

# Kinetic Analysis of the Mechanisms of Ignition and Combustion of Blended Fuels Comprising Hydrocarbons and Hydrogen

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## 1 Introduction

For past years, a great deal of interest has been expressed to the study of features of ignition and combustion of blended fuels consisting of hydrocarbons and hydrogen. The experimental and numerical studies [1-3] demonstrated that admixture of hydrogen to methane and propane increases the flame speed and extends the flammability thresholds. In addition, in some temperature range ( $T=1000-1600$  K), the blended propane-hydrogen fuel ignites much faster than pure propane [3, 4]. However, as was revealed recently in the course of numerical simulations, both propane-hydrogen and n-heptane-hydrogen blends ignite slower than individual hydrocarbons at low temperature ( $T<1000$  K) [3, 5]. Moreover, even at high temperature ( $T>1600$  K), there exist some interesting features in the selfignition of blended propane(n-heptane)-air fuel: a small admixture (~1–2% per mass) of propane to hydrogen results in shortening the ignition delay. The magnitude of boundary temperature  $T_l$  in low temperature range ( $T<T_l$ ), at which the ignition delay for pure propane becomes smaller than that for propane-hydrogen blend, depends on pressure of the fuel-air mixture and on the composition of blended fuel. Identical dependence exists for boundary temperature  $T_h$  in the high temperature range. Because the values of  $T_l$  and  $T_h$  are determined by the features of kinetic mechanisms of hydrogen and each individual hydrocarbon oxidation, one can suppose that the temperature range, in which the specific features of the ignition of blended fuels come into play, can distinguish substantially for different hydrocarbons.

Nowadays, in practical devices a number of hydrocarbons are applied as a fuel. There are methane or natural gas, propane, gasoline (consisting mostly of n-heptane and i-octane) and kerosene (n-decane is considered as a surrogate of commercial aviation kerosene Jet-A). Blended hydrocarbon-hydrogen fuels are considered as very promising ones for different types of internal combustion engines [6, 7]. However, up to now the comparative analysis of the features of ignition and combustion of blended fuels comprising different hydrocarbons and hydrogen has not been conducted. Moreover, it is unclear how these features influence the formation of pollutants, mostly  $\text{NO}_x$  and CO.

The goal of this paper is to analyze the kinetic mechanisms of the selfignition of such fuel blends as i-octane-hydrogen and n-decane-hydrogen that can be very effective as alternative fuels for internal combustion and gas turbine engines and to compare the combustion and emission characteristics of these blended fuels.

## 2 Kinetic Model

The analysis was based on the detailed reaction mechanisms for i-octane and n-decane oxidation reported by Curran et al. [8] and Titova et al. [9], respectively. These mechanisms include both high and low temperature channels of chain mechanism development and describe the specific behavior of the temperature dependence of induction time  $\tau_{in}$  called negative temperature coefficient that takes place at low temperatures. These mechanisms were updated towards accounting for the novel data on hydrogen chemistry reported recently in [10]. As an example of good prediction ability of these mechanisms, figure 1 shows the measured in [11, 12] and predicted values of ignition delay (induction time)  $\tau_{in}$  as a function of initial temperature  $T_0$ .

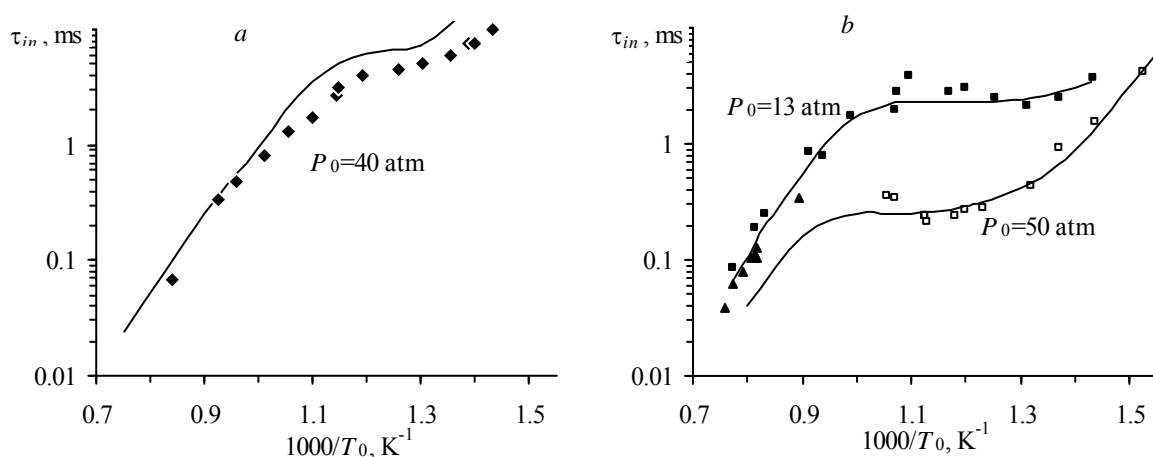


Figure 1. Ignition delay  $\tau_{in}$  in the stoichiometric i-C<sub>8</sub>H<sub>18</sub>-air (a) and n-C<sub>10</sub>H<sub>22</sub>-air (b) mixtures as a function of initial temperature  $T_0$  at specified pressure value  $P_0$ : points are the experimental data [11] (a) and [12] (b), curves are the predictions.

## 3 Results and discussion

### 3.1 Ignition

Let us consider at first, how the addition of H<sub>2</sub> to i-octane and n-decane can influence on the ignition delay. Shown in figure 2 are the  $\tau_{in}(T_0)$  dependences for the stoichiometric i-C<sub>8</sub>H<sub>18</sub>-H<sub>2</sub>-air and n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub>-air mixtures with 0, 15, 90 and 100% H<sub>2</sub> content in the fuel blends at  $P_0=10$  bar. One can see that both for i-C<sub>8</sub>H<sub>18</sub>-H<sub>2</sub> and for n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blends there exists the specific feature in the  $\tau_{in}(T_0)$  behavior. In the some temperature range ( $T_0 < 1000$  K), pure i-octane and pure n-decane or i-C<sub>8</sub>H<sub>18</sub>-H<sub>2</sub> and n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blends with small content of H<sub>2</sub> (10-30% per fuel mass) ignites faster than hydrogen. This effect is much more pronounced for the n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blend. So, at  $T_0=800$  K, the  $\tau_{in}$  value for n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blended fuel with 15% H<sub>2</sub> content is by a factor of 100 smaller than that for pure hydrogen. For the i-C<sub>8</sub>H<sub>18</sub>-H<sub>2</sub> fuel blend with 15% H<sub>2</sub>, this difference does not exceed a factor of 5. At higher initial temperature ( $T_0 > 1000$  K), there exists the temperature range  $T_l < T_0 < T_h$  (the value of  $T_h$  depends on the H<sub>2</sub> mass fraction), where pure hydrogen ignites faster than pure i-octane and n-decane as well as i-C<sub>8</sub>H<sub>18</sub>-H<sub>2</sub>, n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blends. At  $T_0 > T_h$ , the induction time for fuel blends becomes again smaller than that for pure hydrogen. These features are caused by the strong interaction of chain mechanisms of the oxidation of hydrogen and hydrocarbons. Consider this interaction for the n-C<sub>10</sub>H<sub>22</sub>-H<sub>2</sub> blend, as an example.

As is known, in the H<sub>2</sub>-air mixture, the chain process is initiated due to following reactions



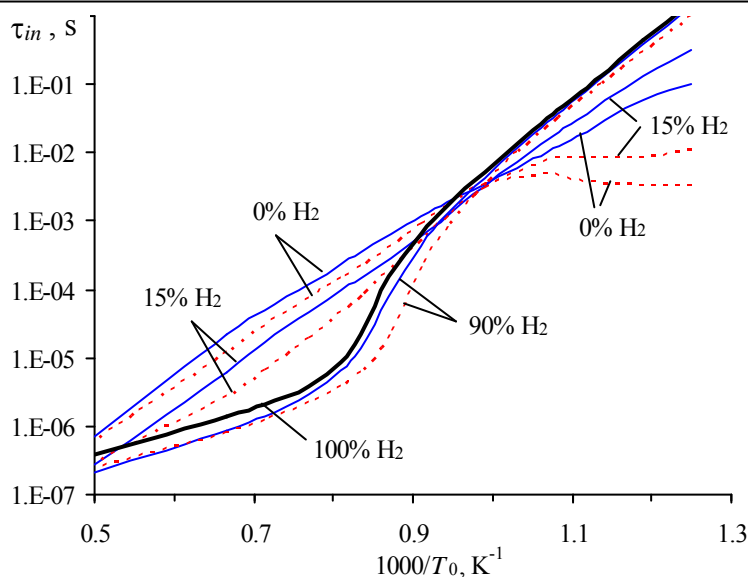


Figure 2. Ignition delay  $\tau_{in}$  in the stoichiometric  $i\text{-C}_8\text{H}_{18}\text{-H}_2\text{-air}$  (solid curves) and  $n\text{-C}_{10}\text{H}_{22}\text{-H}_2\text{-air}$  (dotted curves) mixtures with 0, 15, and 90%  $\text{H}_2$  content per fuel mass at  $P_0=10$  atm. Thick line corresponds to the  $\tau_{in}(T_0)$  dependence in the  $\text{H}_2\text{-air}$  mixture.

Then, H atom reacts rapidly with  $\text{O}_2$



and atomic oxygen interacts with molecular hydrogen in the course of reaction



with the formation of highly reactive OH radical and H atom. The latter again interacts with  $\text{O}_2$  molecule. Thus, the processes R3 and R4 form chain-branching mechanism. However, the reactions R1 and R2 proceeds rather slowly due to their high energy barrier ( $E_a=53443$  and  $95565$  kcal/mole, respectively). At low temperature ( $T_0 < 900$  K) the chain termination reaction

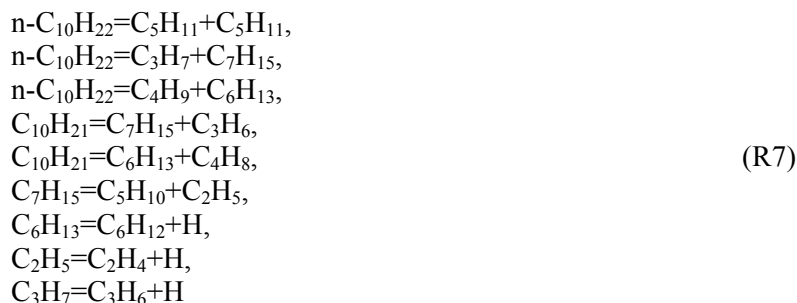


delays the ignition and results in the increase of induction time.

The development of chain mechanism in the  $n\text{-C}_{10}\text{H}_{22}\text{-air}$  mixture is initiated by the oxidation processes



and, at moderate ( $T_l < T_0 < T_h$ ) and high ( $T_0 > T_h$ ) initial temperatures, also by the sequence of dissociation reactions



that produce highly reactive atomic hydrogen and alkyl radicals. It is worth noting that reactions R6-R14 are endothermic, and their occurrence leads to the decrease in the temperature. At high initial temperature ( $T_0 \sim 2000$  K), these reactions proceeds with high rates, and the temperature can fall down notably before the ignition event.

The appearance of H atoms initiates the reaction of chain propagation



At low temperature ( $T_0 < 900$  K) the chain mechanism development in n-decane-air mixture occurs through the formation of alkyl-peroxide radical



that due to consecutive processes of intramolecular isomerization, addition of the second  $\text{O}_2$  molecule, second intramolecular isomerization and, finally, two-stage dissociation results in the formation of three radicals (carbonyl radical and two hydroxyl radicals OH), which substantially accelerates oxidation of n-decane at low temperatures.

When adding some amount of hydrogen to n-decane, the chain mechanism occurs via the competition of chain reactions that take place both in n- $\text{C}_{10}\text{H}_{22}$ -air and in  $\text{H}_2$ -air mixtures.

The chain mechanism in blended n- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$ -air mixture is initiated by the process R6 and, at  $T_0 > T_l$ , additionally by the reactions R7, because the rates of reactions R6 and R7 are higher than those of reactions R1 and R2. The presence of molecular hydrogen in blended fuel ensures the chain mechanism development at  $T_0 > T_l$  through the reactions R3 and R4, whose rates are greater than the rate of the process R8. As a result, in the range  $T_l < T_0 < T_h$  the ignition of n- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$  blended fuel occurs faster than that of pure n- $\text{C}_{10}\text{H}_{22}$ . At very high temperature  $T_0 > T_h$ , high rates of dissociation reactions R7 ensure such a great concentration of H atoms that the blended n- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$  fuel ignites even rapidly than pure hydrogen.

It should be emphasized that at small n- $\text{C}_{10}\text{H}_{22}$  content in the blended (2-10% per fuel mass), there exists some interesting feature: the induction time even at  $T_0 > T_l$  in the n- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$ -air mixture is shorter than that in the  $\text{H}_2$ -air mixture.

Analogous processes occur during the oxidation of i- $\text{C}_8\text{H}_{18}$ - $\text{H}_2$  blend. However, because the dissociation reactions of i- $\text{C}_8\text{H}_{18}$  and its derivatives proceed with low rates, the  $\tau_m$  values in the i- $\text{C}_8\text{H}_{18}$ - $\text{H}_2$ -air mixture are somewhat greater than those in i- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$ -air one with identical  $\text{H}_2$  content in the fuel. Therefore, one can conclude that, though the mechanisms of the oxidation of fuel blends composed of hydrogen and alkanes are similar, nevertheless, because the reactions of chain initiation and chain propagation occur with different rates for alkanes with different structure, the ignition characteristics of blended  $\text{C}_n\text{H}_{2n+2}$ - $\text{H}_2$  fuel can distinguish substantially for various alkanes at the identical composition of blends.

At low initial temperature  $T_0 < T_l$ , the addition of hydrogen to alkane (and, as consequence, the decrease of alkane content in the fuel) results in the decrease of the concentration of alkyl-peroxide radicals formed during low-temperature channel of alkane oxidation (reaction R9) and, as a result, in the smaller rate of OH radical formation. This delays the ignition at low temperature.

### 3.2 Flame speed

Computations showed that an admixture of hydrogen to i- $\text{C}_8\text{H}_{18}$  and n- $\text{C}_{10}\text{H}_{22}$  leads to the increase of the flame speed. This is clearly seen from figure 3, where the variation of laminar flame speed  $U_n$  vs. fuel-air equivalence ratio  $\phi$  is shown for the stoichiometric n- $\text{C}_{10}\text{H}_{22}$ - $\text{H}_2$ -air mixture with different  $\text{H}_2$  content in the fuel. It is also seen that flammability limits in the fuel-lean and fuel-rich regions are notably broader for the fuel blend than those for burning of the pure n- $\text{C}_{10}\text{H}_{22}$ . The strongest effect is observed for the fuel-rich mixture. So, if for the fuel-lean mixture ( $\phi=0.7$ ) the addition of 80%  $\text{H}_2$  to n- $\text{C}_{10}\text{H}_{22}$  increases  $U_n$  value by 25%, for the fuel-rich ( $\phi=1.3$ ) mixture this rise amounts to 35%. For the mixture with  $\phi=1.4$ , this effect is much higher, and the increase in the  $U_n$  value achieves 45%. For the i- $\text{C}_8\text{H}_{18}$ - $\text{H}_2$ -air mixture the analogous tendencies are observed. However, the rise in the  $U_n$  value is somewhat smaller. The increase in the flame speed in the case of burning of blended hydrocarbon-hydrogen fuels is due to the formation of additional amounts of highly reactive H and O atoms and OH radicals in the hot flame region that results in the rise of diffusion rate of these species from the hot flame region to the cold one.

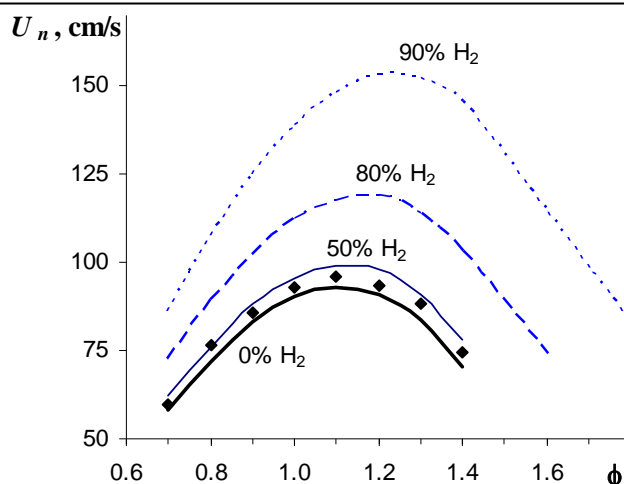


Figure 3. Laminar flame speed  $U_n$  as a function of fuel to air equivalence ratio  $\phi$  for the  $n\text{-C}_{10}\text{H}_{22}\text{-H}_2\text{-air}$  mixture with 0, 50, 80 and 90%  $\text{H}_2$  content per fuel mass at  $T_0=300\text{ K}$  and  $P_0=1\text{ atm}$ . Points are experimental data [13] for the  $n\text{-C}_{10}\text{H}_{22}\text{-air}$  mixture; curves are the predictions of this work.

Extended flammability thresholds in the blended fuels makes it possible to burn leaner or much more rich mixtures compared to pure *i*-octane and *n*-decane. The computations showed, that admixture of  $\text{H}_2$  to *i*-octane and *n*-decane up to 50% content per fuel mass do not result in the growth of NO concentration in the flame. For the fuel-lean mixture with  $0.6 < \phi < 1$ , thermal mechanism is mostly responsible for the NO formation, though at  $\phi \sim 0.6$  both prompt and  $\text{N}_2\text{O}$  mechanisms contribute to NO production. The possibility of burning leaner fuel/air mixture upon usage of blended fuel makes it possible to reduce NO emission notably keeping the same value of  $U_n$  as in the case of burning of  $i\text{-C}_8\text{H}_{18}(n\text{-C}_{10}\text{H}_{22})\text{-H}_2\text{-air}$  mixture with greater  $\phi$ . This also allows one to reduce CO emission.

## 4 Conclusions

Numerical analysis of the features of ignition and chain mechanism development during oxidation of blended fuels composed of *i*-octane(*n*-decane) and hydrogen was conducted on the basis of detailed reaction mechanisms involving both high and low temperature channels of  $i\text{-C}_8\text{H}_{18}$  and  $n\text{-C}_{10}\text{H}_{22}$  oxidation. It was shown that both for the  $i\text{-C}_8\text{H}_{18}\text{-H}_2$  and for  $n\text{-C}_{10}\text{H}_{22}\text{-H}_2$  blends, there exists the temperature range, where the ignition of the fuel blend occurs faster compared to pure alkanes. The broad of this range has low and high temperature boundaries ( $T_l$  and  $T_h$ , respectively) and depends strongly on the type of primary alkane,  $\text{H}_2$  content in the blend and initial pressure of the fuel/air mixture. At  $T_0 < T_l$ , the ignition delay of blended  $i\text{-C}_8\text{H}_{18}(n\text{-C}_{10}\text{H}_{22})\text{-H}_2$  fuel is longer than that of pure alkane under study. It is remarkable that for the pressure higher atmospheric one, at  $T_0 > T_l$ , the addition of small amount of alkane (2-10%) to hydrogen leads to shortening the ignition delay. It was shown that the addition of hydrogen both to *i*-octane and to *n*-decane increases the flame speed and extends the flammability limits. However, the notable effects achieve at rather high  $\text{H}_2$  content (higher than 50% per fuel mass).

## 5 Acknowledgement

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