



Autoignition of kerosene (Jet-A)/air mixtures behind reflected shock waves



Victor P. Zhukov^{*}, Vladislav A. Sechenov, Andrey Yu. Starikovskiy¹

Moscow Institute of Physics and Technology, Dolgoprudny 141700, Russia

HIGHLIGHTS

- We have measured ignition delay times for aviation kerosene (Jet-A) at pressures of 10 and 20 atm.
- The obtained data are in a good agreement with the results of other groups.
- We report a correlation equation for the ignition delay times at temperatures from 1040 to 1380 K.
- The measured ignition delay times are given in Annex tables.

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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 °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. Ignition delay times have been measured using OH^{*} emission at 309 nm and –CH₃ absorption at 3.39 μm. The obtained results are in agreement with the results of other groups. The experimental data have been summarized in a single expression:

$$\tau_{\text{ign}} = 1.31 \times 10^{-3} [\mu\text{s}] \cdot (P/1 [\text{atm}])^{-0.67} \cdot \phi^{-0.6} \cdot \exp(30.4 [\text{kcal/mol}]/RT),$$

where ϕ is the equivalence ratio. The measured ignition delay times for Jet-A/air mixtures are given in Annex tables.

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1. Introduction

There has been a massive technology development in the direction of alternative fuels in the last decade. In certain cases conventional fuels have persisted in spite of the technology development. To date no alternative to turbojet engines in air transport has been found; however, airplanes, already today, can be fueled with synthetic jet fuels or with jet biofuels. Nevertheless, on a global scale aviation kerosene will remain playing a major role for a long time. The performance of internal combustion engines depends heavily on the combustion characteristics of fuel. 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 a large number of hydrocarbons. Progress in science and technology has 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. Thus the goal of the present work has been to measure the ignition delay times of Jet-A/air mixtures in the range of pressures of 10–20 atm.

Jet-A is a mixture of a very large number of substances including large hydrocarbons, for example, hexadecane C₁₆H₃₄. Hexadecane (as all large hydrocarbons) has a very low saturated vapor pressure at ambient temperature and boils at very high temperature: 287 °C. For large hydrocarbons the study of gas phase ignition requires the heating of an experimental setup in order to prepare a homogeneous gas phase fuel mixture at the desired pressure. Most of the works on the combustion of kerosenes have been performed in two-phase mixtures with droplets or liquid films or in highly diluted mixtures. The extensive review of these works

^{*} Corresponding author. Present address: Institute of Space Propulsion, German Aerospace Center (DLR), Lampoldshausen, 74239 Hardthausen, Germany. Tel.: +49 6298 28 633; fax: +49 6298 28 458.

E-mail address: vpzhukov@gmail.com (V.P. Zhukov).

¹ Present address: Princeton University, Princeton, NJ, USA.

on kerosenes was done by Dagaut and Cathonnet [1] (a less extensive overview can be found also in [2]).

In the present work we studied the ignition of gaseous Jet-A/air mixtures at pressures of 10 and 20 atm in a heated shock tube. Dean et al. [3] and Vasu et al. [2] carried out similar studies using a similar experimental setup. Dean et al. [3] 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 °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 °C) during 3–5 h 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, and pressure, each of which should reach its pre-defined level. Dean et al. [3] estimated their experimental error at 10–15%.

Vasu et al. [2] 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 shock tube differs distinctly from the shock tube used by Dean et al. [3]. It is relatively long (the length equals to 100 calibers) and has the smaller diameter; however, the experiments were carried out by Vasu et al. [2] at the higher pressures (≥ 19 atm), at which the diameter of the shock tube is enough. The tube was wrapped with copper sheets and heated to 100 °C using 13 separate heaters. The shock tube was evacuated to pressures below 10^{-5} Torr prior the experiments. The mixture was prepared at the temperature of 125 °C during 3 h. 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. [2] did not take account of any gas dynamic effects in a special way, but included them into experimental uncertainty which amounts 15%.

In a recent study Wang and Oehlschlaeger [4] reported autoignition studies of conventional and Fischer–Tropsch jet fuels in total amount five different fuel compositions (including Jet-A). The measurements of ignition delay times were made in a heated shock tube at pressures from 8 to 39 atm in a wide temperature range 650–1380 K at equivalence ratios from 0.25 to 1.5. The driven section of the shock tube has an inner diameter of 5.7 cm and a length of 4.11 m. During the experiments the shock tube was heated up to the temperature of 135–140 °C; the mixing vessel was heated to a temperature of 140–150 °C. Ignition delay times were determined by monitoring the emission of OH^* through a UV window in the end wall. The pressure behind the reflected shock wave was monitored too. The obtained experimental data cover the low-temperature kinetics, the region of a negative temperature coefficient (NTC), and the high-temperature kinetics. (In the NTC region activation energy takes negative values.) Wang and Oehlschlaeger provided the correlation relation of the ignition delay times of Jet-A/air mixtures at $T > 1000$ K: $\tau_{ign} \propto P^{-0.75} \cdot \phi^{-0.58}$. It was shown that the studied jet fuels, which have the different composition, have the same ignition delay times at high temperatures ($T > 1000$ K); however, in the NTC region and at low temperatures the effect of fuel composition is very distinctive. Unfortunately the authors presented the experimental data only in form of graphs what makes difficult the comparison with other data later, nevertheless they did the comparison with the data of Dean et al. [3] and found that their own data lie higher than the data of Dean et al.

Recently Kumar and Sung [5] studied the autoignition of jet fuels (Jet-A and JP-8) in a heated rapid compression machine (RCM). The experiments were performed at pressures of 7, 15, and 30 bar in the temperature range from 650 to 1100 K. The experimental results demonstrate a two-stage ignition. Kumar and Sung also observed the negative temperature coefficient (NTC) behavior at 7 bar while the effect becomes smaller at higher pressure. Already at 15 bar the slope of the Arrhenius curves is not negative in the NTC region but goes to zero. Ignition delay times were measured using pressure traces. The results obtained at 7 bar were compared with the results obtained in the shock tube by Dean et al. [3]. The data obtained in the heated RCM and in the heated shock tube agree with each other; however, the quantitative comparison of the data is, unfortunately, not possible. The data sets were acquired in the different temperatures ranges which do not overlap and have a gap of ~ 100 K between each other.

Heated shock tubes have been known since the sixties (of the past century). They were used in studies on the subject of matter under extreme conditions for the US and Soviet space programs. In combustion studies they were introduced by Pfahl et al. [6] who studied the self-ignition of *n*-decane and α -methyl-naphthalene in homogeneous mixtures with air at pressures up to 50 bar.

In the present study, we have used a shock tube which was already used by us in the normal and heated regimes. Using this tube we measured in previous studies [7–11] the ignition delay times of *n*-alkanes from methane to *n*-decane in mixtures with air in a range of temperature of 800–1700 K and pressure of 2–500 atm. The ignition delay times at high pressures were also measured for methane in a “conventional” shock tube by Petersen et al. [12] and for *n*-decane in a heated shock tube by Pfahl et al. [6]. The results of our measurements in the normal regime for methane [7] and in the heated regime for *n*-decane [11] agree very well with the data of Petersen et al. [12] and of Pfahl et al. [6], consequently. In the present work we have retained to the same proven and reliable experimental procedure as in our past studies [7–11].

2. Experimental methods

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

2.1. Experimental setup

The heated 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.

The shock tube is equipped with sapphire windows. The diagnostics consists of laser schlieren systems, infrared (IR) absorption and ultraviolet (UV) emission diagnostics (Fig. 2). An observation point located at the distance of 7 mm from the end wall. The UV diagnostic consists of a grating monochromator equipped with a

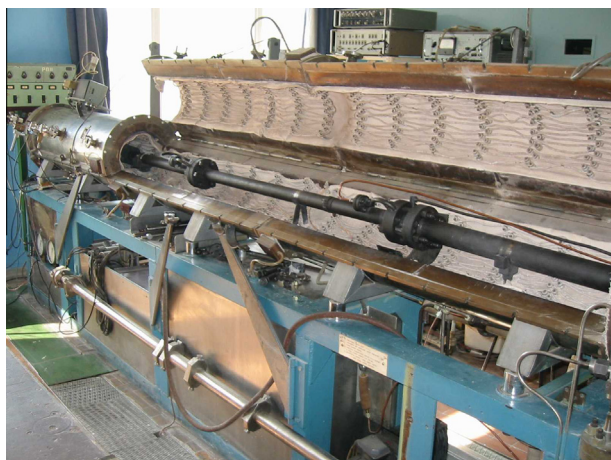


Fig. 1. Photograph of shock tube placed in open heater (closed during experiments).

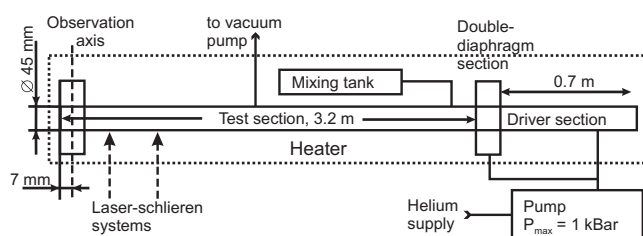


Fig. 2. Scheme of experimental setup.

photomultiplier tube. This setup enables the recording of the time-resolved emission profile of electronically excited 309 nm ($A^2\Sigma^+ - X^2\Pi$). The IR absorption diagnostic consists of an infrared He–Ne laser ($\lambda = 3.3922 \mu\text{m}$, which corresponds to the absorption in the asymmetric ν_3 mode of $-\text{CH}_3$ group) and an IR detector based on a PbSe photoresistor. The IR detector records the intensity of the laser beam passing through the shock tube. While it has a very nonlinear response, it can register the passage of shock waves. The time interval between the reflected shock wave and the emission peak at 309 nm was defined as ignition delay time (or induction time). While the weak chemiluminescence of OH^* may be observed at early stages of ignition, the maximum 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 accompanied by the drop of the absorption at $\lambda = 3.3922 \mu\text{m}$. However, the fall of the absorption has not been used for the definition of ignition delay times due to the irregular shape of the absorption signal, see Fig. 3.

2.2. Mixture preparation

The amount of Jet-A in a mixture was determined by the charge volume while the amount of air was defined by pressure readings. To estimate the mixture composition the charge volume of Jet-A was translated to the charge mass. The measured density of the fuel was equal to $0.80 \pm 0.03 \text{ g/ml}$ at 26°C which conforms to specification ASTM D 1655 for Jet-A. The chromatogram of the used kerosene sample is presented in Fig. 4. The six large peaks seen on the chromatogram correspond to normal alkanes with carbon number of $\text{C}_{10} - \text{C}_{15}$. In fact, the used sample of Jet-A was the same as in the work of Dean et al. [3]. For this reason, we have used the chemical formula $\text{C}_{11}\text{H}_{22}$ for Jet-A, which is the same as in work [3]. This formula was suggested earlier by Gueret et al. [13]. However,

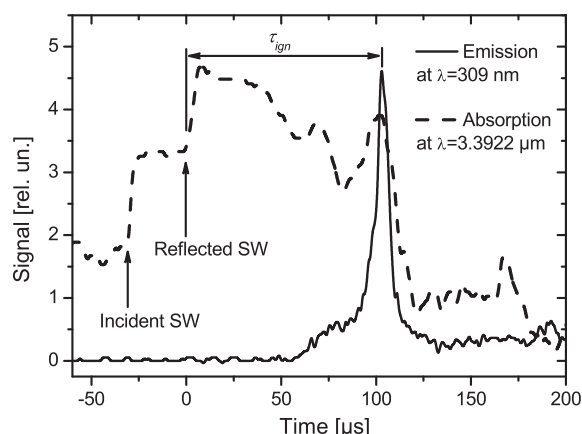


Fig. 3. Emission and absorption signals; definition of ignition delay time.

Vasu et al. [2] used the formula $\text{C}_{11}\text{H}_{21}$ following the recommendations of Edwards and Maurice [14]. As for air, it was approximated in the calculations of the mixture composition and the parameters behind shock wave by the following composition: $\text{N}_2 : \text{O}_2 : \text{Ar} = 78.12 : 20.95 : 0.93$. The amount of fuel was chosen always in such a way that the charge volume 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 of mixture composition amounts to 5%.

Mixture of Jet-A with air was prepared in a stainless steel mixing tank which was placed inside the heater alongside with the shock tube during the experiments. For the filling process the mixing tank was dismantled. The shock tube and the mixing tank were cleaned to remove possible remains of kerosene, soot, or other deposits after each experiment. Before the experiments, the shock tube and the mixing tank were evacuated up to the pressure of $3\text{--}4 \times 10^{-2} \text{ Torr}$. 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 topped up with dried air up to a desired pressure. The volume of the mixing tank is smaller by factor of three compared to the volume the shock tube, therefore the mixing tank should be filled up to the pressure which exceeds the initial pressure P_1 at least four times. (P_1 is a pressure of gas in front of the incident shock wave.)

After being filled 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 opened for the manipulation with the shock tube as in Fig. 1.) The tube and the mixing tank were heated to 150°C . This temperature was maintained during a whole experiment. Stirring of the mixture 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 methodological study was carried out before the main series of the experiments. The objectives of the study was to investigate the effects of the heating and 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 $\pm 25^\circ\text{C}$ around the reference temperature. The influence of the heating temperature on the measurements was not observed in the studied range (at least it is not visible on the background of the random scatter of data), thus the heating temperature was set at 150°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.

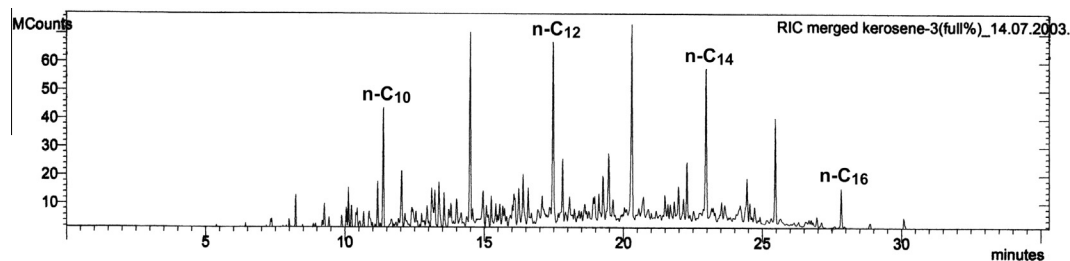


Fig. 4. Chromatogram of the Jet-A sample.

An effect was observed only at the minimum level of stirring. At the medium intensity of stirring the results of the measurements were same to those 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 for about 45 min, but not longer than an hour in order to avoid fuel cracking.

2.3. Interpretation of shock tube data

Fig. 3 displays typical experimental oscillograms, which correspond to the experiment with the stoichiometric mixture of Jet-A and air at a pressure of 20 atm and a temperature of 1133 K behind the reflected shock wave. On the oscillogram the instants of shock wave passages are seen by the absorption jump at $3.3922 \mu\text{m}$. The first absorption jump corresponds to the incident shock wave. (The increase of density behind the shock front leads the increase of the absorption.) After the time required for passing the distance from the observation point to the end wall and back, the second absorption jump corresponding to the reflected shock wave can be seen. From this moment onward the counting of ignition delay time begins and ends with the maximum of OH^* emission.

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 $15 \mu\text{s}$, that long enough to reach the full vibrational relaxation in a fuel/air mixture, in which the kerosene fraction is greater than 0.6% [15]. 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 ($\Delta t \sim 30 \mu\text{s}$). 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, pressure, and the velocity of the incident shock wave at the end wall, whose 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 [16,17], respectively. The properties of gas mixture were derived from the properties of the components, assuming that the gas mixture is an ideal mixture of ideal gases.

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 first at the end wall 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 $+7 \mu\text{s}$. This effect is discussed in detail by us in [9]. When the ignition delay time in fuel/air mixtures (i.e. in mixtures with large energy release) amounts to only several microseconds, another effect has an impact 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 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 [18]. At the conditions of the present experiment the temperature rise does not exceed 15 K at times of $\sim 400 \mu\text{s}$ (i.e. $dT/dt \leq 0.04 \text{ K}/\mu\text{s}$) and it is included in the experimental uncertainty. Without tailoring the time available for measurements amounts 500–600 μs in the present shock tube.

The relatively small size of the used shock tube allowed to place the tube together with the mixing tank into a single heater. The experiments with low volatile liquids require the cleaning of the experimental setup after each experiment. The compact size of the setup simplified maintaining the uniform temperature of the experimental setup during the tests and the following cleaning procedure.

3. Results and discussion

The results of the measurements at pressure of 10 and 20 atm are presented in Figs. 5 and 6, respectively. The main features of

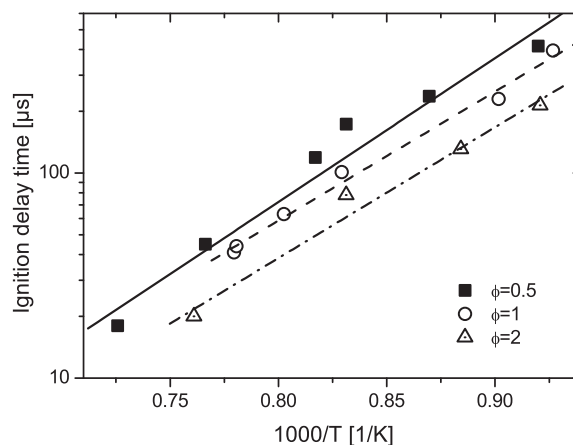


Fig. 5. Ignition delay times for Jet-A/air mixtures at 10 atm.

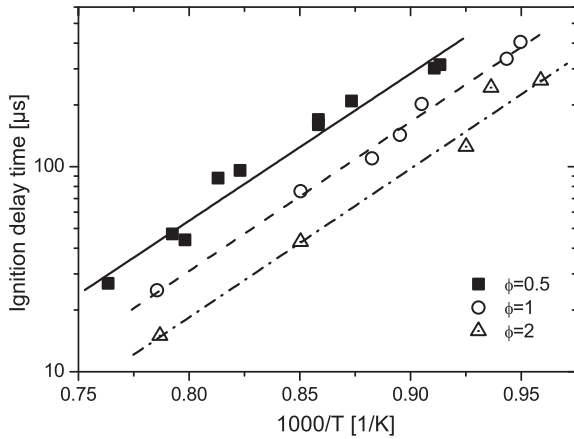


Fig. 6. Ignition delay times for Jet-A/air mixtures at 20 atm.

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:

$$\tau_{\text{ign}} = 1.31 \times 10^{-3} [\mu\text{s}] \cdot (P/1 [\text{atm}])^{-0.67} \cdot \phi^{-0.6} \cdot \exp(30.4 [\text{kcal/mol}]/RT). \quad (1)$$

The correlation has been determined by the minimization of the root-mean-square deviation; the coefficient of determination (R^2) amounts to 96.4%. (The quality of the experimental data and the correlation equation are discussed at the end of this section.) What is also important is that (1) enables the comparison of the results obtained at other conditions, mostly at different pressures. The obtained expression is in agreement, within the limit of error, with the findings of Wang and Oehlschlaeger: $\tau_{\text{ign}} \propto P^{-0.75} \cdot \phi^{-0.58}$, $E_a \approx 30 \text{ kcal/mol}$ for $T > 1000 \text{ K}$ [4].

Using Eq. (1), the limitations of the derived correlation expression should be considered. 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. For example, the data obtained by Vasu et al. [2] were measured at lower temperatures and characterized by a slightly different dependence on pressure ($\tau_{\text{ign}} \sim 1/P$), 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. Moreover, ignition delay times obviously do not follow the Arrhenius law in the NTC region. At temperatures higher than 1400 K Eq. (1) might also not be valid. The high temperature kinetics of alkanes (which amounts to approx. 60–70% of Jet-A) is characterized by a specific dependence on equivalence ratio. While at high temperatures the ignition delay times of lean mixtures are shorter than the times of rich mixtures, it is opposite to the observed behavior of Jet-A/air mixtures at temperatures below 1400 K. Thus Eq. (1) should not be used outside the studied range: below 1000 K and above 1400 K. This recommendation is also supported by the experimental data of other groups [2–4].

The comparison of our ignition delay times measurements with results of other groups [2–4] is shown in Figs. 7 and 8 (data [2–4] are scaled using $\tau_{\text{ign}} \propto P^{-0.67}$ to $P = 10.7$ and $P = 20.5$ atm, respectively). Our experimental data agree well with the data of Vasu

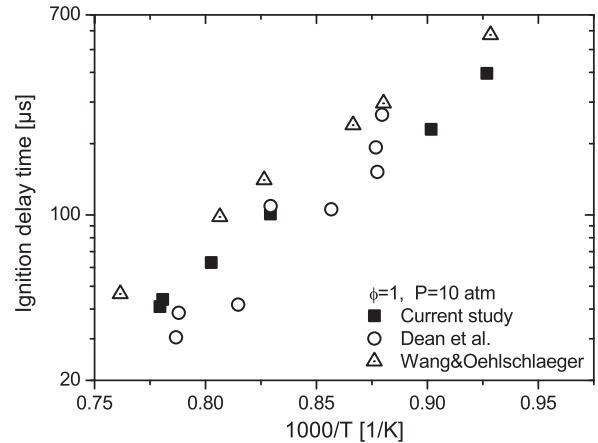


Fig. 7. Comparison of current stoichiometric Jet-A/air ignition delay time measurements at 10 atm with shock tube measurements of other groups [3,4].

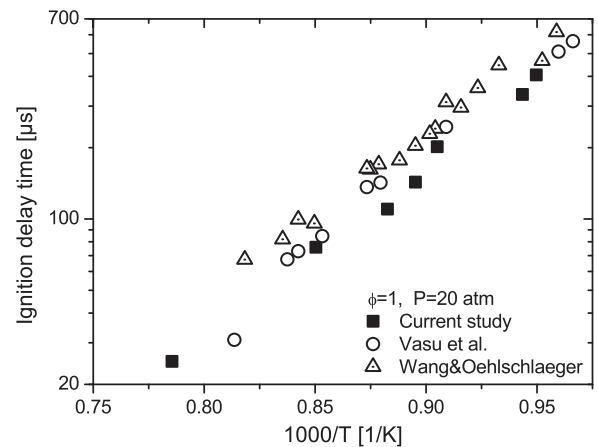


Fig. 8. Comparison of current stoichiometric Jet-A/air ignition delay times measurements at 20 atm with shock tube measurements of other groups [2,4].

et al. [2], see Fig. 8. The data of Wang and Oehlschlaeger [4] lie above and parallel to our data, demonstrating (within limit of statistical error) the same dependence on pressure, temperature and stoichiometry: $\tau_{\text{ign}} \propto P^{-0.75} \cdot \phi^{-0.58}$, $E_a \approx 30 \text{ kcal/mol}$ [4]. The data of Dean et al. [3] lie below, so our data lie somewhere in the middle of the results of Wang and Oehlschlaeger and Dean et al., see Fig. 7. The results obtained by Dean et al. [3] call our attention to the unusual correlation equation for ignition delay times, namely to the dependence on the oxygen concentration:

$$\tau_{\text{ign}} = 1.41 \times 10^{-13} [\text{s}] \cdot (\text{Jet-A} [\text{mol/cm}^3])^{-0.76} \cdot (\text{O}_2 [\text{mol/cm}^3])^{0.33} \cdot \exp(32.6 [\text{kcal/mol}]/RT). \quad (2)$$

According to (2) the reaction rate should decrease with the increase of oxygen concentration. Alkanes are the largest fraction of Jet-A, and they also are the most chemically reactive part of the fuel [1]. Therefore, the experimental data for Jet-A should not contradict to the well-known regularities of the alkane kinetics, i.e. ignition delay times should not go up with the increase of the oxygen concentration in mixture. Dean et al. [3] performed the experiments at different equivalence ratios but at the same pressure. Therefore, the dependence on the oxygen concentration cannot be derived correctly from their data, but only the dependence on the equivalence ratio. Dean et al. [3] reported also about the substantial decrease of the activation energy at $T > 1400 \text{ K}$. However, this phenomenon was observed only at short ignition delay times ($\tau_{\text{ign}} \leq 10 \mu\text{s}$) and

at a strong ignition regime, what points to the possible impact of the gas dynamic effects on the experimental results, which were discussed in the previous section. Wang and Oehlschlaeger have the stronger discrepancy with the data of Dean et al. than us, see Fig. 7. They explain the discrepancy in ignition delay times by the possible development of a detonation wave in the experiments of Dean et al., i.e. using the same arguments as us. Dean et al. also performed the experiments at times more than 1 ms in the shock tube with the length of 5.5 m, likely requiring tailoring. However, they did not report the usage of this procedure in their work [3]. Moreover their propane data indicate the possible existence of the under-tailored regime in their experiments at residence times longer than 1 ms (the Arrhenius plot suddenly changes the slope and goes up at $\tau_{\text{ign}} > 1$ ms).

The data of Wang and Oehlschlaeger [4] are not only above our data but also above the data of Vasu et al. [2]. Indeed, Wang and Oehlschlaeger studied Jet-A composite blend POSF 4658. However, the difference in the results cannot be explained by the use of different kerosene samples. Wang and Oehlschlaeger, and Vasu et al. compared the measurements for different jet fuels, and both found that “at temperatures greater than 1000 K, the differences in fuel composition have no discernible influence on reactivity” [4]. In their article Wang and Oehlschlaeger explained this difference in the measurements by the use of different chemical formulas for Jet-A. (Wang and Oehlschlaeger used $\text{C}_{10.17}\text{H}_{19.91}$ while Vasu et al. [2] used $\text{C}_{11}\text{H}_{21}$; we and Dean et al. used $\text{C}_{11}\text{H}_{22}$.) However, this explanation does not work in our case. If we would use the molecular weight of 142 g/mol for the kerosene, it would increase the molar fraction of kerosene in the fuel mixture by 8.5%, but the stoichiometry would remain unchanged. In the current work (in contrast to other works) the amount of kerosene in mixture has been measured out by mass but not by partial pressure. Although the difference between the current measurements and the measurements of Wang and Oehlschlaeger exists, it lies within the limits of the experimental uncertainty.

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. In the simulations the most important thing is the correct estimation of the temperature rise during induction period. The ignition delay times of hydrocarbons are characterized by a strong temperature dependence (in our case $E_a \approx 30$ kcal/mol), so even a small temperature rise during the ignition reduces the ignition delay. Most of the researchers use the model of a constant volume reactor with adiabatic walls for these calculations (for example Vasu et al. [2]). 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 and shortens the ignition delay time. Less common are the conditions of constant pressure which give longer ignition delay time (the example of the usage can be found in [19]). The real conditions behind the reflected shock wave lie somewhere in the middle. The impact of boundary conditions (constant volume or constant pressure) becomes significant when the temperature of mixture rises during the induction period. The difference between the results obtained at constant pressure and constant volume may reach 50% for undiluted fuel–air mixtures in the NTC region. Therefore, for undiluted fuel–air mixtures we recommend to perform both calculations in order to get the idea about the magnitude of the effect. When the difference in the results are large, the feasible solution could be the use of the some average value with respect to the both boundary conditions. At times longer than 0.5 ms the effect of the interaction between the reflected shock wave and boundary layers becomes visible. It manifests itself in the slow rise

of pressure behind the reflected shock wave with time (0.4–1.2% per 100 μs in a 5-cm-diameter shock tube according to the measurements of Peterson and Hanson [18]). Thus, for ignition delay times longer than 1 ms it is necessary to take into account the real pressure history. The useful discussions about this phenomenon can be found in [20,21].

Peculiarities of the shock tube technique, namely the running of experiments at a fixed pressure in the driver section, result in 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 (on average $\Delta\tau = 4 \mu\text{s}$), comparing the results of experiment and kinetic modeling, 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. The ignition delay times for Jet-A also depend on the mixture composition (and its uncertainty) but not as strong as on temperature. 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 plot it vertically. The total relative error can be found by the formula:

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

where α , β , and E_a are the coefficients of expression $\tau_{\text{ign}} = A \cdot P^\alpha \cdot \phi^\beta \cdot \exp(E_a/(R \cdot T))$. As one can see the total experimental error amounts to around 20% with the main contribution given by the parametric error of the temperature. This is clearly demonstrated in Fig. 9. The graph shows the scattering of the experimental data around the correlation curve (Eq. (1)). In Fig. 9 the shift of the curve by 1.5% along the horizontal axis corresponds to the shift by $\approx 20\%$ along the vertical axis. The graph also shows that all experimental points are scattered near the correlation (Eq. (1)) within the limits of 20%, and only four points lie outside the 20% margins. In modeling it is necessary to understand that the mixture composition in the experiments is derived from the chemical formula

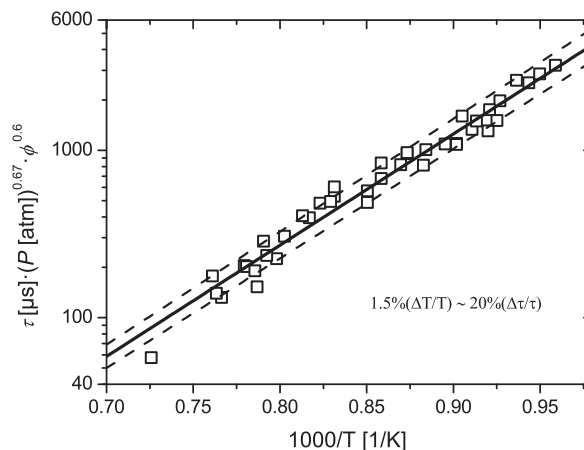


Fig. 9. Scattering of the obtained experimental data around the correlation curve: $\tau [\mu\text{s}] \cdot (P [\text{atm}])^{0.67} \cdot \phi^{0.6} = 1.31 \times 10^{-3} \cdot \exp(15300/T)$; thin dash lines: $y = 1.31 \times 10^{-3} \cdot \exp(15300/(T \pm 1.5\%))$.

C₁₁H₂₂ for Jet-A, which may be different in reality. However, this uncertainty is completely covered by the total error.

4. Conclusions

The ignition delay times have been measured for the lean, stoichiometric and rich mixtures of Jet-A with air ($\phi = 0.5, 1, 2$) at pressures of 10 and 20 atm in the overall temperature range of 1040–1380 K. The measurements have been performed in the heated shock tube behind the reflected shock wave at the heating temperature of 150 °C. The experimental data lie in the intermediate region between the regions of the high temperature kinetics and of the negative temperature coefficient. The measured ignition delay times agree well with the shock tube data of Vasu et al. [2]. The current measurements are in the good qualitative agreement with the measurements of Wang and Oehlschlaeger [4]. The agreement with the data of Dean et al. [3] is not perfect. The discrepancy with the data of Dean et al. at $\tau_{\text{ign}} < 100 \mu\text{s}$ have been explained by the possible impact of the gas dynamic effects.

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: $\tau_{\text{ign}} = 1.31 \times 10^{-3} [\mu\text{s}] \cdot (P/1 [\text{atm}])^{-0.67} \cdot \phi^{-0.6} \cdot \exp(30.4 [\text{kcal/mol}]/RT)$.

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 to around 20%.

Ignition delay times for Jet-A/air mixtures at pressures of 10–20 atm were also measured by other groups [2–4]. The measurements performed using different heated shock tubes have resulted in the scattering of experimental data relative to each other. At the moment, the data obtained in the present study is an important contribution to the existed data on ignition of undiluted Jet-A/air mixtures in the pressure range of 10–20 atm.

The obtained experimental data are given in Appendix A.

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Appendix A. Experimental data

see Tables A.1, A.2, A.3, A.4, A.5, and A.6.

Table A.1
Ignition delay times for Jet-A/Air mixtures at $\phi = 0.5$ and $P = 10$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1203	10.0	0.64	99.36	173
1224	11.2	0.64	99.36	119
1150	11.9	0.64	99.36	237
1087	10.3	0.64	99.36	416
1378	10.6	0.64	99.36	18
1305	9.3	0.64	99.36	45

Table A.2
Ignition delay times for Jet-A/Air mixtures at $\phi = 1$ and $P = 10$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1283	11.0	1.27	98.73	41
1281	9.72	1.27	98.73	44
1246	10.6	1.27	98.73	63
1206	10.7	1.27	98.73	101
1109	10.3	1.27	98.73	230
1079	11.0	1.27	98.73	396

Table A.3
Ignition delay times for Jet-A/Air mixtures at $\phi = 2$ and $P = 10$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1131	11.3	2.51	97.49	131
1314	14.0	2.51	97.49	20
1086	12.4	2.51	97.49	214
1203	11.4	2.51	97.49	78

Table A.4
Ignition delay times for Jet-A/Air mixtures at $\phi = 0.5$ and $P = 20$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1310	21.7	0.63	99.37	27
1253	21.3	0.63	99.37	44
1098	17.1	0.63	99.37	302
1165	18.0	0.63	99.37	170
1145	20.2	0.63	99.37	209
1215	20.8	0.63	99.37	96
1095	19.1	0.63	99.37	314
1165	16.1	0.63	99.37	160
1230	18.3	0.63	99.37	88
1262	20.6	0.63	99.37	47

Table A.5
Ignition delay times for Jet-A/Air mixtures at $\phi = 1$ and $P = 20$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1176	20.4	1.27	98.73	76
1133	20.0	1.26	98.74	110
1060	20.7	1.25	98.75	336
1117	20.9	1.26	98.74	143
1273	20.7	1.26	98.74	25
1053	18.7	1.26	98.74	406
1105	22.3	1.26	98.74	202

Table A.6
Ignition delay times for Jet-A/Air mixtures at $\phi = 2$ and $P = 20$ atm.

<i>T</i> (K)	<i>P</i> (atm)	Jet-A (% vol.)	Air (% vol.)	τ_{ign} (μs)
1043	22.4	2.54	97.46	263
1081	21.9	2.54	97.46	125
1068	18.5	2.54	97.46	243
1176	20.0	2.54	97.46	43
1271	17.0	2.54	97.46	15*
1109	27.1	2.54	97.46	78†
1145	29.4	2.54	97.46	66†

† Not plotted in Fig. 6.

* The emission peak has an irregular shape, $\Delta\tau = \pm 7 \mu\text{s}$.

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