Kinetic Modelling of n-Decane Ignition at High Pressure

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1   Introduction

Investigations of ignition of mixtures of n-decane with air are of great interest. n-Decane and other normal alkanes: nonane, undecane, dodecane and others form a significant part of total amount of fossil fuels. Normal alkanes are the main components of diesel fuels and aviation kerosene. In recent times there has been considerable interest in the developing of a HCCI engine (Homogeneous Charge Compression Ignition – HCCI), which promises reduced emissions and increased efficiency. In order to successfully operate an HCCI engine it is necessary to obtain a full agreement of ignition delay time with engine speed at all loads. A particular interest is presented by ignition delay time of heavy normal alkanes within the following range of parameters: temperatures of 800–1600 K, pressures of 10–80 atm, and equivalence ratio of 0.5–1. Aim of this work is an answer for a question: "How do modern kinetic models describe ignition of n-decane at high pressure?"

Most of authors of reaction mechanisms of oxidation of n-decane uses the experimental data of Pfahl et al. [1] for a validation. Pfahl et al. [1] measured ignition delay time of mixtures of n-decane with air by using a preheated shock tube. The experimental data covers temperature range from 700 K to 1300 K and consists of two sets corresponded to pressure of 13 and 50 atm. There are also recent, mostly unknown, shock tube experimental data of Zhukov et al. [2] presented on the last European Combustion Meeting. A similar experimental technique was used in both works. Zhukov et al. [2] measured ignition delay time of lean and stoichiometric mixtures of n-decane–air at pressures of 13 and 80 atm. In this work a comparison between the new experimental data [2] and well-known kinetic models [3]–[6], and the existed experimental data [1] is performed.

These well-known kinetic mechanisms [3]–[6] realize a different approaches. Zhao et al. developed a kinetic mechanism of oxidation and pyrolysis of n-decane. A detailed reaction mechanism was developed consisting of 494 reactions with 69 species. An assumption of equilibrium between alkyl radicals allowed authors to obtain a reduced mechanism with 407 reactions and 52 species. The model was validated using data from flow reactor data, shock tube, burner-stabilized flame. Lindstedt and Maurice [4] developed a detailed surrogate chemical-kinetic model for aviation fuels. This model consists of two components: n-decane and toluene. The sub-mechanism of n-decane was used to represent the combustion of all non-aromatic components in kerosene with toluene representing the aromatic component. The model was validated against temperature and concentration profiles for n-decane and kerosene laminar flames. Bikas and Peters [5] compiled and successfully validated a kinetic mechanism for the combustion of n-decane for a wide range of combustion regimes. The semi-detailed reaction mechanism involves approximately 600 reactions and 67 species. The relatively small dimensions of the reaction mechanism is explained by using a lumped sub-mechanism for the low-temperature oxidation. The validation was performed by using results of experimental measurements in a shock-tube, a jet-stirred reactor, a flat-flame burner and a premixed flame. Furthermore the authors of the mechanism later developed a new version [7]. Battin-Leclerc et al. [6] showed another approach of developing a kinetic mechanism for oxidation of
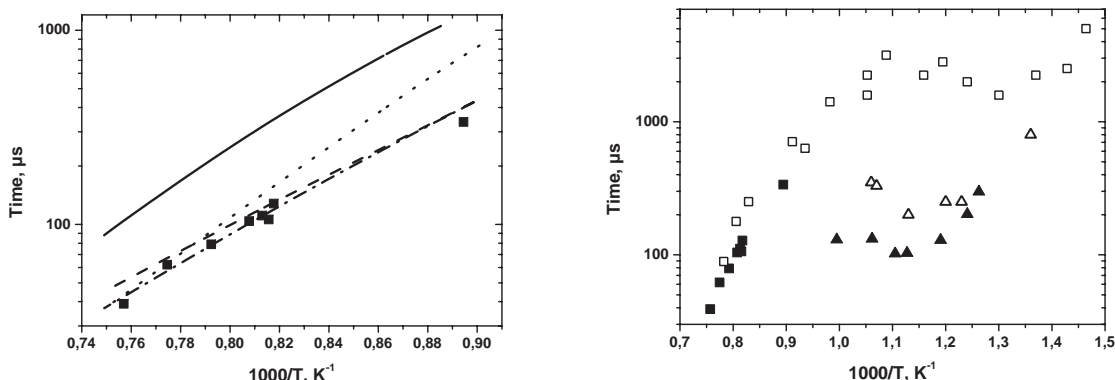
Figure 1: Ignition delay time of stoichiometric mixture of n-decane(1.33%) with air. Symbols – experimental data: solid squares – 13 atm [2]; open squares – 12 atm [1]; solid triangles – 80 atm [2]; open triangles – 50 atm [1]. Lines – modelling (p=13 atm): solid line – EXGAS-ALKANES [8]; dot line – "Zhao" [3]; dash-dot line – "Lindstedt" [4]; dash line – "Peters" [7].

n-decane. A computer package EXGAS-ALKANES was used for an automatic generation of detailed kinetic mechanism. A modelling study of oxidation and combustion of n-decane in a jet-stirred reactor and a premixed laminar flame in a temperature range from 550 to 1600 K was performed. A low-temperature oxidation mechanism of n-decane consists of 7920 reactions with 1216 species. A fresh version [8] of the mechanism was used in the current work.

2   Modelling

n-Decane ignition was simulated by using Chemkin software. The conditions behind the reflected shock waves were assumed as homogeneous adiabatic reactor at constant volume.

In previous study [9] calculations of ignition delay time were performed in assumption of constant pressure. Most of researches use a constant volume assumption. A difference in ignition delay time in the assumption of constant volume and constant pressure is small, because of small temperature variation during the induction period. Actually the both assumptions are not correct for the concerned system (ignition of air-fuel mixture behind reflected shock wave). It is supposed that the average value of ignition delay time calculated at constant volume and at constant pressure is close to the actual conditions in this system. In this work a constant volume assumption was used in order to be consistent with other authors [7, 3, 8].

In the calculations, the ignition delay time was determined as the point of temperature increase up to 500 K relative to initial temperature, which amounts to one third of the total calculated rise in temperature.

3   Results and Discussion

A comparison between predictions of different kinetic models and experimental data at a pressure of 13 atm is presented on Fig. 1. Kinetic mechanisms [7, 4] show very good agreement with experimental data throughout the whole temperature range 1100–1300 K. The mechanism of Zhao et al.[3] has some qualitative disagreement with the experimental data [2], which leads to a discrepancy with the experimental data at temperatures below 1200 K. That is not surprising, because such a disagreement with
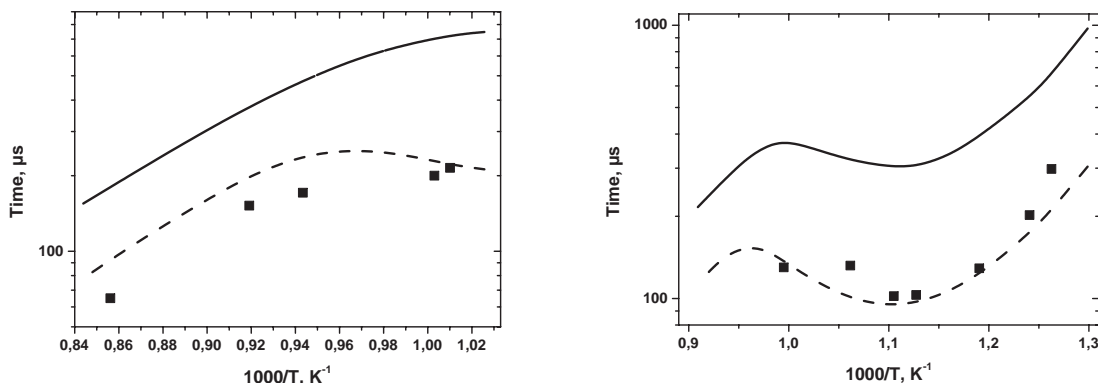
Figure 2: Ignition delay time of lean mixture (left side) and stoichiometric (right side) of n-decane with air at 80 atm. Symbols – experimental data [2], Lines – modelling: solid line – EXGAS-ALKANES [8]; dash line – "Peters" [7].

experimental data [1] was shown by the authors of the mechanism in their work [?]. The mechanism generated by EXGAS-ALKANES predicts ignition delay times, which are twice lager than those measured experimentally.

The models [7, 8] have a validity range below 1000 K. These models were used in the simulation of experimental data in the intermediate temperature range and at high pressure (Fig. 2). Both models [7, 8] have qualitative agreement with the experimental data. The model [7] reproduces the experimental data very well. The model [6] overpredicts the experimental data by 2–3 times. The models predicts a wider range of NTC (Negative Temperature Coefficient) behavior than measured in the work [2], where the high temperature limit of the NTC effect lies at slightly lower temperature. A predicted amplitude (depth of pothole on Fig. 2) of NTC effect are close to the measured values.

In spite of an apparent agreement between the experimental data and some models [7, 4] all kinetic models [3, 4, 7, 8] predict longer ignition delay times for n-decane–air mixture than were measured in work [2]. Actually it was the comparison of different values: ignition delay times in the experimental work [2] was defined as a time of maximum of OH* emission at 309 nm, but calculated ignition delay time is defined as a time of temperature increase up to 500 K from initial temperature. Firstly, the considered models cannot predict emission profile of OH(A→X). Secondly, these kinetic models predict maximum of all radical concentrations at the same time with temperature rise, so the both definitions should agree indeed. That is why this definition of ignition delay time was chosen.

The kinetic models [3, 4, 7, 8] were tested against the earlier work of Pfahl et. al [1]. The current experimental data agreed well with results of the previous work (see Fig. 1, but there is a propensity of the data from the work of Pfahl et. al [1] to be slightly slower than that of Zhukov et al. [2] in the temperature range 1100–1300 K. This propensity results in the overpredictions by the all models in comparison with the experimental data of Zhukov et. al [2]. It is possible to estimate a value of random error of the data [2] from the scattering of experimental data on the plots. This value amounts 20% that is not enough to overlap the data of Pfahl et. al [1]. Nevertheless, the models of Zhao et al. [3] and Battin-Leclerc et al. [6] visibly predict longer ignition delay times that data of Pfahl et. al [1] also.

In comparison to other heated shock tubes a tube, which was used for measurements in work [2], has some advantages. The measurements were performed by using two different techniques: absorbtion measurements at 3.3922 μm (CH$_3$- group) and emission measurements at 309 nm (OH*). The measurements [2] were performed through a side wall at a distance of 7 mm from the end plate at an observation time of 400 μs. These allowed to use of the ideal theory for the calculations of the conditions behind the

reflected shock wave. The experimental setup was used previously for measurements of ignition delay time of low alkanes [9] and this data agrees very well with the results of other groups (Hanson's group). The shock tube is placed into a heater as whole and internal dimensions more greater than dimensions of the shock tube, which provides a uniform temperature field.

Taking into account that the calculation were made under assumptions of constant volume we can conclude that the considered kinetic models [3, 4, 7, 8] overpredict ignition delay time of n-decane mixtures in air.

4   Conclusions

The existed kinetic mechanisms of oxidation of n-decane are in need of further development. Used methods on their constructions are correct, and only qualitative improvement is required.

The kinetic mechanism generated by the EXGAS-ALKANES package predict a longer ignition delay times than measured in the both experimental works [1, 2]. It has only very good qualitative agreement with the experimental data on ignition of n-decane, whereas EXGAS-ALKANES shows very good agreement with experimental data for pentanes [8]. The mechanisms [3, 4, 7] agree with the experimental data [2] very well. The mechanism [7] has a good agreement with experimental data on n-decane ignition in the whole studied range of conditions: 13–100 atm, 800–1300 K, ϕ=0.5–1.

It is possible to use lumped mechanisms in order to predict integral parameters like temperature or ignition delay time in a temperature range which corresponds either high-temperature oxidation or low-temperature oxidation regions. Indeed, it is admissible to use extensively verified models of oxidation of smaller hydrocarbons like n-heptane, which has similar kinetic behavior, instead of kinetic models of n-decane oxidation.

The kinetic model with lumped reactions [7] shows the best agreement with experimental data among considered models [3, 4, 7, 8]. It is obvious that it is easier to fit a smaller kinetic model to an experimental data. Nevertheless, the software packages like EXGAS-ALKANES [6] for automatically generation of kinetic mechanisms give some benefits. It is possible to generate a mechanism, which will be adapted to desire conditions. They cover not only one hydrocarbon, but a whole set of hydrocarbons and allow to perform a comparative study of hydrocarbons combustion.

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