

Auto-ignition of aromatic and aliphatic Diesel fuel components: High-pressure shock-tube experiments and kinetic modeling for toluene and n-heptane

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The auto-ignition of toluene and n-heptane as model fuels for Diesel fuel components have been studied in a high-pressure shock tube under engine-relevant conditions. Toluene/air and n-heptane/air mixtures as well as toluene/n-heptane/air (10/90% and 40/60% by volume) have been investigated over a wide temperature range (700 – 1200 K), $\phi = 1.0$ and 0.5 and 40 bar behind reflected shock waves. A kinetic mechanism based on the detailed Lawrence Livermore PRF (primary reference fuel) mechanism [1] extended with a toluene submechanism has been tested against the experimental ignition delay times and calculations for engine-relevant pressures and temperatures have been performed. The temporal variation in toluene concentration in the pre-ignition phase is determined relative to the base fuel and the pressure rise induced by the heat release.

Introduction

Since many years, n-heptane is used as model fuel for Diesel to simplify kinetic modeling. Toluene can be found as aromatic compound in some Diesel fuels, and is also used as a fluorescent species for fuel concentration imaging studies. The ignition behavior of each component and their interaction in mixtures is interesting for the improvement of existing chemical reaction mechanisms. The visualization of the fuel distribution during combustion processes is of practical interest, too. Therefore, the fluorescence of toluene that might be added or is already contained in Diesel fuels, can be used by laser induced fluorescence (LIF) imaging measurements [2]. For these measurements the interaction of toluene with the fuel oxidation chemistry is crucial for two reasons: (i) a tracer that is added to the base fuel should not modify the ignition properties of the fuel and (ii) the lifetime of the fluorescing component relative to either the lifetime of the parent fuel or to the profile of heat release must be known for an adequate interpretation of the measured signals.

Toluene auto-ignition has been subject of several experimental and numerical studies. Most of these studies (e.g. [3,4]) focus on the oxidation of toluene in dilute mixtures for low pressures and high temperatures in shock tubes. Only few investigations under engine-relevant conditions and mixtures of toluene with model fuels are found in literature. For these conditions, the chemical reaction mechanisms are not satisfactorily validated against experimental data.

Few papers addressed the interaction of fluorescence tracers and fuels. A recent study investigated the stability of biacetyl relative to reference fuels based on simulations so far, however, without experimental validation [5].

Experimental

Ignition delay time measurements have been performed in a heatable high-pressure shock tube. The maximum test time is extended up to 15 ms by driver gas tailoring [6]. The initial temperature is set to 80°C to ensure total evaporation of the test gas mixtures. A detailed description of the shock tube and the preparation of the mixtures can be found in [7]. The temperature and pressure behind the reflected shock wave were computed from the incident shock velocity, its attenuation and the initial conditions T_1 and the filling pressure p_1 using a one-dimensional shock tube code (shock tube code of the CHEMKIN-package [8]). The ignition delay time τ_{ign} is defined as the period between the arrival of the reflected shock wave in the measuring region and the steepest increase in the CH* chemiluminescence signal.

Chemical reaction mechanism

For the simulations, we used the detailed Lawrence Livermore PRF mechanism [1] augmented by a toluene submechanism of Andrae et al. [9].

Numerical simulations

Numerical simulations based on a homogeneous reactor model were performed to theoretically determine ignition delay times. All simulations used an adiabatic constant-volume model. The chemical source term was evaluated using the reaction mechanism described above.

Several simulations were run in a parametric study with initial conditions set according to the shock-tube experiments: Simulations were run with pure n-heptane and toluene and with mixtures with various toluene concentrations. Global maps were derived to investigate the influence of toluene on the ignition properties of n-heptane.

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A comparison of the development of toluene and n-heptane during ignition and combustion in an engine is shown in Fig. 1. The data are from a numerical simulation using a homogeneous reactor model for the engine. A stoichiometric n-heptane / toluene (90/10% by volume) / air mixture (initially at 350 K, 1 bar) is compressed adiabatically according to a prescribed volume-pressure history simulating an engine with a compression ratio of 12 and a speed of 2000 min^{-1} .

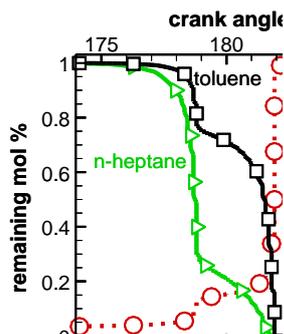


Fig. 1: Relation between the relative concentrations of n-heptane and toluene during the ignition and combustion in an engine (simulation), shown as temporal profiles, along with the corresponding simulated pressure curve.

Fig. 1 shows the disappearance of n-heptane and toluene on a time axis compared to the pressure rise as an indication of the second ignition stage. It can be seen that under the chosen conditions, there is an initial decrease in toluene concentration that is synchronized to the decay of the base fuel. About 60% of the initial toluene, however, survives until the onset of the second-ignition stage. This indicates that in a case with homogeneous fuel distribution, the measurement of toluene concentration (e.g. via LIF) directly yields information about both, the location of first and second ignition. For an inhomogeneous case further experiments are needed to investigate if both effects can be separated.

Results and Discussion

Ignition delay times were determined for pure n-heptane and toluene/air mixtures and for n-heptane/toluene (90/10vol% and 60/40vol%) / air mixtures for $\phi = 1.0$ and 0.5 and $p_5 = 40 \pm 2$ bar over a wide temperature range of 700–1200 K.

Fig. 2 shows the comparison of measured and simulated τ_{ign} for n-heptane with and without different concentration of toluene and for pure toluene for $p_5 = 40$ bar and $\phi = 1.0$ (upper part) and 0.5 (lower part). A pronounced s-shaped curve is observed for low toluene concentrations due to the main component n-heptane in simulations and measurements as well, indicating a NTC (negative temperature coefficient) behavior. With increasing toluene concentration, this effect decreases and

for pure toluene in air, a linear behavior in the Arrhenius-diagram is observed. Also, with increasing toluene concentration, the ignition delay times increase with increasing toluene concentration. For pure toluene/air mixtures, a linear behavior of τ_{ign} is observed in the Arrhenius-diagrams.

The absolute values of τ_{ign} for lean mixtures are longer. The influence of 10vol% toluene on τ_{ign} is small for the stoichiometric mixtures. The lean mixture is slightly influenced by the toluene doping. The strongest increase of τ_{ign} is found for $T_5 = 740$ K.

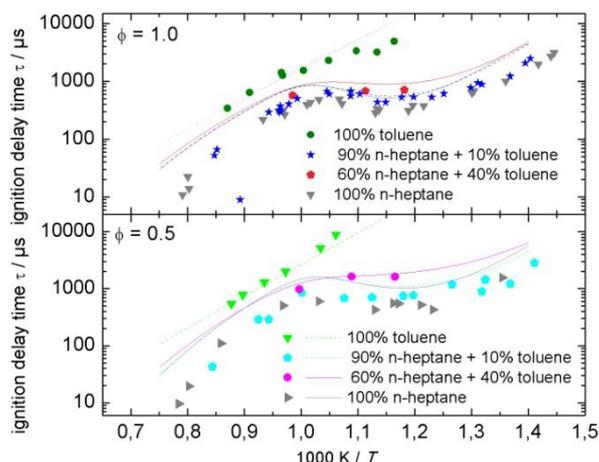


Fig. 2: Comparison of simulated (lines) and measured (symbols) τ_{ign} for $\phi = 1.0$ (upper part) and $\phi = 0.5$ (lower part) and $p_5 = 40$ bar. The simulations show good agreement with the experimental τ_{ign} . Small toluene concentrations do not show strong influence on the ignition of n-heptane.

The simulations overpredict the measured τ_{ign} for pure n-heptane and n-heptane with small toluene concentrations. Qualitatively, simulations and experiments show the same trends for all conditions. By “tuning” some sensitive reactions in the mechanism, better agreement in the absolute values of τ_{ign} can be achieved even for low toluene concentrations. Therefore, the pre-exponential factor A in the Arrhenius-expression of the chain branching reaction $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$ is increased. Importantly, this “tuned” mechanism essentially predicts the same change (relative to the pure fuel) of ignition delay when toluene is added, like the original mechanism.

To gain a more complete picture of the influence of toluene on the auto-ignition behavior of n-heptane, a map of the ratio $\tau_{\text{n-heptane + toluene}} / \tau_{\text{n-heptane}}$ is simulated to determine the relative effect of toluene on the ignition delay (Fig. 3). If this ratio is larger than one, toluene has a decelerating effect, if it is smaller than one, toluene has an accelerating effect on the ignition delay.

For toluene concentrations < 20%, the influence of toluene is quite weak (mostly less than 5%, only for $820 \text{ K} < T < 920 \text{ K}$ almost 30%). For more than

20% toluene, τ_{ign} is only by a factor of about 1.5 larger than for pure fuel. The strength of the influence of toluene depends on temperature. For 30% toluene, there is a factor 1.5 increase at 850 K, while at 1000 K, the same toluene concentration has no influence at all ($\tau/\tau(\text{pure fuel}) \approx 1$ at 30% at 1000 K). In the lower-temperature range, toluene concentrations > 30% cause a rapid increase in τ_{ign} up to a factor of 4 at 60% and 850 K, for instance. Above 950 K, the increase is far less pronounced: At 1000 K, even with 80% toluene, the ignition delay compared to pure n-heptane increases only by a factor of 1.3.

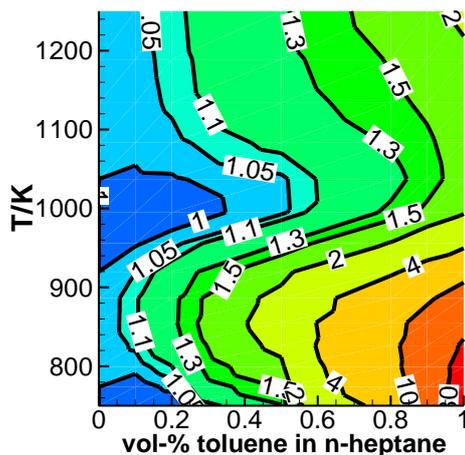


Fig. 3: Global map of the influence of toluene on τ_{ign} of n-heptane for $p = 40$ bar, $\phi = 1.0$ (simulation). The contours give the ratio $\tau/\tau_{\text{pure fuel}}$.

The overall shape of the function shows that the dependence of ignition delay on the toluene concentration is highly nonlinear and also strongly temperature-dependent. Especially, the ignition delay for n-heptane/toluene mixtures can in general not be determined by simply interpolating between ignition delays of pure fuel and pure toluene.

Conclusions

Ignition delay times for toluene/n-heptane mixtures (10/90% and 40/60% by volume) have been determined in a heatable high-pressure shock tube under engine-relevant conditions ($p = 40$ bar) for various equivalence ratios $\phi = 0.5$ and 1.0 over a wide temperature range (700–1200 K). The results were compared to ignition delay times of pure toluene and n-heptane fuels under identical conditions.

The detailed Lawrence Livermore PRF mechanism, augmented by a toluene submechanism by Andrae et al. [9], was used in this study. The comparison of simulated and measured ignition delay times shows good agreement, although the simulations systematically slightly overpredict the measured τ_{ign} for small toluene concentrations.

Simulations and experiment agree that at 40 bar for small toluene concentrations (<10% by volume) the effect of toluene on the auto-ignition of

n-heptane is negligible. A stronger influence of toluene is observed for seeding levels >40% for $T < 950$ K, while at temperatures above 1000 K, the effect is much weaker.

Global maps of ignition delay times have been computed for the mixtures and help reducing the number of required measurements for validating and/or improving the mechanism by revealing the temperatures and pressures where experimental effort should be spent.

As a result found in simulations and already confirmed by experiments, the effect of toluene on ignition delay is small (not more than ~20% alteration of ignition delay compared to pure n-heptane), if the amount of toluene in the mixture does not exceed 10% by volume. Therefore, for applications with toluene as a tracer for laser-induced fluorescence experiments (e.g. in engines) with low concentrations, no significant alteration of the auto-ignition behavior of n-heptane is expected near 40 bar. Future experiments and simulations will be performed with Diesel fuels to investigate the transferability from n-heptane to complex Diesel fuels.

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