Ignition Delay Times of Kerosene(Jet-A)/Air Mixtures

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Abstract

Ignition delay times have been measured for gas-phase mixtures of aviation kerosene Jet-A with air at pressures of 10 and 20 atm. The experiments have been carried out in a heated shock tube at a heating temperature of 150 ^{0}C. The measurements have been performed for the lean, stoichiometric and rich mixtures ($\phi = 0.5, 1, 2$) behind the reflected shock wave in the temperature range of 1040–1380 K. The obtained experimental data have been summarized in a single expression:

$$\tau_{ign} = 1.32\text{e-}3[\mu\text{s}] \cdot (P/1[\text{atm}])^{-0.67} \cdot \phi^{-0.6} \cdot exp(30.4[\text{kcal/mol}]/(R\cdot T)),$$

where ϕ is the equivalence ratio.

1. Introduction

There is a massive technology development in the direction of alternative fuels last decade. In certain cases conventional fuels hold own in spite of the technology development. Up to the present moment the alternative to turbojet engines and aviation kerosene has not been found. The performance of internal combustion engines depend heavily on the combustion characteristics of large hydrocarbons, so there is demand for an extension of knowledge of the combustion of fuels to new areas. Research of ignition of Jet-A, which is the most common grade of aviation kerosene, is particularly important. Most of real fuels are complicated mixtures of large number of hydrocarbons. Progress in science and technology enabled the development of detailed chemical kinetic mechanisms for oxidation of individual hydrocarbons, alcohols, and ethers. The next step is development of kinetic mechanisms for oxidation of real fuels. This step requires not only experimental data on ignition of individual components of a fuel, but also the data on ignition of the fuel itself.

Jet-A is a mixture of a very large number of substances including large hydrocarbons, for example, hexadecane $C_{16}H_{34}$. Hexadecane (as all large hydrocarbons) has a very low saturated-vapour pressure at ambient temperature and boils at very high temperature: 287 ^{0}C. For large hydrocarbons the study of gas phase ignition requires heating of an experimental setup in order to prepare a homogeneous gas phase fuel mixture at desired pressure. Therefore, most of the works on kerosene (or Jet-A) combustion have been performed with droplets or liquid films (the overview of these works can be found in [1]).

In the current work we studied the ignition of gaseous Jet-A/air mixtures at pressures of 10 and 20 atm in a shock tube. (The results presented in the current work were obtained by us in summer 2003.) Later Dean et al. [2] and Vasu et al. [1] carried out similar studies using heated shock tubes. Dean et al. [2] performed the measurements of ignition delay times of Jet-A/air mixtures behind the reflected shock wave at pressure of 8.5 atm. The shock tube had a diameter of 76 mm and length of 5.5 m. The driver section was separated from the driven section not by a membrane, but by a special high-pressure valve for the controlled firing. The experiments were performed at preheating temperatures of 75–100 ^{0}C. Four independent electric circuits were used for the uniform heating of the tube. The mixing tank was heated up to the boiling temperature of Jet-A (160 ^{0}C) during 3–5 hours before the tests. The ignition delay times were defined using three different criteria: C_2 luminosity at 516.5 nm, wideband emission at 380–480 nm or pressure, each of which should reach its pre-defined level. Dean et al. [2] estimated their experimental error as 10–15%.

Vasu et al. [1] measured ignition delay times for gaseous mixtures of Jet-A and JP-8 with air behind the reflected shock wave in a heated shock tube. The measurements were performed at temperatures of 715–1229 K, pressures of 17–51 atm, at equivalence ratios of 0.5 and 1, and the volume fraction of air of 10% and 21%. The driven section of the shock tube has an inner diameter of 5 cm and a length of 5 m. The tube differs distinctly from the tube used by

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Dean et al. [2]. It is relatively long (the length equals to 100 calibers). It has the smaller diameter, but the experiments were carried out by Vasu et al. [1] at the higher pressures (≥19 atm). The tube was wrapped with copper sheets and heated to 100 ^{0}C using 13 separate heaters. The shock tube was evacuated to pressures below 10^{-5} Torr before experiments. The mixture was prepared at the temperature of 125 ^{0}C during 3 hours. The ignition delay time was defined as a time of the steep rise of pressure and OH^* emission. The observation point was located at 10 mm from the endwall. Vasu et al. [1] did not take account of any gas dynamic effects by a special way, but included them into experimental uncertainty which amounts 15%.

2. Experimental methods

The measurements of ignition delay times for Jet-A/air mixtures have been carried out in a heated shock tube behind the reflected shock wave. Shock tube has some advantages for the investigations of ignition: 1) the influence of high pressures and temperatures on tube walls and windows lasts for a short time interval; 2) required thermodynamic parameters of test gas behind the incident and reflected shock waves can be obtained by a variation of initial conditions: pressure, temperature, composition of mixture, and driver gas pressure; 3) the gas behind the reflected shock wave is stagnate and uniform in space.

The preheated shock tube (Fig. 1) is made of stainless steel and has an inner diameter of 45 mm. The 0.7 m long driver section is separated from the 3.2 m long test section by a double-diaphragm chamber. The shock tube is placed inside a heater, which allows the heating of the tube up to the temperature of 900 K. Eight thermocouples are placed along the tube at different points for the temperature control. The heater is divided into three independent sections. A preset temperature is maintained along the tube with the accuracy of ±5 K with the help of a special automatic system.

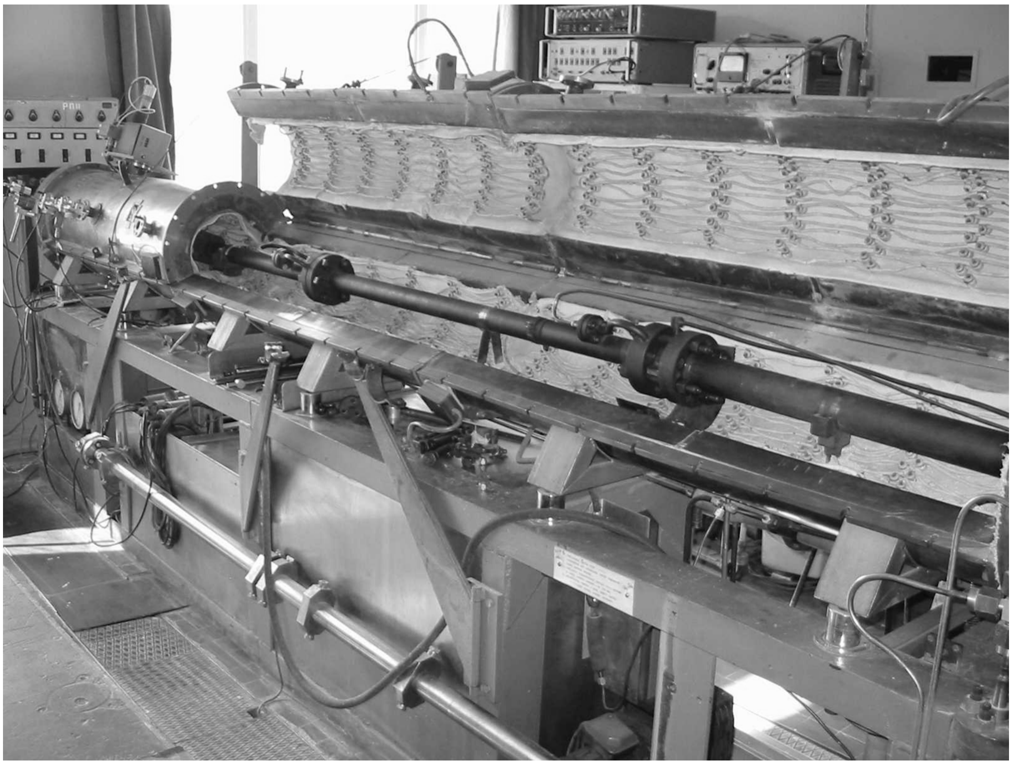

Figure 1: Photograph of shock tube placed in open heater (closed during experiments).

The shock tube is equipped with sapphire windows. The diagnostics consists of laser-schlieren systems, infrared (IR) absorption and ultraviolet (UV) emission spectroscopies (Fig. 2). The measurements of ignition delay times have been performed at 7 mm from the endwall. The UV diagnostic system consists of a grating monochromator equipped with a photomultiplier tube. The setup enables the recording of the time-resolved emission profile of electron-excited OH ($A^2\Sigma$ – $X^2\Pi$) at wavelength of 309 nm. The IR absorption diagnostics consists of an infrared He-Ne laser (λ=3.3922 µm, which corresponds to the absorption in the asymmetric ν_3 mode of CH_3 group) and an IR detector based on PbSe photoresistor. The passage of the shock waves through the observation axis has been identified by the steep rise of the absorption. The time point of ignition has been defined as the emission peak at 309 nm, which has been always synchronous with the considerable decrease of the absorption at λ=3.3922 µm, see Fig. 3. While the chemiluminescence of OH^* may be observed at early stages of ignition, the peak of the chemiluminescence corresponds to the moment of the maximum rate of free radical formation (more precisely of OH^* radical formation). In the experiments the peak of the chemiluminescence was always synchronous with the drop of the absorption. Moreover, the emission peak is repeatable in the experiments while the moment of the emission onset has been always different.

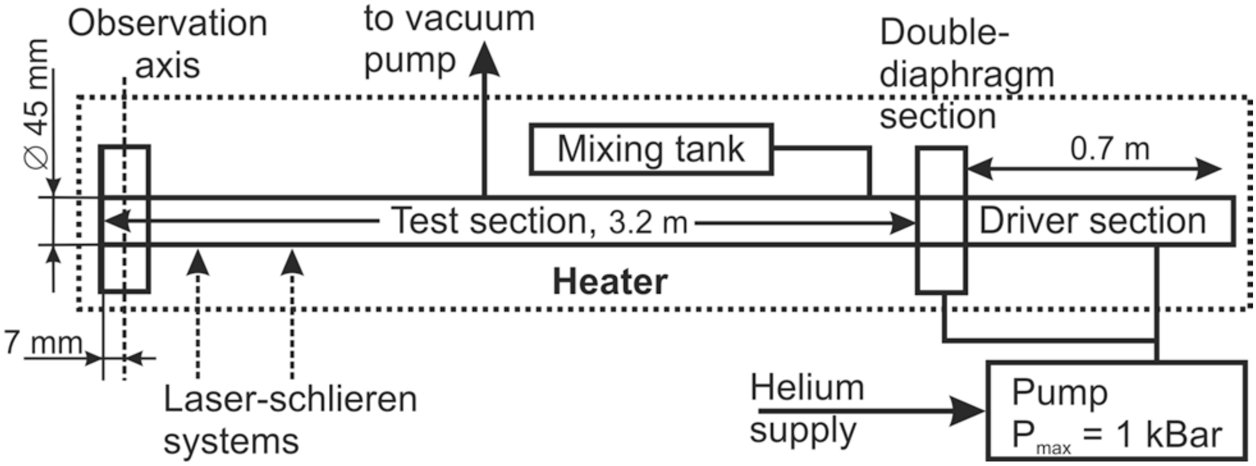

Figure 2: Scheme of experimental setup.

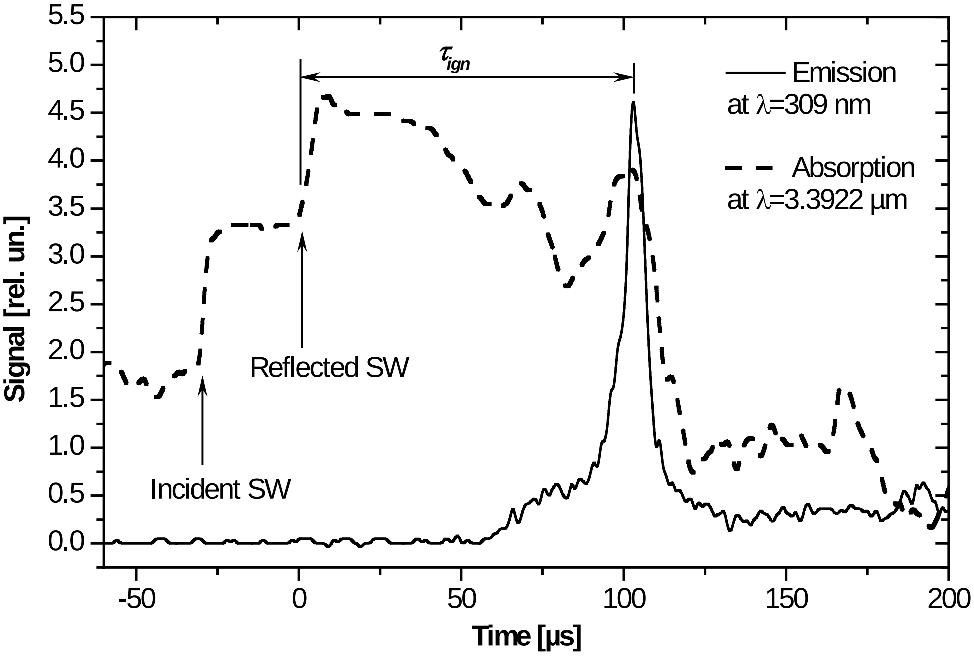

Figure 3: Emission and absorption signals; definition of ignition delay time.

The amount of Jet-A in a mixture was determined by the charge volume; the amount of air was defined by pressure. To estimate the mixture composition the charge volume of Jet-A was recalculated to the charge mass. The measured density of the fuel was equal to 0.80±0.03 g/ml at 26 ^{0}C what conforms to specification ASTM D 1655 for Jet-A. The chromatogram of the used kerosene sample is presented in Fig. 4. The four large peaks on the chromatogram correspond to alkanes with carbon number of C_{11}–C_{14}. In fact, the used sample of Jet-A was the same as in the work of Dean et al. [2]. In the current work the fuel composition was approximated by a chemical formula of $C_{11}H_{22}$. As for air it was approximated in the calculations of the mixture composition and the parameters behind shock wave by the following composition: N_2:O_2:Ar = 78.12:20.95:0.93. The amount of fuel was taken in such a way that the charge volume was always equals to the whole-number of scale points. Thus the stoichiometry of some mixtures is not exact and may differ from the exact value by a small percentage. The total error in the mixture composition amounts 5%.

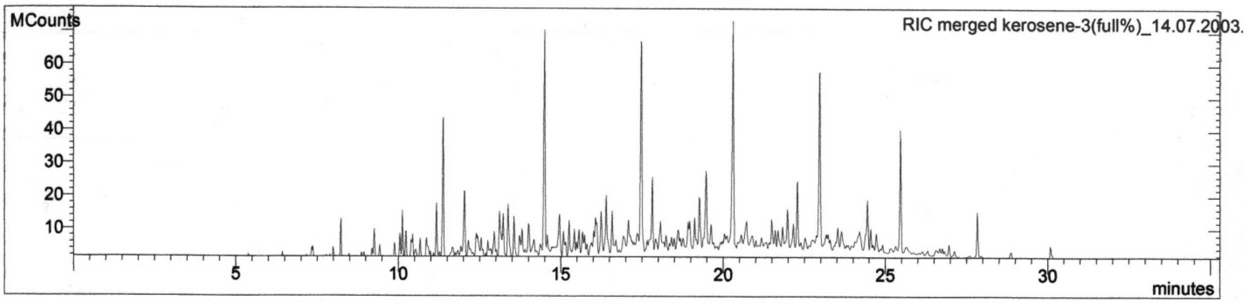

Figure 4: Chromatogram of the Jet-A sample.

Mixture of Jet-A with air was prepared in a stainless steel mixing tank which can be placed inside the heater alongside with the shock tube. The volume of the mixing tank is smaller by factor of 3 than the volume the shock tube, so the pressure of the mixture in the mixing tank is at least four times larger than the initial pressure P_1. The shock tube and the mixing tank were cleaned to remove possible remains of kerosene, soot, or other deposits every time between the experiments. Before the experiments the shock tube and the mixing tank were evacuated up to the pressure of $3–4\cdot10^{-2}$ Torr. The vacuum sealing of the experimental setup was provided by annealed copper gaskets. After the outgassing the mixing tank was filled with dried air up to the atmospheric pressure then a desired amount of liquid Jet-A was injected inside the mixing tank. Finally, the mixing tank was filled with dried air again up to a desired pressure.

After filling with kerosene and air the mixing tank was placed into a heater and connected with the shock tube. (The sections of the heater can be open for the manipulation with the shock tube as in Fig. 1.) The tube and the mixing tank were heated to 150 ^{0}C. This temperature was maintained during a whole experiment. The stirring is provided by a rolling of a brass ball with a diameter of 43 mm inside the mixing tank, which can be tilted about horizontal axis of the tank.

After the short series of preliminary experiments a special methodologic study was carried out before the main series of the experiments. The objectives of the study were to investigate the effects of the heating and of the stirring on the experimental results. For this purpose, the heating temperature and the stirring intensity were varied. The heating temperature was varied in the range of ±25 ^{0}C around the reference temperature. The influence of the heating temperature on the measurements was not observed in the studied range (was not visible on the background of the random scattering of data), so the heating temperature was preserved as 150 ^{0}C. To study the effect of stirring the measurements of ignition delay times were performed at three levels of stirring intensity: normal (highest), reduced twice, and reduced four times. The effect was observed only at the minimum level of stirring. At the medium intensity of stirring the results of the measurements were same as at the maximum intensity. However, during the experiments the intensity of stirring was maintained at the highest (normal) level. During the stirring the fuel mixture was exposed to the high temperature in the mixing tank about for 45 minutes but not longer than for an hour to avoid fuel cracking.

The goal of the experiments was to measure the ignition delay times of Jet-A/air mixtures behind the reflected shock wave in the range of pressures of 10–20 atm. The ignition delay times were defined by the emission peak at 309 nm as written above, see Fig. 3. The parameters of gas behind the shock waves were calculated using the one-dimensional shock wave theory on the assumption of a full relaxation and a “frozen” chemistry. The measured ignition times are greater than 15 μs, that is long enough to reach the full vibrational relaxation in a fuel/air mixture, in which the kerosene fraction is greater than 0.6%. The rate of chemical reactions depends on temperature exponentially, as a consequence the kinetics behind the incident shock wave is much slower than that behind the reflected shock wave. The ignition delay times behind the incident shock wave would be greater than 1 ms at the hottest conditions of our experiments. This time is much greater than the time between the incident and reflected shock waves ($\Delta t \sim 30$ μs). Moreover, the assumption about the “frozen” chemistry was confirmed by experimental observations: the chemiluminescence of OH^* radical was not observed behind the incident shock wave. The conditions behind the reflected shock wave were determined from the initial temperature and pressure and the velocity of the incident shock wave at the end wall, which value was obtained by the extrapolation with regard for the attenuation of the incident shock wave in the shock tube. The thermodynamic properties of Jet-A and of the components of air were taken from [3] and [4], respectively.

The results of measurements behind the reflected shock wave are affected by gas dynamic effects. Two of them play major roles at the condition of the performed experiments. The ignition of fuel mixture behind the reflected shock wave occurs at the end wall at first and then the combustion products expand and push the fresh mixture from the end wall. As a result, the ignition delay times are shorter when they are measured through the side wall rather than at the end wall. For this reason all the measured ignition delay times were corrected by +7 μs. This effect is discussed in detail by us in [5]. When the ignition delay time in fuel/air mixtures (i.e. in mixtures with large energy release) amounts only several microseconds, another effect takes action in shock tubes. At the very short ignition delay times the pressure rise is so strong during the ignition of fuel mixture that it produces a strong pressure wave running ahead the ignition wave and behind the reflected shock wave. Finally, this pressure wave catches the reflected shock wave and forms the detonation wave. Therefore, the very short ignition delay times cannot be taken into account as far as the ignition occurs at the conditions far from predicted by the one-dimensional shock wave theory. Unfortunately, the time available for the measurements is also limited from above in the shock tube as well. Due to the interaction of the reflected shock wave with the boundary layer the temperature and the pressure are not constant and rise behind the reflected shock wave. At the conditions of the current experiment the temperature rise does not exceed 15 K at times of ~400 µs (i.e. $dT/dt \leq 0.04$ K/µs) and it is included in the experimental uncertainty. Without *tailoring* the time available for measurements amounts 500–600 µs in the used shock tube.

The current experimental setup was also used in the experiments on the ignition of methane [6] and of n-decane [7] in air using the conventional and heated regimes respectively. The results of measurements [6,7] agree well with the results of other scientific groups. The relatively small size of the used shock tube allowed to place the tube together with the mixing tank into the heater. The experiments with low volatile liquids require the cleaning of the experimental setup after each experiment. The compact size of the setup eased the maintaining the uniform temperature of the experimental setup during the tests and the cleaning procedure after them.

3. Results and discussion

The results of the measurements at pressure of 10 and 20 atm are presented in Fig. 5 and 6, respectively. The main features of the obtained results are: the quasi-Arrhenius dependence on temperature; the positive dependence on pressure (ignition delay times are smaller at higher pressure); and the positive dependence on the stoichiometry. The experimental data can be presented in the form of the correlation expression which allows to summarize the results of all experiments in a form convenient for further application:

$$\tau_{ign} = 1.32\text{e-}3[\mu\text{s}] \cdot (P[\text{atm}])^{-0.67} \cdot \phi^{-0.6} \cdot exp(30400[\text{cal/mol}]/(R \cdot T[\text{K}])). \qquad \textbf{(1)}$$

What is also important is that Eq. (1) enables the comparison of the results obtained at other conditions, mostly at different pressures.

Using Eq. (1), it should be realized the limitations of the derived correlation expression. The experimental results have been obtained in a transient region between the regions of the high temperature kinetics and the negative temperature coefficient (NTC) where the dependences of ignition delay times on temperature, pressure, and the stoichiometry are completely different. (The existence of NTC region for Jet-A/air mixtures was shown by Vasu et al. [1].) Thus Eq. (1) should not be used outside the studied range: below 1000 K and above 1400 K. This rule is supported by the comparison with the results of other groups. The data obtained by Vasu et al. [1] were measure at lower temperatures and characterized by the dependence of $\tau_{ign} \sim 1/P$, which is representative of the low temperature kinetics. At low temperature the chain branching is degenerate and radicals are formed in the decomposition of the derivatives of the parent fuel, thus the rate of ignition is proportional to the fuel concentration or pressure when the equivalence ratio is fixed. At higher temperatures ($T > 1400$ K) Eq. (1) might be also not valid. Dean et al. [2] reported about the different dependence of the ignition delay times for Jet-A/air mixtures on initial conditions at this region.

The obtained experimental data agree well with the data of Vasu et al. [1], however the agreement with the data of Dean et al. [2] is not full. First of all, the data obtained by Dean et al. call our attention by an interesting correlation namely by the dependence on the oxygen concentration:

$$\tau_{ign} \sim (\text{Jet-A }[\text{mole/cm}^3])^{-0.76} \cdot (O_2\ [\text{mole/cm}^3])^{0.33} \cdot exp(E_a/T[\text{K}])), \qquad \textbf{(2)}$$

where E_a is an activation energy. Thus the reaction rate should decrease with the increase of oxygen concentration according to Eq. (2). However, the experiments were performed at different stoichiometry but at the fixed pressure. Therefore the dependence on the oxygen concentration cannot be derived properly from the data but only the dependence on the equivalence ratio. Dean et al. [2] reported also about the substantial decrease of the activation energy at $T > 1400$ K. However, this phenomenon was observed only at short ignition delay times ($\tau_{ign} \leq 10$ µs) and at a strong ignition regime what points at the possible impact of the gas dynamic effects which were discussed in the previous section. Dean et al. also performed the experiments at times more than 1 ms in the shock tube with the length of 5.5 m what likely requires tailoring. However, they did not report about the usage of this procedure in their work [2]. Moreover their propane data indicate on the possible existence of the under-tailored regime in their experiments at residence times longer or equal to 1 ms. Alkanes are the largest fraction of Jet-A, but also they are the most chemically reactive part of the fuel [8]. Therefore the experimental data for Jet-A should not contradict to the well-known regularities of the alkane kinetics.

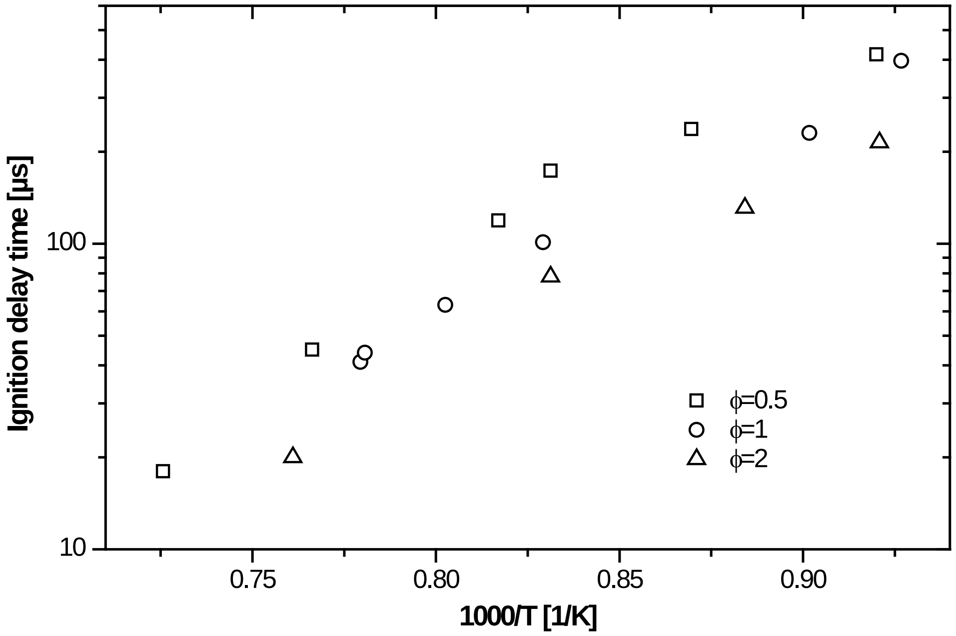

Figure 5: Ignition delay times for Jet-A/air mixtures at 10 atm.

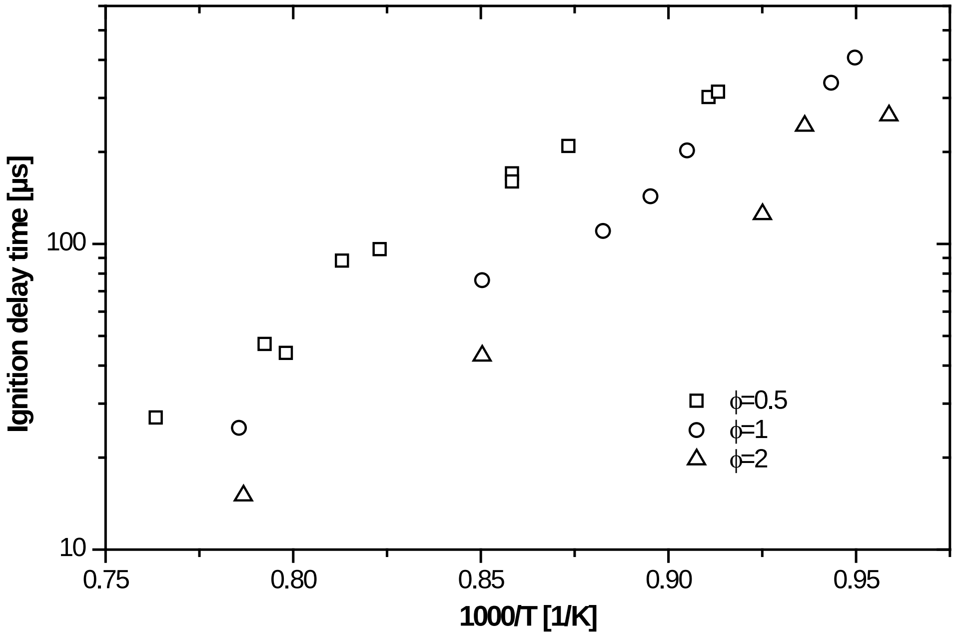

Figure 6: Ignition delay times for Jet-A/air mixtures at 20 atm.

The experiments on the ignition of Jet-A/air mixtures have been carried out to obtain the data for the validation of kinetic mechanisms. The performed shock tube experiments can be simulated using simple tools, nevertheless it is necessary to understand the peculiarities of these experiments which could result in a systematic difference with the experimental data. First, it is the model of the shock tube as a chemical reactor. Most of the researchers use the model of a constant volume reactor with adiabatic walls. Although the shock tube is neither a constant volume reactor nor a constant pressure reactor, nevertheless we recommend to use the assumption of a constant pressure. In the simulations of ignition it is important to estimate correctly the temperature rise during the ignition. The ignition delay times of hydrocarbons are characterized by the strong temperature dependence (in our case $E_a \approx 30$ kcal/mol), so even the small temperature rise during the ignition reduces the ignition delay. The assumptions of a constant volume disregard the expansion work of a gas, thus it leads to the larger temperature rise during the induction period. Vasu et al. [2] use the model of a constant volume reactor, however if it would be true, we would see more than a threefold pressure increase after the ignition what it is not observed on their graphs.

Peculiarities of the shock tube technique, namely the running of experiments at a fixed pressure in the driver section, lead to a weak trend for pressure on the Arrhenius plot: the points at low temperatures correspond to a slightly lower pressure than the points at high temperatures. This can easily be taken into account in the calculations of ignition delay times using not the average pressure but the pressures of individual experimental points.

While the ignition delay times were measured with the small error, comparing the results of the experiment and of the modelling, it is necessary to take into account a parametric error originating from the evaluation error for the conditions behind the reflected shock wave. The measurement uncertainty of the velocity of the incident shock wave leads to 1.5% error in the temperature and 3% error in the pressure. Not so strong as on temperature the ignition delay times for Jet-A depend also on the mixture composition (and its uncertainty). While the temperature uncertainty may be plotted horizontally on the Arrhenius plot, the other errors may not. It is more convenient to collect all uncertainties into one total error and lay off it vertically. The total relative error can be found by the formula:

$$\frac{\Delta\tau_{total}}{\tau}\% = \sqrt{\left(\frac{\Delta\tau}{\tau}\right)^2 + \left(\alpha\frac{\Delta P}{P}\right)^2 + \left(\beta\frac{\Delta\varphi}{\varphi}\right)^2 + \left(\frac{E_a}{RT}\cdot\frac{\Delta T}{T}\right)^2} \approx \sqrt{\left(\frac{4\ \mu s}{\tau\ [\mu s]}\cdot 100\%\right)^2 + 4 + 9 + \left(\frac{15300\ K}{T\ [K]}\cdot 1.5\%\right)^2}, \quad \textbf{(3)}$$

where α, β, and E_a are the coefficients of expression $\tau = A \cdot P^{\alpha} \cdot \phi^{\beta} \cdot exp(E_a/(R \cdot T))$. As one can see the total error amounts around 20% and the main contribution is given by the parametric error of temperature. In modelling it is necessary to understand that the mixture composition is derived from the chemical formula $C_{11}H_{22}$ for Jet-A which may be different in reality. However, this uncertainty is already included into the error.

4. Conclusions

The ignition delay times were measured for the lean, stoichiometric and rich mixtures ($\phi = 0.5, 1, 2$) of Jet-A with air at pressures of 10 and 20 atm in the overall temperature range of 1040–1380 K. The measurements were performed in the heated shock tube behind the reflected shock wave at the heating temperature of 150 ^{0}C. The experimental data lie in the transient region between the regions of the high temperature kinetics and the negative temperature coefficient; they complement the “low temperature” data of Vasu et al. [1] and the “high temperature” data of Dean et al. [2].

The ignition delay times of Jet-A/air mixtures have the quasi-Arrhenius dependence on temperature and decrease with pressure and the equivalence ratio. The experimental data may be approximated by the correlation expression: $\tau_{ign} = 1.32e\text{-}3[\mu s] \cdot (P[atm])^{-0.67} \cdot \phi^{-0.6} \cdot exp(30400[cal/mol]/(R \cdot T[K]))$. The main contribution in the overall experimental error is given by the parametric uncertainty of the temperature behind the reflected shock wave. The total experimental error amounts around 20%.

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