratio  $\varepsilon$ , the initial values of  $P_0$  and  $T_0$  were selected as to provide  $\varepsilon = 7$  and  $\varepsilon = 10$ . The hydrocarbon fuel was *n*-heptane and *n*-dodecane. In all the calculations, the volume fraction of the hydrocarbon in the ternary mixture did not exceed 0.22% and the mass fraction was not more than 10%.

The calculation results are displayed in Fig. 6. It can be seen that even small concentrations of the hydrocarbon markedly inhibit the combustion of hydrogen in hydrocarbon–hydrogen–air homogeneous ternary mixtures. The maximum reduction in the flame speed reaches 30–40%. This result should be taken into account when discussing the prospects of changeover to hydrogen-fueled ICEs. The inevitable ingress of lubricating oil into the cylinder can substantially alter the combustion characteristics.

#### CONCLUSIONS

Numerical simulations of the ignition and combustion of hydrocarbon–hydrogen–air ternary homogeneous and hybrid (gas–drop) mixtures for three hydrocarbon fuels (*n*-heptane, *n*-decane and *n*-dodecane) were for the first time performed. The simulation is carried out based on a comprehensively tested DCM of the oxidation of *n*-dodecane, which includes mechanisms of the oxidation of *n*-decane, *n*-heptane, and hydrogen as constituent parts.

It is shown that the addition of hydrogen to a hydrocarbon–air homogeneous mixture at  $T_0 < 1050$  K increases the total ignition delay time; i.e., hydrogen acts as an ignition inhibitor. At low temperatures, even ternary mixtures with a very high concentration of hydrogen show a multistage ignition, with the temperature dependence of the ignition delay featuring a NTC region. On the contrary, at  $T_0 > 1050$  K, the addition of hydrogen to a hydrocarbon–air homogeneous mixture reduces the total ignition delay time; i.e., hydrogen acts as an autoignition promoter. However, at very high initial temperatures, an increase in the hydrogen concentration may again lead to an increase in the ignition delay time: under these conditions, the presence of small hydrocarbon additive accelerates the reaction due to the rapid thermal decomposition of hydrocarbon molecules with the formation of large concentrations of active species.

Adding hydrogen to a hydrocarbon–air hybrid (gas–drop) mixture leads to similar effects as in homogeneous mixtures: at  $T_0 < 1050$  K, hydrogen additives increase the ignition delay time for ternary gas–drop mixtures, reducing it at  $T_0 > 1050$  K. Hydrogen additives affect not only the overall ignition delay time, but also the duration of the intermediate stages of the multistage process of ignition of drops. In addition, the rate of evaporation of hydrocarbon droplets increases with the hydrogen concentration, as do the masses of fuel vapor and hydrogen peroxide accumulated by the time of ignition.

Calculations of the structure and speed of the laminar flame in hydrocarbon–hydrogen–air homogeneous ternary mixtures with low hydrocarbon concentrations showed that the hydrocarbon significantly inhibits the combustion of hydrogen, with the maximum reduction in the flame speed reaching 30–40%. All these effects should be kept in mind when discuss-

ing the prospects for the practical use of hydrogen-containing fuel mixtures, as well as in solving the issues of fire and explosion safety.

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