

REACTION MECHANISMS OF *iso*-OCTANE AND *n*-HEPTANE
AUTOIGNITION UNDER CONDITIONS RELEVANT TO
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Introduction

The kinetic schemes employed in studying combustion processes in SI engines must take into account the phenomenological features typical for hydrocarbon fuel oxidation at high pressures and moderate temperatures. This implies that both low- and high-temperature oxidation mechanisms should be incorporated into a kinetic scheme [1]. Combination of the two subschemes can provide a model of two-stage auto-ignition. Hydrocarbons exhibiting two-stage auto-ignition are known to be characterized by substantial widening of self-ignition limits. According to the qualitative analysis [1] and quantitative estimations [2], abnormal combustion in SI engines ('knock') can be caused by two-stage autoignition of unburnt mixture pockets.

This paper deals with a new detailed reaction mechanism developed for studying autoignition of *iso*-octane, *n*-heptane and their mixtures under conditions similar to those in the end gas of SI engines. To implement the mechanism in multidimensional fluid dynamic codes, its systematic reduction has been performed.

Reaction Mechanism

Modeling of two-stage autoignition of hydrocarbon fuels is based on the well-known principle discussed elsewhere [1, 3]. At low temperatures, chain branching is assumed to proceed via alkyl peroxide decomposition, whereas at larger temperatures decomposition of hydrogen peroxide and reactions involving formaldehyde are dominant. With a further temperature increase, the branching tends to proceed mainly through the reaction of H atom with oxygen. The transition between the branching mechanisms is a result of the temperature increase in the course of decomposition of the alkyl peroxide radical RO₂.

The kinetic mechanism of *iso*-octane and *n*-heptane oxidation includes two groups of reactions.

The first one is the autoignition group including 29 reactions involving 13 reactants. The autoignition group includes reactions describing cool flames and two-stage autoignition at certain critical values of Arrhenius parameters. It includes competing reactions (specific for *iso*-octane and *n*-heptane) which ensure the transition between low- to high-temperature oxidation mechanisms. In addition, a few empirical reactions

are included to reduce C_7 and C_8 to C_1 and C_2 hydrocarbons. The autoignition sub-scheme under consideration differs from the existing reaction mechanisms, although the basic steps involved are represented by well-known processes.

The second group of reactions is the detailed mechanism of oxidation of C_1 and C_2 hydrocarbons containing 255 reactions involving 30 reactants [4]. In the present paper, it is modified for the use at high initial pressures.

Validation of the reaction mechanism was performed by comparing the predicted autoignition delay times to the available measurement data. The ignition delay times are calculated for constant-volume conditions.

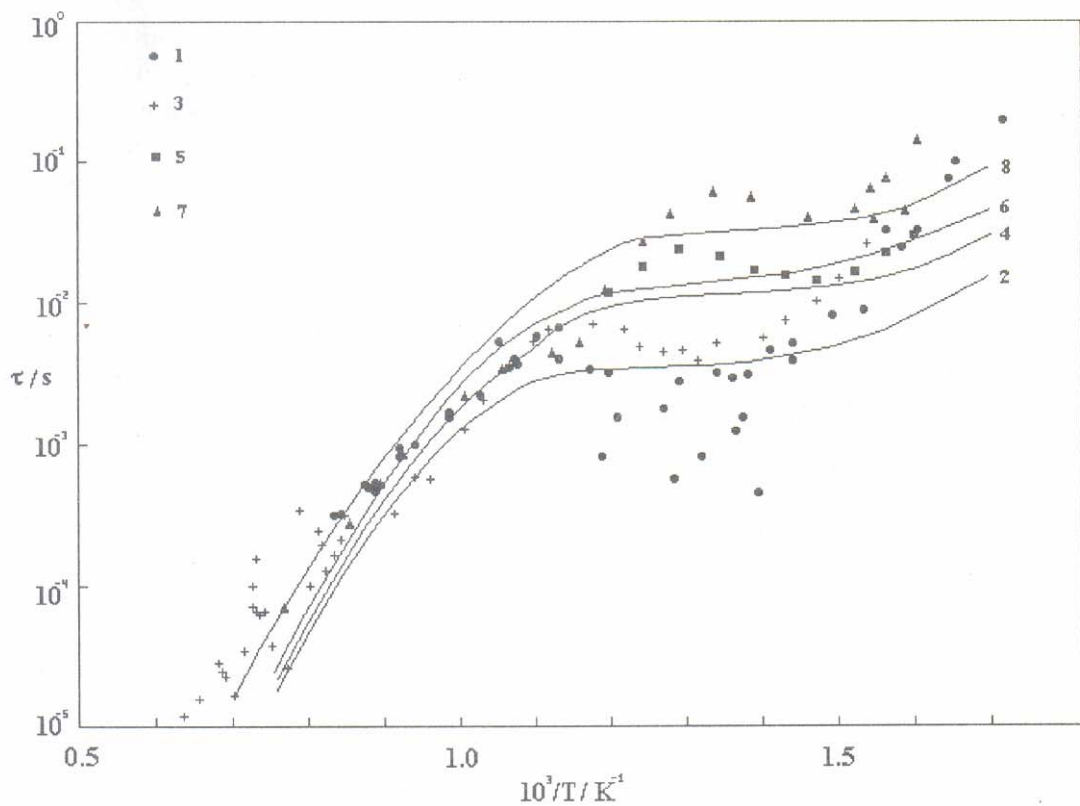


Figure 1: Comparison of predicted (curves) and measured (points) ignition delays for stoichiometric *n*-heptane-*iso*-octane-air mixtures at initial pressure 15 bar. 1, 2 — *n*-heptane-air; 3, 4 — 40% *n*-heptane + 60% *iso*-octane-air; 5, 6 — 10% *n*-heptane + 90% *iso*-octane-air; 7, 8 — *iso*-octane-air.

Validation

To compare the predicted results to the measured data, experimental studies using rapid-compression and shock-tube techniques were considered. Of interest are the experimental conditions close to those in the end gas in SI engines, namely, the temperatures $600 \text{ K} < T < 1200 \text{ K}$, the pressures $15 \text{ bar} < p < 100 \text{ bar}$, and the equivalence ratios $0.5 < \phi < 2.0$.

An example of the comparison of the predicted and measured results is shown in Fig. 1. The predicted curves are compared to the available experimental data for the ignition delays of stoichiometric mixtures of *n*-heptane (1, 2), 40% *n*-heptane + 60% *iso*-octane (3, 4), 10% *n*-heptane + 90% *iso*-octane (5, 6) and *iso*-octane (7, 8) with air at the initial pressure $p = 15 \text{ bar}$ over a wide range of initial temperatures.

Figure 1 exhibits a significant scatter of the measured results for *iso*-octane (3 groups of points: Halstead et al, Teichmann, and Fieweger et al) and for *n*-heptane (5 groups: Ciezki et al, Teichmann, Taylor et al, Scheuermeyer et al, and Roegerer). For similar initial conditions, the ignition delay times differ by a factor of 2 to 7. Moreover, different authors observed qualitatively different dependencies of $\lg \tau$ vs. $1/T$ for *iso*-octane. The discrepancies observed are most likely due to the difference in experimental and measuring techniques and the definitions of ignition delay employed in the respective studies.

It is evident that the *iso*-octane-air mixture exhibits longer ignition delays than the *n*-heptane-air and blended fuel-air mixtures. The difference is more pronounced at low temperatures. At high temperatures, the ignition delays for different fuel-air mixtures become close. Clearly, all the predicted curves are *S*-shaped. This is an evidence of two oxidation mechanisms involved, namely, low-temperature ($T < 700 \text{ K}$) and high-temperature ($T > 900 \text{ K}$). Between these temperature ranges, there is a transition region where the process of autoignition is two-staged.

Mechanism Reduction

Implementation of a reaction mechanism in a multidimensional fluid dynamic code requires reducing it to the shortest possible scheme. The reduction procedure employed has been reported in [5].

The use of the procedure resulted in developing a reduced reaction mechanism including 21 reactions involving 13 reactants. This mechanism shows a good agreement with experimental data and with the results obtained using the complete reaction mechanism.

Conclusion

A detailed reaction mechanism has been developed and validated with the view of studying autoignition of *iso*-octane, *n*-heptane and their mixtures in air in a wide range of initial conditions in terms of temperature (600–1200 K), pressure (15–100

bar), and equivalence ratio (0.5-2.0). The mechanism includes 284 reactions involving 43 reactants. A reduced reaction mechanism including 21 reactions among 13 reactants has also been developed. It approximates, with a good accuracy, the results of detailed calculations, based on the complete reaction mechanism, within the ignition delay time.

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THE KINETIC MODELING OF LAMINAR FLAMES OF H₂S AND CS₂

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This work completes the first stage of the development of the detailed kinetic mechanisms of self-ignition and combustion of relatively simple sulphur-containing gas-phase molecular systems: H-S-O and C-S-O. Experimental studies of gas-phase hydrogen sulfide oxidation (H-S-O) and carbon disulfide oxidation (C-S-O) were conducted in a number of works. Some of these works were reviewed in [1, 2], where detailed kinetic mechanisms of these processes were also suggested and kinetic simulation of self-ignition