

Diesel Fuel Surrogate Oxidation Mechanism with Application to Spray Combustion Modelling

¹A. Häggström, ²V. Golovitchev

1 Scania CV AB – Södertälje – SWEDEN

2 Chalmers University of Technology – Göteborg – SWEDEN

ABSTRACT

A numerical study has been carried out on the application of a detailed chemistry mechanism for diesel fuel surrogate to spray combustion modelling. The fuel surrogate vapour is represented by a mixture of 70 % n-heptane and 30 % toluene and is modelled on the basis of detailed mechanisms for n-heptane and toluene, individually developed. The mechanism is validated using shock-tube auto-ignition data and reduced using sensitivity analysis. The diesel surrogate mechanism developed consists of 68 species and 280 reactions. The mechanism is implemented into the KIVA-3V [1] code for spray combustion modelling in a constant-volume vessel.

Using the diesel surrogate model, the essential features of fuel auto-ignition at engine relevant conditions are reasonably well reproduced. The aliphatic fuel component controls spray auto-ignition, while the aromatic one significantly contributes to soot formation. The effect of toluene on auto-ignition is predicted as moderate, since its ignition is promoted by a radical pool formed by easily oxidised n-heptane.

INTRODUCTION

Diesel oil is characterized by an enormous variation of its chemical makeup. In order to model combustion processes within a realistic computational time, a simplified model of the diesel fuel is needed. The ignition behaviour, combustion process development and emission formation, especially soot, depend on the fuel properties to a significant degree. Therefore it is important to have a realistic diesel fuel surrogate model. Diesel fuel surrogate models consisting of single component aliphatic hydrocarbons, such as n-heptane or n-dodecane, have been used in the Computational Fluid Dynamic (CFD) modelling of diesel spray combustion. However, since real diesel oil is a mixture of different hydrocarbons, both aliphatic and aromatic, modelling of diesel fuel as a single component, pure aliphatic substance is unlikely to reproduce accurately all of its properties.

This motivates the development of a diesel fuel surrogate model consisting of both aliphatic and aromatic components. In this model, the fuel vapour is represented by a mixture of 70 % n-heptane and 30 % toluene and the chemical mechanism integrates the kinetics of fuel component combustion with kinetics of Polycyclic Aromatic Hydrocarbon (PAH) formation as soot precursors.

The mechanism developed has been implemented into the KIVA-3V combustion code and numerical solutions have been used to evaluate auto-ignition of real diesel oil in a constant-volume vessel.

DIESEL FUEL SURROGATE MODEL

Currently, only single component fuels are implemented in the KIVA-3V library. The thermodynamic properties of diesel fuels in the liquid phase are represented by those of real

diesel oil, i.e. the enthalpy-temperature curve is similar to n-dodecane with enthalpy of formation of -9.8 kcal/mole.

Since diesel surrogate vapour is represented by a mixture of n-heptane and toluene, it is assumed that the combination of their respective properties will give a good approximation of real diesel oil properties. The choice of n-heptane is motivated by its cetane number around 56, which is similar to the cetane number of real diesel oil. This promotes correct auto-ignition behaviour. In order to get a more accurate prediction of soot formation, the aromatic hydrocarbon is also included in the model. Toluene, which is a product of benzene alkylation, has been selected as the aromatic component in the diesel fuel surrogate makeup. The presence of toluene does not affect significantly ignition delay time because its oxidation is promoted by high radical concentrations, produced when n-heptane oxidation proceeds.

The main reaction pathways for n-heptane combustion are well established [2] and in addition to its reduced mechanism, the simplified reaction scheme of toluene oxidation [3] is included into the diesel surrogate model. The toluene oxidation promotes direct formation of acenaphthylene, A2R5, which is a gaseous precursor of soot. Soot formation is modelled as a finite-rate transition of A2R5 to graphite. The complete mechanism, in which the dominant reaction rate coefficients are tuned on a basis of a sensitivity analysis [4], consists of 68 species and 280 reactions and has been validated using auto-ignition shock tube experimental data.

RESULTS AND DISCUSSION

Shock tube auto-ignition calculations

The suggested reaction mechanism is evaluated by comparing predicted ignition delay times with shock tube experiments for n-heptane [5] and toluene [6], respectively.

Comparisons of calculated and experimental ignition delay times for different temperatures and n-heptane/air compositions are shown in Fig. 1. The predictions are in reasonable agreement with the experimental data

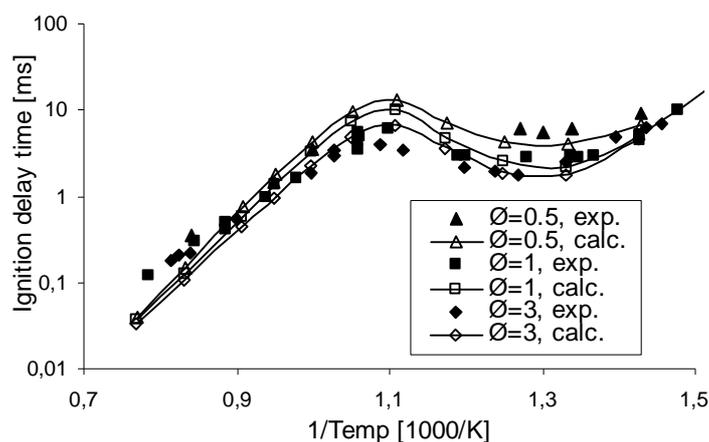


Fig. 1 Ignition delay times for n-heptane in shock tube experiments. $p_0=13.5$ atm.

Experimental and calculated data for toluene ignition delay times for different pressures and compositions, summarized in Table 1, are compared in Fig. 2. The calculated values agree well with the experimental data.

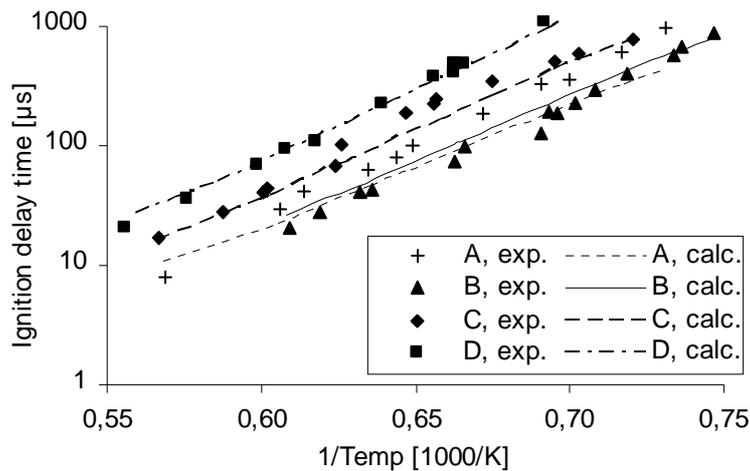


Fig. 2 Ignition delay times for toluene in shock tube experiments. The experimental conditions are summarized in Table 1.

Table 1. Mixture compositions and initial pressures for shock tube experiments.

Case	p (atm)	\emptyset	$C_6H_5CH_3$ (%)	O_2 (%)	Ar (%)
A	2.8	1	1.495	13.45	85.055
B	2.3	0.33	0.497	13.51	85.993
C	6.8	1	0.497	4.48	95.023
D	2.3	1	0.497	4.48	95.023

Fig. 3 presents calculated ignition delay times for stoichiometric mixtures of n-heptane, toluene and the diesel fuel surrogate. This illustrates that the auto-ignition behaviour of the fuel surrogate model is mainly characterised by the properties of n-heptane.

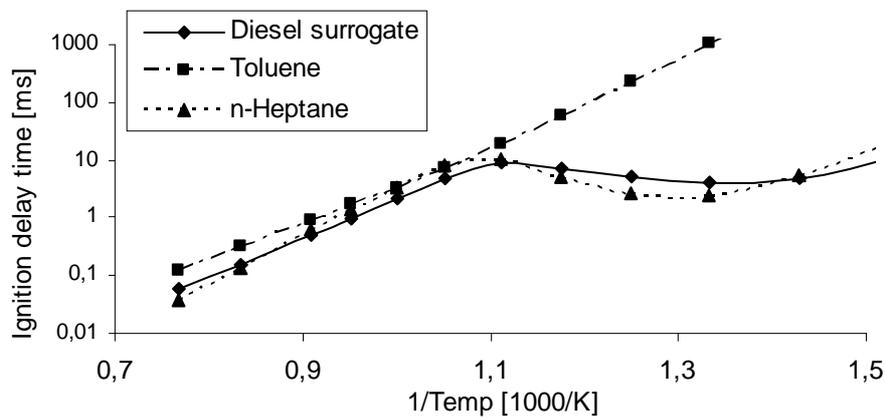


Fig. 3 Calculated ignition delay times for n-heptane, toluene and diesel surrogate combustion in air. $p_0=13.5$ atm. Equivalence ratio, $\emptyset=1$.

Constant volume spray combustion

The model predicts accurately shock-tube n-heptane and toluene auto-ignition, but the important question is whether the fuel surrogate model can reproduce the ignition properties of real diesel oil at engine relevant conditions. This is evaluated by simulation of constant-

volume spray auto-ignition experiments. Calculations of ignition delay times in a constant volume vessel were carried out using the KIVA-3V code.

Constant volume experimental data are available in [7], where ignition delay times were measured for different initial temperatures for both turbulent and non-turbulent cases. In the experiments, diesel fuel (6 mg) has been injected with the injection duration 1.27 ms. To simulate different levels of turbulence, different initial values of turbulent kinetic energies are used in the calculations, while the initial turbulent length scale is kept constant. The ignition delay time was defined as the time for the average temperature to increase by 1% of its initial level. The results are presented in Fig. 4 and the predictions show reasonable agreement with the experimental data.

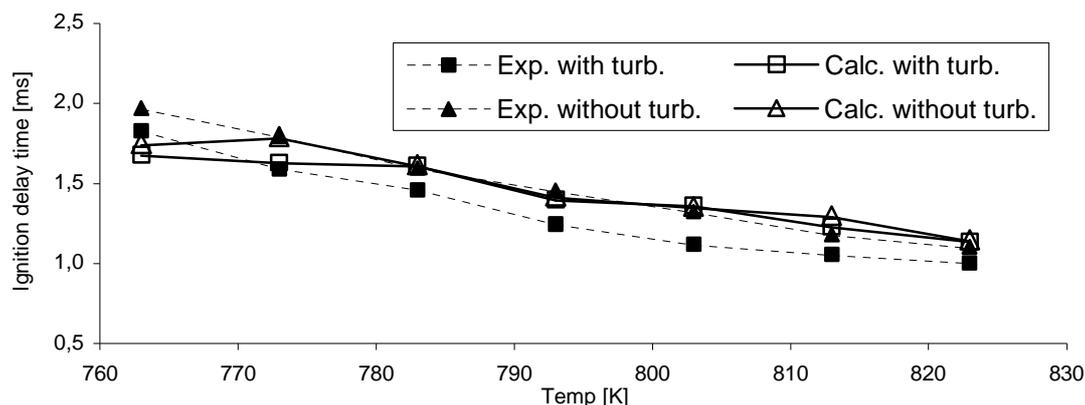


Fig. 4 Ignition delay times for constant volume ($p_0=50$ atm.) combustion; comparisons between experimental data and simulations.

CONCLUSIONS

A diesel fuel surrogate model has been developed, consisting of 68 species and 280 reactions representing the oxidation kinetics of a mixture of 70 % n-heptane and 30 % toluene. The model has been validated by comparison of simulated ignition delay times for the fuel components with shock tube experimental data.

The validated model has been integrated into the KIVA-3V code to simulate diesel spray combustion in a constant-volume vessel. Comparisons with spray auto-ignition experimental data show that the model reproduces reasonably well the diesel spray auto-ignition process.

REFERENCES

1. Amsden A.A., *KIVA-3V: A Block-structured KIVA Program for Engines with Vertical or Canted Valves*, LA-13313-MS (1997).
2. Glaude P.A., Warth V., Fournet R., Battin-Leclerc F., Côme G.M., Scacchi G., *Bull. Soc. Chim. Belg. vol. 106*, **6**: 343 (1997)
3. Emdee J.L., Brezinsky K., Glassman, I., *Journal of Physical Chemistry*, **96**: 2151(1992).
4. Lutz A.E., KEE R.J, Miller J.A., *SENKIN: A FORTRAN Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis*, SAND87-8248, Sandia National Laboratories (1994).
5. Ciezki H., Adomeit G., *Combustion and Flame*, **93**: 421 (1993).
6. Burcat A., Snyder C., Brabbs T., *Ignition Delay Times of Benzene and Toluene with Oxygen in Argon Mixtures*, NASA Technical Memorandum, N86-25431 (1986).
7. Breuer A., et al., *Investigations of the Influence of Turbulence and Type of Fuel on the Evaporation and Mixture Formation in Fuel Sprays*, 8th Periodic Report, IDEA (1992).