COMBUSTION, EXPLOSION, AND SHOCK WAVES

Promotion of the High-Temperature Autoignition of Hydrogen–Air and Methane–Air Mixtures by Normal Alkanes

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Abstract—Numerical simulations are performed to examine the effect of small additives of heavy hydrocarbons on the high-temperature autoignition of homogeneous hydrogen–air and methane–air mixtures. The kinetic calculations are carried out using a previously developed detailed mechanism of the oxidation and combustion of normal alkanes. It is shown that the behavior of hydrogen–hydrocarbon–air ternary mixtures is ambiguous. Large hydrocarbon additives of *n*-heptane and *n*-hexadecane to a hydrogen–air mixture promote its autoignition at low temperatures and inhibits it at high temperatures, whereas in a definite high-temperature range, small additives of hydrocarbons can promote rather than inhibit the autoignition. The autoignition of methane–air mixtures is promoted by additives of heavy hydrocarbons in all cases.

INTRODUCTION

The literature has repeatedly reported on the prospects of using hydrogen–hydrocarbon–air ternary mixtures in solving practical problems in the power and transport industries, for example, for reducing the emission of toxic substances from combustion processes, for improving the stability of combustion in flow, etc. (see, e.g., [1–3]). In [4–6], we performed numerical simulations of the autoignition and combustion of homogeneous hydrogen–air mixtures with homogeneous or heterogeneous (in the form of droplets) additives of hydrocarbons (for example, *n*-heptane and *n*-decane) and revealed a number of interesting effects. On the one hand, it was shown [4] that, at temperatures lower than $T_0 = 1050$ K, the presence of a hydrocarbon in a hydrogen–air mixture shortens the ignition delay time compared to that characteristic of the hydrogen–air mixture without additive, i.e. hydrocarbon additives promote the autoignition of hydrogen–air mixtures. On the other hand, at temperatures above $T_0 = 1050$ K, the presence of hydrocarbons in a hydrogen-air mixture makes the autoignition delay longer than that for the hydrogen–air mixture without additive, i.e. hydrocarbon additives inhibits the autoignition of hydrogen–air mixtures. More detailed studies carried out in [5, 6] have shown that the conclusion drawn in [4] on the inhibitory effects of a hydrocarbon on the autoignition of hydrogen–air mixtures at high temperatures is ambiguous. It turned that, at high temperatures, addition of a small amount of a hydrocarbon in a hydrogen–air mixture can not only

inhibit, but also promote its autoignition. This fact is important for understanding the physicochemical processes in the detonation wave.

The aim of the present work was to theoretically study the effect of promotion of the high-temperature autoignition of homogeneous hydrogen–methane–air mixtures by small additives of hydrocarbons.

CALCULATION RESULTS

The kinetic calculations of the autoignition delay times for hydrogen–heavy hydrocarbon–air and methane–heavy hydrocarbon–air ternary mixtures were performed using the detailed reaction mechanisms of the oxidation and combustion of *n*-heptane [7] and *n*-hexadecane [8] implemented in the KINET code, developed by M.G. Neigauz. This kinetic code, based on the exponential function linearization method [9], solves the differential equations of material and heat balance for a mixture of ideal gases under constant pressure ($P = $ const),

$$\frac{d\rho_j}{dt} = \sum_i w_{ij}, \qquad (1)$$

$$\rho c_\mathrm{p} \frac{dT}{dt} = \sum_{i,j} \Delta H_{ij} w_{ij}, \qquad (2)$$

at the initial conditions $\rho_j(0) = \rho_{j0}, j = 1, 2, ..., N$ and $T(0) = T_0$, where ρ_j is the partial density of the *j*th component, *t* is the time, ρ is the density of the mixtures,
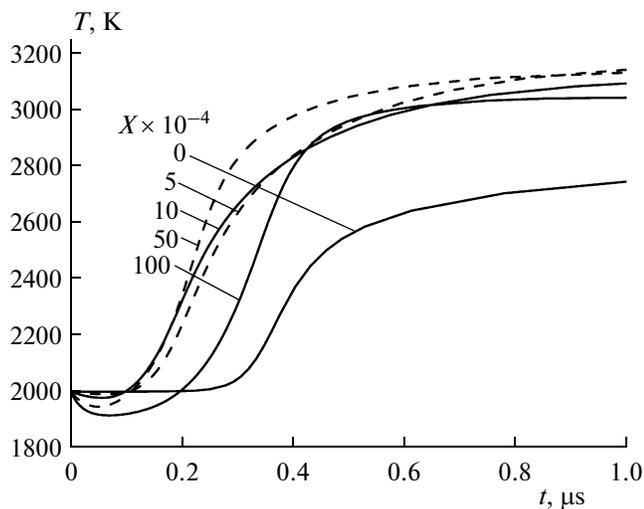
Fig. 1. Calculated temperature−time dependence for the autoignition of a hydrogen−air stoichiometric mixture at different volume fractions of *n*-heptane vapor additive. The initial temperature $T_0 = 2000$ K, pressure $P = 15$ atm.
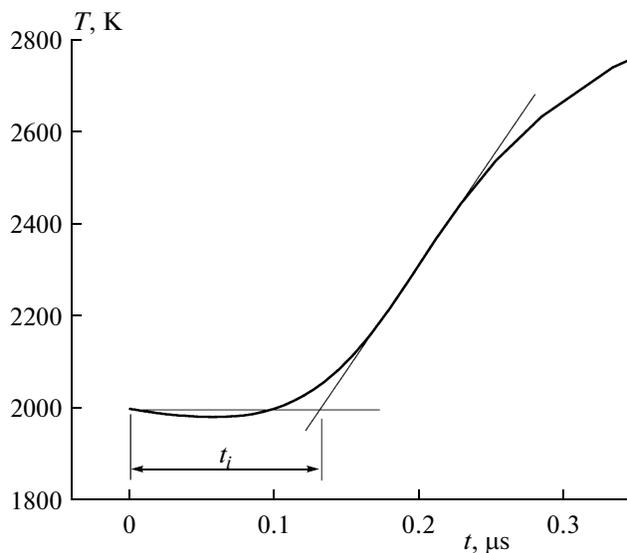

Fig. 2. Determination of the ignition delay time from the temperature−time dependence.

c_p is the heat capacity of the mixture at constant pressure, T is the temperature, w_{ij} and ΔH_{ij} are the rate and heat of the *i*th reactions involving the *j*th component, the subscript 0 designates time $t = 0$. The pressure, density, and temperature of the mixture are related by the equation of state a mixture of ideal gases, $P = \rho RT$, where R is the universal gas constant.

Figure 1 displays the temperature time history for the autoignition of a hydrogen−air stoichiometric mixture with different additives of *n*-heptane vapor.

The quantity X is the fraction of *n*-heptane−air stoichiometric mixture in a hydrogen−*n*-heptane−air stoichiometric mixture. It can be seen that small additives shorten the ignition delay time and reduce the temperature of the mixture in the beginning of the process. This is due to the fact that the added hydrocarbon readily decomposes, producing atomic hydrogen and other radicals, which initiate the process of chain-thermal autoignition.

Figure 2 shows how the ignition delay time is determined: from the point of intersection of the $T_0 = \text{const}$
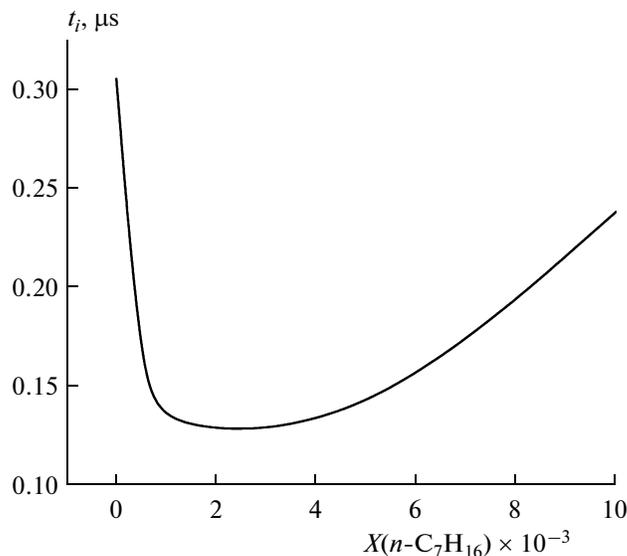

Fig. 3. Calculated dependence of the self-ignition delay time for a stoichiometric hydrogen−air mixture on the volume fraction of added *n*-heptane. The initial temperature $T_0 = 2000$ K, pressure $P = 15$ atm.
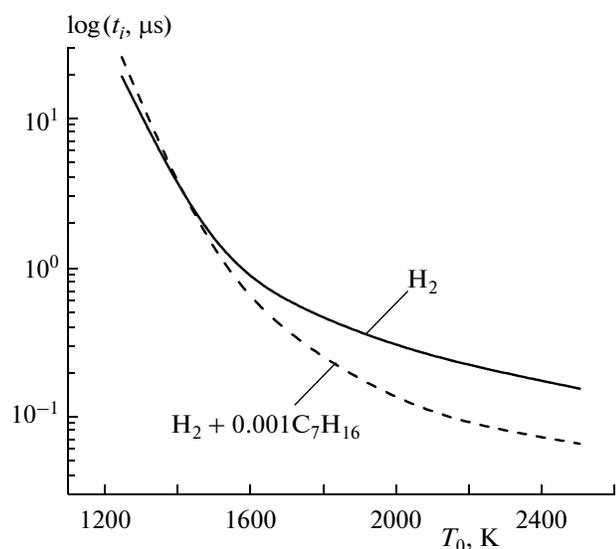
Fig. 4. Effect of initial temperature on ignition delay time for a hydrogen–air stoichiometric mixture without ($X = 0$) and with a n-heptane additive ($X = 0.001$). Pressure $P = 15$ atm.
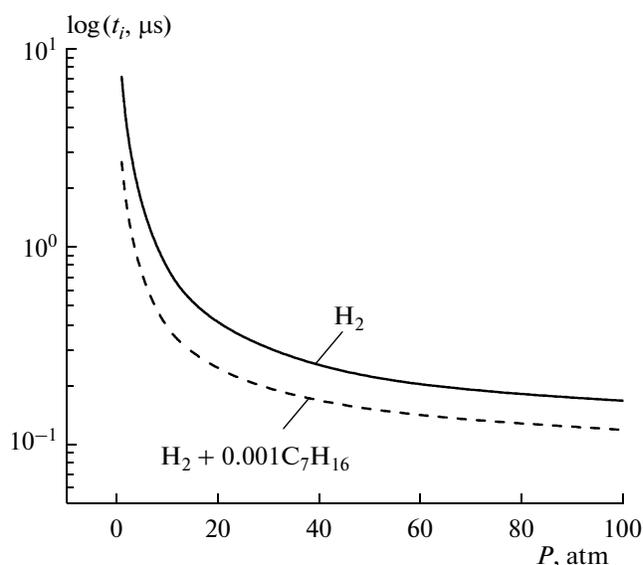

Fig. 5. Effect of pressure on the ignition delay time for a hydrogen–air stoichiometric mixture without ($X = 0$) and with a n-heptane additive ($X = 0.001$). The initial temperature $T_0 = 1750$ K.

straight line and the tangent to the inflection point in the temperature T versus time t dependence. Figure 3 demonstrates the calculated dependence of the autoignition delay time for a hydrogen–n-heptane–air stoichiometric mixture on the amount of added n-heptane vapor (volume fraction X) at $T_0 = 2000$ K and $P_0 = 15$ atm. As can be seen, at $X > 0.002$, the promoting effect weakens. Note that, at the given temperature and pressure, the ignition delay time for the n-heptane–air stoichiometric mixture is much longer than that for the hydrogen–air stoichiometric mixture. The elongation of the autoignition delay time for ternary mixtures at $X > 0.002$ is due to increasing role of chain termination by hydrocarbon radicals and molecules. At high values of X, n-heptane vapor additives begin to inhibit the process of autoignition of the hydrogen–air mixture.

Figure 4 shows the calculated effect of the initial temperature T_0 on the ignition delay time for a hydrogen–air stoichiometric mixture without additives ($X = 0$) and with an n-heptane additive ($X = 0.001$) at a pressure of $P = 15$ atm. Under these conditions, the promotion effect was observed only at temperatures of $T_0 > 1400$ K.

Figure 5 demonstrates how the pressure P influences the ignition delay time for a hydrogen–air stoichiometric mixture without additives ($X = 0$) and with a n-heptane additive ($X = 0.001$) at an initial temperature $T_0 = 1750$ K. It is seen that, in the pressure range from 1 to 100 atm, the promoting effect of a small n-heptane additive at specified values of X and T_0.

Figure 6 compares the calculated dependences of the autoignition delay time for a hydrogen–air stoichiometric mixture on the content of n-heptane and

n-hexadecane additive at $T_0 = 2000$ K and $P_0 = 15$ atm. Note that, at these pressure and temperature, the autoignition delay time for the n-hexadecane-air stoichiometric mixture is only slightly longer than that for the stoichiometric hydrogen–air mixture. Therefore, the minimum in the curve corresponding to the hydrogen–n-hexadecane–air stoichiometric mixture is achieved at a significantly higher X value than the minimum in the curve corresponding to the hydrogen–n-heptane–air ternary mixture, outside the graph in Fig. 6.
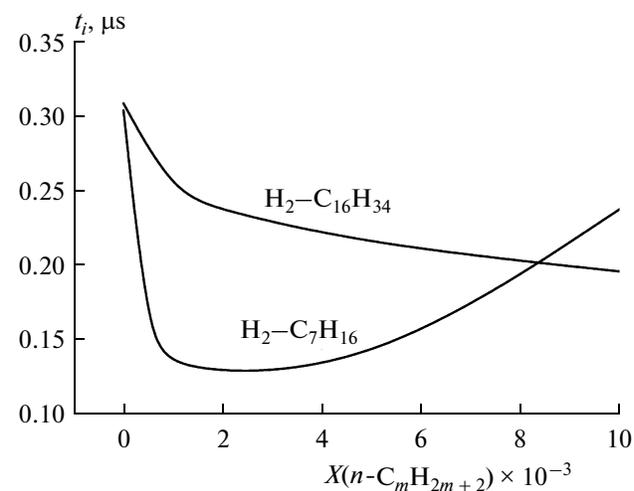

Fig. 6. Calculated dependences of the autoignition delay time for a stoichiometric hydrogen–air mixture on the volume fraction of vaporous n-hexadecane and n-heptane additives. The initial temperature $T_0 = 2000$ K, pressure $P = 15$ atm.
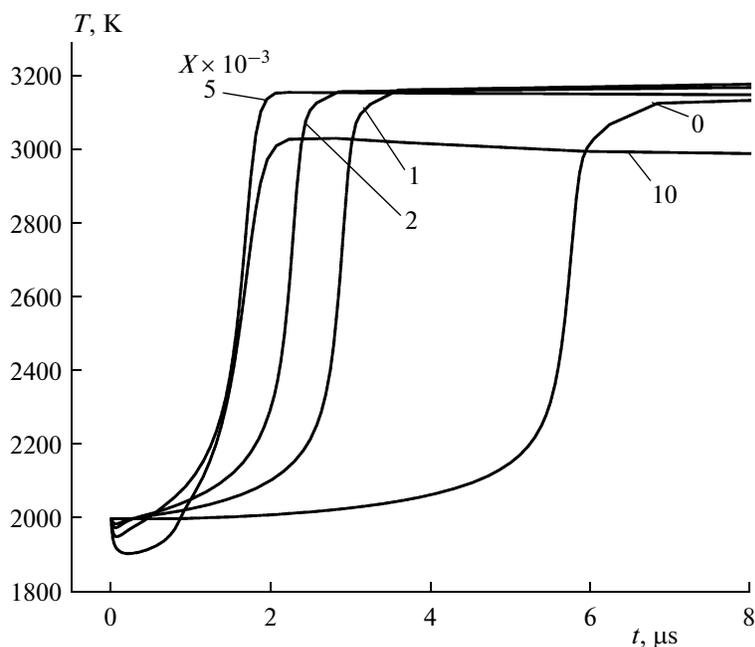
Fig. 7. Calculated temperature–time dependence for the autoignition of a stoichiometric methane-air mixture containing different volume fractions of added *n*-heptane. The initial temperature $T_0 = 2000$ K, pressure $P = 15$ atm.

In addition to studying the effect of small additives of hydrocarbons on the high-temperature self-ignition of hydrogen–air mixtures, we investigated the effect of such additives on the autoignition of methane–air mixtures. Figure 7 shows the calculated temperature versus time dependence for autoignition of a meth-ane–air stoichiometric mixture containing various amounts X of *n*-heptane vapor at $T_0 = 2000$ K and $P = 15$ atm, while Fig. 8 displays the corresponding calculated dependence of the ignition delay time of the ternary mixture on X. As can be seen, the autoignition delay time shortens significantly in the presence of very small *n*-heptane additives.
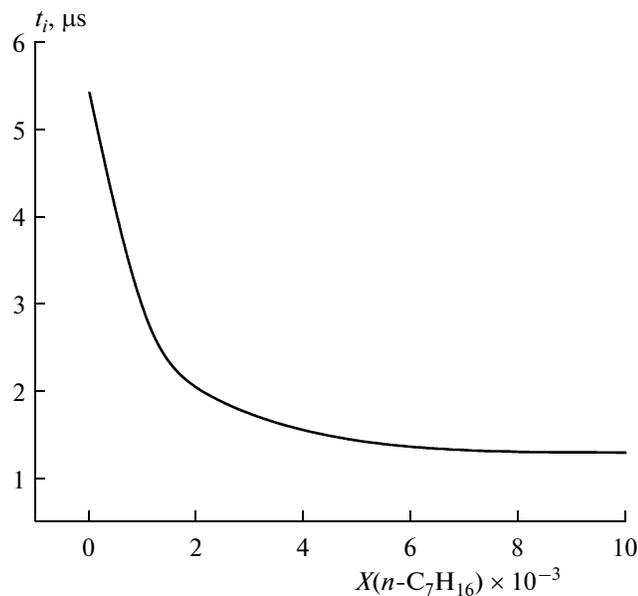

Fig. 8. Calculated dependences of the autoignition delay time for a stoichiometric methane–air mixture on the volume fraction of added *n*-heptane. The initial temperature $T_0 = 2000$ K, pressure $P = 15$ atm.

CONCLUSIONS

Thus, using calculations based on a detailed kinetic mechanism of the oxidation of higher hydrocarbons (*n*-heptane, *n*-hexadecane), including the mechanisms of the oxidation of methane and hydrogen as constituent parts, we demonstrated that, within a definite high-temperature range, small additives of hydrocarbon can promote the autoignition of hydrogen–air and methane–air mixtures. The phenomenon of promotion and inhibition of autoignition has been extensively studied experimentally and interpreted based on the theory of chain reactions [10]. The above calculation results are in qualitative agreement with the conclusions drawn from a general analytical study of the promotion of the self-ignition of model systems with linear- and branched-chain mechanisms of the process [11, 12], but need, however, experimental verification. The investigated range of microsecond-scale ignition delays is of interest for the gas dynamics of reacting flows, in particular for describing detonation phenomena, especially in places of collision of transverse waves in multi-detonation structures.

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