

Special Cases Affecting the Low-Temperature Ignition of Evaporated Hydrocarbon-Air Mixtures in a Rapid Compression Machine

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1 Introduction

Experimental ignition delay studies on simple hydrocarbons are of considerable theoretical interest, and have a practical application for the construction and verification of detailed kinetic mechanisms. These mechanisms, in turn, are the basis for developing oxidation kinetics of multicomponent surrogate mixtures that are designed for ignition and combustion simulations of real fuels. Some of the main components of surrogates of gasoline, kerosene and diesel fuel are iso-octane, *n*-heptane, and *n*-decane [1–3]. However, there is a significant lack of experimental data on the ignition delay time of the *n*-decane/air mixture at temperatures below 1000 K. It is connected with certain difficulties in carrying out experiments with *n*-decane due to its low saturated vapor pressure (about 120 Pa) at ambient temperature. For this reason, ignition delay time was measured in heated shock tubes (ST) at high-to-intermediate temperatures [4–10] and in heated rapid compression machines (RCM) at low temperatures [11, 12]. However, only in one of these studies measurements were carried out for a wide temperature range of 650–1300 K [4] behind the reflected shock wave under the tailored interface conditions. These results together with the data for *n*-heptane [8, 13] and iso-octane [14] demonstrate clear negative temperature coefficient (NTC) behavior for hydrocarbons at temperatures below 1000 K. An analysis of gas parameters: pressure, temperatures and mixture compositions, behind reflected shock wave (ST) or at the end of compression stroke (RCM) shows that in most studies ignition delay time was measured under supersaturation conditions when the partial vapor pressure *n*-heptane and *n*-decane exceeded significantly its saturated value at the wall temperature. Only in papers [5, 9, 13] the vapor supersaturation conditions were not reached due to low fuel concentrations and final gas pressure. The problem of possible fuel vapor condensation near the relatively cold walls of the test volume has not previously been raised anywhere as well as the influence of this process on the local gas mixture parameters and composition has not been estimated. Ignition is known to be very sensitive to even minor changes in local temperature and fuel concentration in the mixture. These changes can be caused by inhomogeneity of hydrocarbon molecules distribution and the latent heat release due to phase transition as well as the presence of contaminated microparticles [15]. Thus, it is important to identify a relationship between physical processes occurring during adiabatic compression and the self-ignition of *n*-heptane, *n*-decane and iso-octane vapors under conditions corresponding to NTC behavior. In the

present study, ignition of *n*-heptane/air, *n*-decane/air and iso-octane/air mixtures was investigated under controlled supersaturated fuel vapor conditions.

2 Experimental procedure

Experimental investigation of self-ignition of lean ($\phi = 0.5$), stoichiometric, and rich ($\phi = 1.5$) *n*-decane/air ($N_2 - 79\%$, $O_2 - 21\%$); lean, stoichiometric *n*-heptane/air and stoichiometric iso-octane/air mixtures was carried out by the rapid compression machine (RCM) (Fig. 1.) under conditions: 580–950 K and 0.8–1.5 MPa. The pressure inside the combustion chamber was measured by a precision high-temperature piezoelectric pressure sensor Kistler 6031U18, with an accuracy of 25 kPa. The temperature of compressed gas was calculated in the adiabatic core approximation, taking into account heat loss, based on the measurement of the initial temperature and the pressure rise at the end of the compression stroke. The chemiluminescence of excited molecules and radicals from the volume, which arises during chemical reactions, was registered by 3 photomultiplier tubes (PMT). The first PMT recorded light in the range of 300–600 nm. The second PMT registered emission at the wave length 394 ± 5 nm, which corresponds to one (395.2 nm) from the most intense bands of formaldehyde HCOH spectrum (cool flame). The third PMT – at 431.5 ± 1.5 nm, corresponds to chemiluminescence of the excited CH radical from state 2Δ to 2Π (hot flame). Quartz window installed in the end wall allows flame imaging during ignition and combustion processes. A high-speed camera FASTCAM SA-Z with a speed of 67,500 frames per second and a resolution of 512×512 pixels and image intensified camera DI-CAM Pro in double frame mode (exposure time is 10 μ s) were implemented to capture low-luminous cool flame and hot flame propagations.

The fuel/air mixture was prepared directly in the RCM compression cylinder to minimize the influence of adsorption and condensation of hydrocarbon vapor and to provide homogeneity of the mixture. The required amount of liquid fuel was placed using a measuring pipette (scale division 0.1 μ l) in the form of a drop on the inner surface of volume when the piston was at the top dead center (TDC). After that, the chamber was hermetically closed by a flange (in about 10 s), and the piston was moved back to its initial position. An additional quantity of synthetic air was supplied to the test volume to achieve the required composition. The compression cylinder, combustion chamber, and quartz window were then heated to 333 K and fuel/air mixture was kept at this temperature for at least one hour.

Ignition delay time τ_0 was determined from the pressure records as the time interval between the pressure maximum during compression, which is realized when the piston reaches the TDC, and the moment of 5 % pressure rise caused by spontaneous ignition. In the case of a two-stage regime, the delays in the appearance of a cool flame τ_1 and the time between the cool and hot stages τ_2 were measured in the same way.

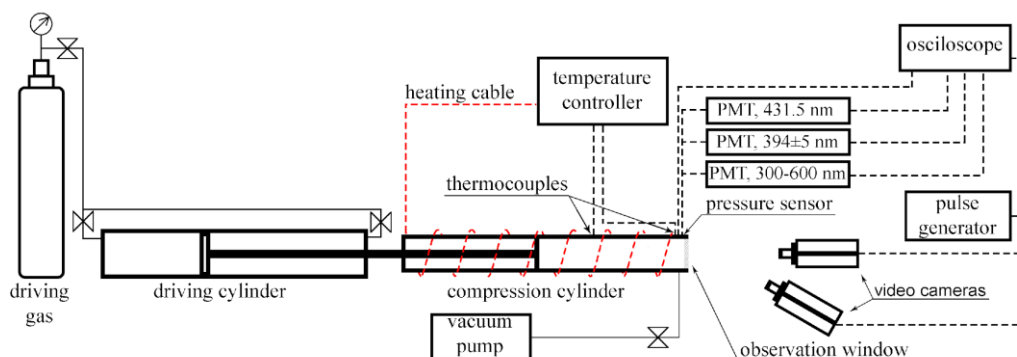


Figure 1: Schematic view of the present rapid compression machine.

3 Results and discussion

Analysis of pressure and chemiluminescence records allowed us to determine the conditions for occurrence of one- and two-stage ignition and to build the corresponding parametric diagram for *n*-decane/air (Fig. 2) self-ignition. It is clearly seen that a fuel-rich mixture is capable of self-ignition at lower temperatures than stoichiometric or lean. The ignition of *n*-decane vapor in air occurs at minimum temperature: $\phi = 0.5 - 655$ K, $\phi = 1 - 630$ K, and $\phi = 1.5 - 600$ K. It was found that for the lean mixture, the two-stage regime is observed at the temperature range of 655–810 K, while for stoichiometric and rich mixtures it appears only at temperatures above 685 K and 695 K, respectively. At lower temperatures, only one-stage ignition is observed for mixtures $\phi = 1$ and $\phi = 1.5$. The minimal self-ignition temperature was determined: for the lean mixture – 630 K, stoichiometric – 600 K, and rich – 580 K.

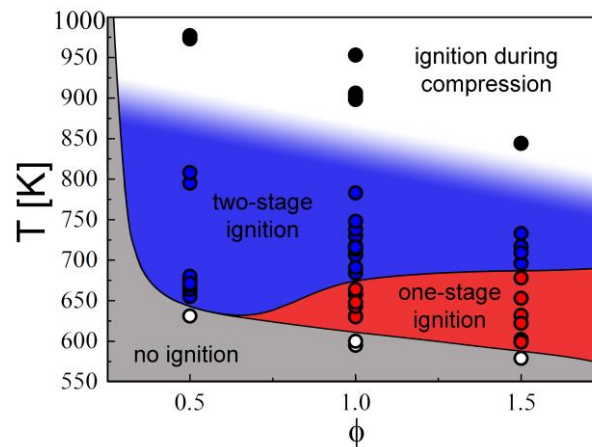


Figure 2: Parametric diagram of self-ignition modes of *n*-decane-air mixture (symbols - experiment).

Additionally, it was found that in most experiments the measured pressure exceeded the one calculated in the approximation of an adiabatic process. This discrepancy can be explained by the condensation of fuel vapors near the cold inner surfaces. Despite the temperature of the mixture reaching 800 K during compression, the walls of the cylinder and combustion chamber as well as the piston face remain at an initial temperature 333 K as the stroke takes no more than 60 ms. Thus, as the mixture is compressed, the ratio α (supersaturation) of the *n*-decane vapor partial pressure to its saturated vapor pressure (at the temperature 333 K) increases. It can reach a value of 3–16 to the piston stop moment, depending on the mixture composition. Therefore, at a certain moment of compression stroke near the walls non-equilibrium condensation of *n*-decane vapor is initiated with the formation of nano- and microdroplets. It leads to decrease of fuel/air equivalence ratio of the mixture and, accordingly, to an increase of its specific heat capacity. The last can explain the excess of measured pressure on the calculated adiabatic one. It also means that local temperature of gas mixture can be rather higher than calculated in the adiabatic core approximation.

Using the condition that the measured pressure should not exceed the adiabatic one, it is possible to introduce the effective composition mixture (ϕ_{eff}), at which the equality of pressures would be realized and the gas temperature would be recalculated (T_{eff}). Figure 3 presents the results of these calculations for experiments with equal postcompression density 5 ± 0.5 kg/m³ of lean ($\phi = 0.5$, blue dots), stoichiometric ($\phi = 1$, green), and rich ($\phi = 1.5$, red) mixture at pressure 0.8–1.2 MPa. The arrows on plot (a) between solid and empty symbols demonstrate the difference between initial and recalculated values of fuel/air equivalence ratio and temperature. It is seen that fuel condensation leads to a significant decrease in the mean *n*-decane vapor concentration and increase in mean mixture temperature. As expected, this effect is more pronounced for experiments with rich mixtures (ϕ changes

from 1.5 to 0.2 and temperature increases by 100 K). For lean mixtures recalculated temperatures are higher by about 15–25 K. As it was mentioned above, generally fuel-rich mixtures are capable to self-ignite easily (at lower temperatures and with shorter delays) than stoichiometric or lean. The unequal displacement of measured ignition delay time τ_0 for different ϕ along temperature scale on Arrhenius-type plot (Fig. 3, *b*) leads to convergence of all points to one line and smooth out NTC-behavior of temperature dependence of *n*-decane ignition delay times.

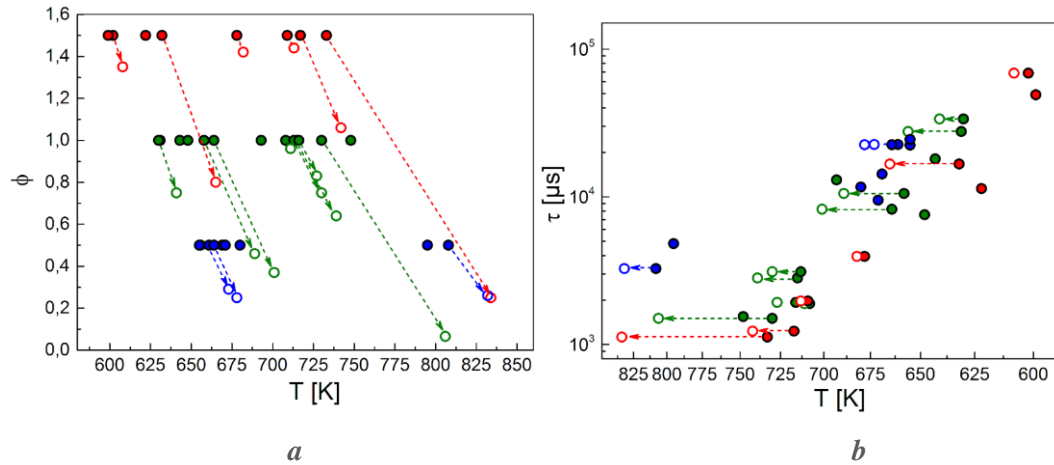


Figure 3: Effect of *n*-decane vapor condensation on the changing fuel/air equivalence ratio and temperature of mixture (*a*) and the position of the measured ignition delay times temperature dependence plot (*b*).

The use of *n*-heptane, which saturated vapor pressure at the temperature of 293 K is 4.72 kPa made it possible to obtain the same mixture temperature when the piston reaches TDC at $\alpha < 1$ and $\alpha > 1$ by varying the initial temperature and the compression ratio. Thus, the results were obtained on the spatial localization of an ignition kernel at different α . In the normal conditions mode ($\alpha < 1$, fuel condensation is excluded), the focus is predominantly located near the piston surface and has a “petal” shape (Fig. 4, *a*), while the fuel condensation ($\alpha > 1$) leads to the formation of a volumetric ignition kernel with a developed surface, which is located randomly in the volume (Fig. 4, *b*). The similar photographs of the ignition kernel position and the subsequent flame front propagation over the volume of the combustion chamber in the modes $\alpha < 1$ and $\alpha > 1$ were obtained at temperatures of 730 and 700 K.

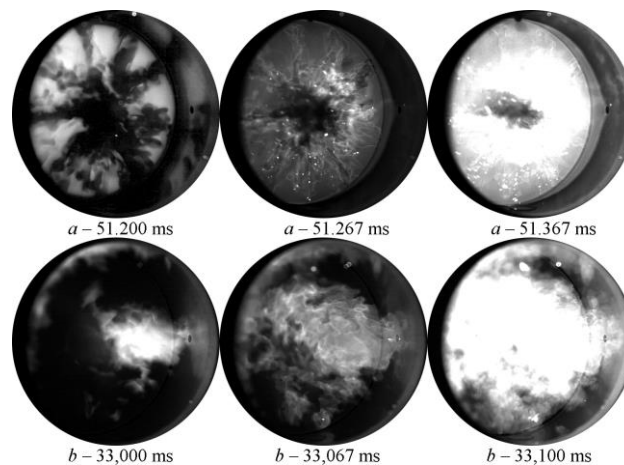


Figure 4: Imaging sequence (view at an angle of 30° to chamber axis) of ignition kernel of a stoichiometric *n*-heptane/air mixture at temperature 800 K and supersaturation $\alpha = 0.88$ (*a*) and $\alpha = 4$ (*b*) (time after end of compression)

In addition, we observed the discrepancy between the localization of the ignition kernel in supersaturated *n*-decane/air and *n*-heptane/air mixtures. In the experiments with *n*-decane vapor, ignition kernel has arisen near the surface of quartz window (at temperature less than 700 K) or the piston (more than 720 K), which corresponds to the normal conditions mode for *n*-heptane with air. It was not possible to carry out experiments with *n*-decane vapor at $\alpha < 1$, as mentioned above, due to the low pressure of its saturated vapor. The observed dependence of ignition kernel localization in various mixtures from supersaturation α requires additional combined experimental and numerical investigation.

The experiments with iso-octane vapor, which is generally less reactive at lower temperatures compared to *n*-heptane and *n*-decane, demonstrated that stoichiometric mixture ignition was occurred at temperatures more than 860 K and pressure of 1.4 MPa and was always initiated by a burning foreign particle. This ignition regime has a pronounced hot-spot character, similar to which was found for gaseous fuels [15]. Therefore, the measured ignition time under these conditions does not depend on temperature and cannot be interpreted as the induction period of a homogeneous mixture.

4 Conclusion

Ignition of *n*-heptane/air, *n*-decane/air and iso-octane/air mixtures was investigated in RCM at pressures varied from 0.8 to 1.5 MPa within the temperature range of 580–950 K. The presence of a non-equilibrium process of vapor fuel condensation in the thermal boundary layer was established. The minimum temperatures of *n*-decane/air mixture ignition and transition from a one- to two-stage ignition were determined: for a rich one – 600 K and 695 K, stoichiometric – 630 K and 685 K, respectively, for lean – only two-stage ignition are observed at range temperature 655–810 K. It leads to a possible heterogeneous distributions of mixture parameters: fuel vapors concentration and the gas temperature in a combustion chamber, an increase in the average temperature by 15–100 K compared to the calculated one, and a decrease in fuel/air equivalence ratio ϕ to 0.2. A regularity in the ignition kernel location depending on temperature, supersaturation and composition of the mixture was found: *n*-decane/air ($\alpha > 1$) – a flat shape near the piston surface (more 720 K) or quartz window (less 700 K), *n*-heptane/air – flat “petal” shape near the surface of the piston ($\alpha < 1$) or randomly located volumetric ignition kernel with a developed surface ($\alpha > 1$). The ignition of iso-octane mixture ($\alpha > 1$) at low temperature and pressures is initiated by the burning contaminated particles of an extraneous substance, that are additional local heat sources.

Acknowledgments

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References

- [1] Gauthier BM, Davidson DF, Hanson RK. (2004). Shock tube determination of ignition delay times in full-blend and surrogate fuel mixtures. *Combust. Flame.* 139: 300.
- [2] Violi A, Yan S, Eddings EG, Sarofim AF, Granata S, Faravelli T, Ranzi E. (2002). Experimental formulation and kinetic model for JP-8 surrogate mixtures. *Combust. Sc. Tech.* 174: 399.
- [3] Edwards T, Maurice Edwards LQ. (2001). Surrogate mixtures to represent complex aviation and rocket fuels. *J. of Propulsion and Power.* 17: 491.
- [4] Pfahl U, Fieweger K, Adomeit G. (1996). Self-ignition of diesel-relevant hydrocarbon-air mixtures under engine conditions. *Sympos. Combust.* 26: 781.

- [5] Horning DC. (2001). A study of the high-temperature auto-ignition and thermal decomposition of hydrocarbons. Stanford university report. No. TSD-135.
- [6] Olchanski E, Burcat A. (2006). Decane oxidation in a shock tube. *Intern. J. Chem. Kinetics*. 38: 703.
- [7] Zhukov VP, Sechenov VA, Starikovskii AY. (2008). Autoignition of n-decane at high pressure. *Combust. Flame*. 153: 130.
- [8] Shen HPS, Steinberg J, Vanderover J, Oehlschlaeger MA. (2009). A shock tube study of the ignition of n-heptane, n-decane, n-dodecane, and n-tetradecane at elevated pressures. *Energy & Fuels*. 23: 2482.
- [9] Dean AJ, Penyazkov OG, Sevruk KL. (2007). Autoignition of surrogate fuels at elevated temperatures and pressures. *Proc. Combust. Inst*. 31: 2481.
- [10] Nie XF, Li P, Zhang CH, Xie W, Li CS, Li XY. (2012). Shock tube study of n-decane ignition at low pressures. *Acta Mechanica Sinica*. 28: 79.
- [11] Strozzi C, Ossman H, Tsuzuki K, Sotton J, Bellenoue M. (2019). Autoignition of n-decane and multi-component surrogates of kerosene in an optical rapid compression machine. *27th Intern. Colloquium on the Dynamics of Explosions and Reactive Systems*.
- [12] Kumar K, Mittal G, Sung CJ. (2009). Autoignition of n-decane under elevated pressure and low-to-intermediate temperature conditions. *Combust. Flame*. 156: 1278.
- [13] Heufer KA, Olivier H. (2010). Determination of ignition delay times of different hydrocarbons in a new high pressure shock tube. *Shock Waves*. 20: 307.
- [14] Atef N, Kukkadapu G, Mohamed SY, Al Rashidi M, Banyon C, Mehl M, Heufer KA, Nasir EF, Alfazazi A, Das AK, Westbrook CK, Pitz WD, Tianfeng L, Farooq A, Chih-Jen S, Curran HJ, Sarathy SM. (2017). A comprehensive iso-octane combustion model with improved thermochemistry and chemical kinetics. *Combust. Flame*. 178:111.
- [15] Leschevich VV, Martynenko VV, Penyazkov OG, Sevrouk KL, Shabunya SI. (2016). Auto-ignitions of a methane/air mixture at high and intermediate temperatures. *Shock Waves*. 26: 657.