Numerical and experimental analysis of propane–hydrogen mixture ignition in air

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Abstract. The addition of hydrogen to the various hydrocarbon fuels being examined as a promising method for increasing the efficiency of the engine while improving their emission characteristics. This work is dedicated to experimental investigation of the ignition delay time C₃H₈–H₂ mixture in the air and analysis of the mechanisms responsible for the acceleration of chain reactions with the addition of hydrogen in propane, based on numerical simulation.

1. Introduction
The literature extensively studied effects of the addition of hydrogen at the time of ignition, flame velocity and flame stability, changes in the concentration of hazardous substances in the combustion products. For example, it was shown experimentally [1] that the addition of hydrogen to methane significantly reduces the ignition delay time in the range of initial temperature 1000–2000 K and a pressure 5–20 bar. A similar tendency was registered by the addition of H₂ to a mixture of 92% methane and 8% ethane at temperature 900–18000 K and pressure 1–16 bar [2], as well as to propane at temperature 1000–1600 K and pressure 1.2–10 bar [3]. Investigations of ignition delay time changes with the addition of hydrogen to heavier hydrocarbons (heptane, i-octane, n-decane) is carried out only on the basis of numerical simulation [4–6]. The presence of a negative temperature coefficient (NTC) according to saturated hydrocarbons CₙH₂n+2 (n ≥ 3) leads to the following characteristics: at relatively high temperature 1000–1600 K the hydrogen additive accelerates ignition and at a low temperature—slows down.

The aim of this work is to measure the ignition delay time C₃H₈–H₂ mixture in the air and analysis of the mechanisms responsible for the acceleration of chain reactions with the addition of hydrogen in propane, based on numerical simulation.

2. Experimental setup
The ignition delay time measurements were carried out in shock tube diameter of 50 mm and a length of 8.5 m. A detailed description of the experimental setup and measurement system is presented in [7]. There were investigated the ignition of the composite fuel C₃H₈–H₂ in the air when the equivalence ratio ϕ = 1. The mole fraction of hydrogen in a fuel amounted to 0, 30,
50 and 70%. Mixtures were prepared on the method of partial pressures and kept for 2 days before use in experiments. The initial pressure of the mixture was controlled to within ±0.2 mm Hg. The parameters of gas behind the incident (SW) and reflected shock waves (RSW) was calculated in the approximation of “frozen” chemistry from the known dependence of the heat capacity changes of the gas temperature and measured with an accuracy of ±0.5% the velocity of SW. Such inaccuracy in determining the velocity of SW leads to ~ 0.75% error in determining the temperature, pressure ~ 1.5% and density ~ 0.7% of the mixture behind the RSW. The compositions of the mixtures and the range of temperature and pressure changes of RSW are shown in table 1.

Measurements of the ignition delay time were performed by photoluminescence of OH radical (transition $^4\Sigma - X^2\Pi$) at a wavelength of $\lambda = 308.9$ nm and the CH radical (transition $^2\Delta - ^2\Pi$) at a wavelength of $\lambda = 431.5$ nm along the axis of the shock tube. To differ the desired wavelength emission were used narrowband filters $\lambda_{\text{max}} = 308.5$ nm, $\Delta \lambda_{0.5} = 1.4$ nm; $\lambda_{\text{max}} = 430.8$ nm, $\Delta \lambda_{0.5} = 2.6$ nm, respectively. Additionally, the $C_2$ molecules emission were registered in the boundary layer at a wavelength of $\lambda = 516.5$ nm using a monochromatic filter $\lambda_{\text{max}} = 516.3$ nm, $\Delta \lambda_{0.5} = 4.6$ nm. The ignition delay time also monitored by measuring the pressure and the ion current on the end wall of the shock tube. It was defined as the time between the arrival of the incident shock wave at the end wall of the shock tube and the beginning of emission at selected wavelengths or the beginning of the pressure increase. The accuracy of determining $\tau_{in}$ is $\sim 15\%$.

Figure 1 shows the dependence of the ignition delay time of the mixture $C_3H_8 - H_2 - air$ with varying degrees of hydrogen in the fuel determined experimentally as the emission of various components (OH, CH and $C_2$), and by the change in pressure. It can be seen that the various criteria for determining $\tau_{in}$ give very similar values, except for the high temperature range and, consequently, low induction time.

At high initial temperature $T_0 > 1100–1200$ K experimental data with good accuracy follow the Arrhenius dependence with $E_a \sim 20\,000$ K. At lower temperatures, when the ignition delay time is $\tau_{in} \sim 1$ ms or more, there is a change in the slope of this dependence with the transition to $E_a \sim 6000–10\,000$ K for mixtures with different concentrations of $H_2$. It is unlikely that the behavior of $\tau_{in}(T_0)$ dependence is associated with a low-temperature oxidation mechanism of propane at temperatures of 900–1100 K and a pressure of 5–10 bar, since the low-temperature oxidation of propane leads to NTC at a lower temperature [8–10]. At the same time the ignition delay in the NTC part of $\tau_{in}(T_0)$ curve for propane is 40–50 ms, even at a pressure of 30 bar [8], which is much higher that measured in this work. The $\tau_{in}(T_0)$ deviation by Arrhenius at low temperature occurs, apparently, because of the influence of non-stationary processes developing in the shock tube at $\tau_{in} > 1$ ms.

On the figure 1, the dotted line corresponds to the temperature $T_{0b}$, below which there were no ignition in experiments. It can be seen that the addition of hydrogen to the propane reduces

| % $H_2$ | Mixture composition $C_3H_8 - H_2 - air$ | $P_0$, bar | $T_0$, K |
| --- | --- | --- | --- |
| 0 | 4% $C_3H_8 + 20.16\% O_2 + 75.84\% N_2$ | 5.8–9.7 | 1098–1780 |
| 30 | 3.81% $C_3H_8 + 1.63\% H_2 + 19.87\% O_2 + 74.69\% N_2$ | 5.7–10.1 | 985–1788 |
| 50 | 3.55% $C_3H_8 + 3.55\% H_2 + 19.52\% O_2 + 73.38\% N_2$ | 5.36–11.2 | 921–1897 |
| 70 | 3.06% $C_3H_8 + 7.1\% H_2 + 18.9\% O_2 + 70.94\% N_2$ | 5.21–10.4 | 923–1746 |
Figure 1. The ignition delay time for a stoichiometric C$_3$H$_8$–H$_2$–air mixture with the mole fraction of hydrogen in the fuel of 0, 30, 50 and 70% depending on the initial temperature $T_0$, defined by OH, CH and C$_2$ emission, and pressure.

The $T_{ib}$ value. The more hydrogen in the fuel, the less $T_{ib}$ value. For pure propane ignition was not observed when $T_0 < 1098$ K, in a mixed fuel C$_3$H$_8$–H$_2$ with the mole fraction of hydrogen 30, 50 and 70% $T_{ib}$ values were 985, 950 and 922 K, respectively.

Figure 2 shows the Influence of addition of H$_2$ to propane at the ignition delay time. It can be seen that the addition of 30% H$_2$ almost no effect on the $\tau_{in}$, supplement with 50% H$_2$—decreases $\tau_{in}$ by 30–35% and the addition of 70% H$_2$—reduces $\tau_{in}$ in 2 times. The same qualitative and quantitative effect was observed in [3] for lean C$_3$H$_8$–H$_2$–O$_2$ mixture, highly diluted with argon.

3. The simulation results and analysis

Modeling of ignition of the mixture C$_3$H$_8$–H$_2$–air was performed using the detailed reaction mechanism of oxidation of propane [11]. Note that this mechanism comprises both high and low temperature oxidation parts of propane that allows with high accuracy (see [11]) describe the experimental data on ignition delay times of C$_3$H$_8$–H$_2$–O$_2$–Ar and air–C$_3$H$_8$ mixtures [7,8,12,13], including at low temperatures, down to $T_0 \sim 700$ K.

The data presented in figure 2 shows that the results of the calculations reproduce well the measured $\tau_{in}$ values when $T_0 > 1100$ K. It is also seen that the calculation does not predict the
Figure 2. The ignition delay time for a stoichiometric C₃H₈–H₂–air mixture as a function of the initial temperature T₀. Symbols—pressure change measuring, lines—the calculation by the model [11] for 0, 30, 50 and 70% H₂ content in fuel (lines 1-4).

Figure 3. Temperature changing during combustion of a stoichiometric mixture C₃H₈–H₂–air with the mole fraction of hydrogen in the fuel of 0, 30, 50 and 70% at T₀ = 1300 K and P₀ = 8 bar. To the right is a fragment of the left figure.

presence of NTC depending τₐₙ(T₀) at 920 < T₀ < 1100 K. This confirms the hypothesis that the deviation of experimental data from the Arrhenius in this temperature range associated with the flow features in the shock tube.

Consider how the addition of H₂ to propane effects on temperature changes and component concentration. Figure 3 shows dependence of the temperature variations of the C₃H₈–H₂–air mixture ignition with different mole fraction of hydrogen in the fuel at T₀ = 1300 K, and P₀ = 8 bar. The right part of figure 3 shows more detailed region at T₀ ~ 1300 K, it is seen that temperature reduces before the mixture ignition. Moreover, in pure propane the temperature decreases to about 5°, but adding H₂ temperature reduction becomes smaller. It is associated with the dissociation of propane, which proceeds with the energy absorption. The smaller propane in a fuel, the lower temperature drop. The calculations also show that the equilibrium temperature of the combustion products is higher when bigger amount of hydrogen
Figure 4. Changing the molar fraction of H atoms in the ignition of a stoichiometric mixture $\text{C}_3\text{H}_8$–H$_2$–air with the mole fraction of hydrogen in the fuel of 0, 30, 50 and 70% at $T_0 = 1300$ K and $P_0 = 8$ bar.

in the mixture.

Figure 4 shows the mole fraction change of H atoms in the tested mixture. It is seen that the change in H concentration in time for all mixtures until $t \sim 10^{-6}$ s with almost identical. However, if $t > 10^{-6}$ s it is observed a more rapid increase in the H concentration in mixtures containing H$_2$. The more H$_2$ in a mixed fuel, the concentration of H increases faster, which leads to earlier ignition. A similar trend holds for the active components such as the O atoms and the radicals OH. To explain this behavior of the concentration of active radicals let us analyze the mechanisms responsible for accelerating ignition of propane in air with the addition of H$_2$.

Oxidation of pure propane and mixed fuel at $T_0 > 1100$ K initiates the process with the participation of C$_3$H$_8$

\[
\text{C}_2\text{H}_5 + \text{C}_3\text{H}_8 = \text{CH}_3, \quad (1)
\]
\[
\text{C}_3\text{H}_8 + \text{O}_2 = \text{C}_3\text{H}_7 + \text{HO}_2. \quad (2)
\]

Subsequent dissociation of alkyl radicals C$_2$H$_5$ and C$_3$H$_7$:

\[
\text{C}_2\text{H}_4 + \text{C}_2\text{H}_5 = \text{H}, \quad (3)
\]
\[
\text{C}_3\text{H}_6 + \text{C}_3\text{H}_7 = \text{H}, \quad (4)
\]

leads to the appearance of the H atoms and an increase in their concentration. H atoms are involved in the reactions to continue

\[
\text{C}_3\text{H}_8 + \text{H} = \text{C}_3\text{H}_7 + \text{H}_2 \quad (5)
\]

and branching

\[
\text{H} + \text{O}_2 = \text{OH} + \text{O}. \quad (6)
\]

Presence of H$_2$ in a mixed fuel on the one hand stimulates the formation of additional reaction of H atoms with a methyl radical

\[
\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}, \quad (7)
\]
Figure 5. Basic processes scheme responsible for the development of the chain mechanism in the C₃H₈–H₂ mixed fuel oxidation at T₀ > 1100 K. The dashed lines marked processes involving H₂ molecules, which affect the ignition acceleration under the presence of hydrogen in the original mixture.

and, on the other hand, is involved in the chain propagation reaction

\[ \text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}, \]  

which is characteristic of hydrogen oxidation.

In pure propane to implement reaction (8) requires a preliminary operation time sufficient H₂ molecules, for example, in the reaction C₃H₈ + H = C₃H₇ + H₂, which is somewhat delaying ignition. Scheme of the main processes responsible for the development of the chain process in a mixture of C₃H₈–H₂–O₂, is shown in figure 5.

4. Conclusion
There were performed experimental and numerical studies of ignition stoichiometric C₃H₈–H₂–air mixture with different content of H₂ in fuel at T₀ = 920–1900 K and P₀ = 5.2–11.2 bar. It has been shown that a significant reduction in the ignition delay time is achieved only at rather high mole fraction of hydrogen in the fuel. At 70% H₂ in the fuel the ignition delay time is reduced to about 2 times as compared with pure propane.

The kinetic model, developed earlier [11], allows to describe the experimental data with high accuracy in the range of parameters where do not influence unsteady effects used to measure \( τ_{in} \) shock tube (typical times \( t \sim τ_{in} \leq 1 \text{ ms} \)). On the basis of numerical analysis found that the main process responsible for the acceleration of the ignition process by adding H₂ to propane is branching reaction H + O₂ = OH + O, the rate of which increases with the content of H₂ in mixed fuel in the temperature range T₀ = 1100–1600 K. In this case the main source of H atoms are alkyl radicals dissociation C₃H₇ and C₂H₅, which arise in the mixture H₂–C₃H₈–air oxidation and decomposition reactions of propane. Another channel of formation of H atoms is the reaction of the methyl radical CH₃ with molecular hydrogen. Thus, there is close cooperation between the kinetics of the oxidation of C₃H₈ and H₂.

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