Detailed Mechanism for n-Heptane and iso-Octane Relevant for HCCI Engine Calculations

S. S. Ahmed, E. Blurock and F. Mauss

Division of Combustion Physics, Lund University of Technology, P.O. Box 118 SE-22100 LUND, Sweden

ABSTRACT

A detailed mechanism for the oxidation of n-heptane and iso-octane mixture, including NO_x chemistry, has been developed and validated against the shock tube experimental data from Fieweger et al. [1, 2] for both low and high temperature regions, lean and rich fuel conditions, a range of octane numbers and pressures from 13 bar to 40 bar. In addition, the mechanism was tested using a zero dimensional HCCI model against engine experiments under a range of octane numbers and initial temperatures.

INTRODUCTION

The Homogeneous Charge Compression Ignition (HCCI) is known for its low pollutant emissions and is an important development for meeting future stricter pollution controls. This work studies the effect of elevated pressure and temperature of the n-heptane and iso-octane mixture in the developing combustion device the HCCI engine. It is done by developing and updating the existing fuel mechanism.

The major draw back of HCCI engines is its difficulty to control the ignition timing. The ignition timing in HCCI is dependent on the autoignition chemistry and not on injection timing as in Diesel engines or spark occurrence as in SI engines. A small change in the inlet conditions can vary the results dramatically. For this reason detailed reaction mechanisms for complex fuels, validated under HCCI engine conditions are needed, to simulate and understand the complex chemical processes that lead to autoignition. As a result of this development an accurate and comprehensive reaction mechanism is provided.

DETAILED MECHANISM

The construction of the detailed mechanism is systematically in accordance with Curran et al. [4] using the reaction classes and rate constants suggested by the authors as a base. Intermediate reactions, considered of low importance for the timing of ignition, are simplified substantially. The mechanism is further divided into sub-mechanisms, for lighter hydrocarbon fuels and for reaction intermediates. The detailed mechanism consists of 140 species and 1275 reactions excluding NO_x sub-mechanism and 157 species and 1547 reactions including NO_x sub-mechanism. In the present detailed mechanism all the reaction paths which are known to be pertinent from both high and low temperature kinetics are included in order to cover the full range of temperature and pressure. Pathways of the mechanism involve the fuel species, iso-octane and n-heptane, and also the lower alkene sub-mechanisms of C_7, C_6 and C_5 species (where the C_4 and below is the part of the base mechanism [5]).

Selected species isomers undergoing same reaction types were lumped. In this lumping procedure, a decision is made whether a distinction between the different isomers is necessary or not. However, a distinction was always made in the reaction coefficients (duplicate reactions with different rate coefficients). The first species that are lumped are the products from Reaction type 12 (Alkyl peroxy radical "RO_2" isomerization). Problems in calculating backward reactions of lumped reactions are avoided, since this reaction class is almost

irreversible. The rate constants of this class are found to be not sensitive for both; shock tube experimental and HCCI engine conditions. All alkenes (C_5, C_6, C_7 and C_8) have been lumped to either linear (C_5H_{10}, C_6H_{12}, or C_7H_{14}) or branched forms (i-C_5H_{10}, i-C_6H_{12}, i-C_7H_{14} or i-C_8H_{16}).

Sensitivity of reaction pathways

The rate coefficients are chosen in accordance with Curran et al. [4]. Differences in the base mechanisms, and in thermodynamic data, made adjustment for some reaction rate coefficients necessary. For this a detailed sensitivity analysis on the reaction types has been performed.

Reaction type 10 (Addition of Alkyl radicals to O_2) and reaction type 23 (O_2QOOH Iso-merization to Ketohydroperoxide + OH) are the most sensitive classes of reactions in terms of their reaction coefficients. We increased the rate constants of both classes by factor 4. This gave the best optimisation of the mechanism for both the shock tube experiments and the engine experiments.

Further, the base mechanism was slightly modified, to include reactions that were found to be important at low temperatures, and to include all branched species that are products of the iso-octane sub-mechanism.

Figure 1: Mechanism

VALIDATION OF MECHANISM

The detailed n-heptane and iso-octane oxidation mechanism has been first validated against the shock tube experimental data from Fieweger et al. [1, 2]. Calculated and experimental ignition delay times have been compared at low and high temperatures. In the negative temperature regime, where the ignition occurs as a two-stage process, we compare in addition the timing of the occurrence of the low temperature oxidation. The mechanism was validated for fuel lean and rich conditions, a range of octane numbers and pressures from 13 bar to 40 bar.

Further validation was done under HCCI engine conditions. NO_x chemistry was included in the mechanism to investigate the influence of rest gas NO_x on ignition timing in HCCI engine. The validation of the mechanism was made for a range of octane numbers and initial temperatures using a zero dimensional HCCI engine model. Experimental data performed at Lund Institute of Technology on a modified Volvo TD100 engine with variable compression ratio and port injected mixture of n-heptane and iso-octane [3] was used.

Constant Volume flow model

Validation of the mechanism was made by comparison between the constant volumes flow model calculations and shock tube experiments from Fieweger et al [1, 2]. The initial temperature range from 700 to 1300 K is set for all the cases. Experiments were considered at 13 to 40 atm, fuel-air equivalence ratios (ϕ) equal to 0.5, 1.0 and 2.0, and RON numbers 0, 20, 40, 60, 80, and 100. In general, there is a good agreement between calculated and experimental ignition delay times. Results for RON 100 and RON 0, ϕ=1, P=40 atm are shown in the figures 2 and 3 as an example.
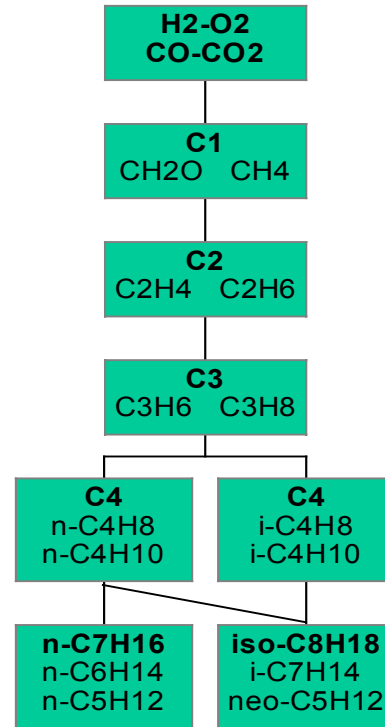
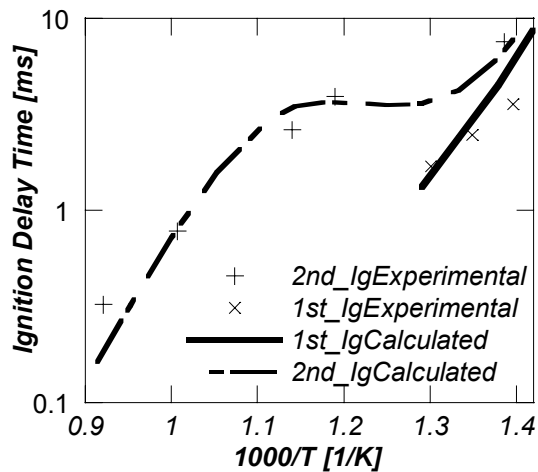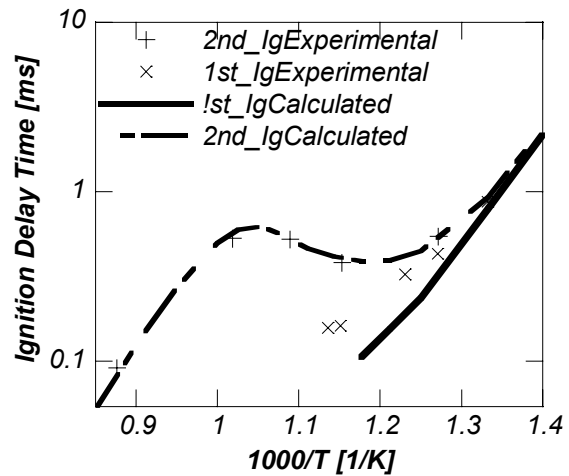*Figure 2: Ignition delay times for iso-octane at P=40 atm and ϕ=1.0.*

Figure 3: Ignition delay time for n-heptane at P=40 atm and ϕ=1.0.

The comparison shows that both the occurrence of the low temperature oxidation reactions (1st ignition delay time) and the final excitation (2nd ignition delay time) is well predicted. The strong increase of the ignition delay with increasing temperature for n-heptane and the weak increase for iso-octane in the negative temperature regime agrees also well with the experiments.

HCCI Engine Model

The mechanism has been further validated against HCCI engine experiments using the same computer program, which was used for the constant volume calculations. For these calculations a zero-dimensional engine model was applied. The model compresses the gas to auto-ignition, using temperature and pressure at a certain crank angle position obtained from engine experiments as initial conditions. Further input parameters of the model are the air-fuel equivalence ratio (λ), the fuel and oxidizer composition, the amount of internal and external EGR, the cylinder wall temperature, the Woschni constants, the chemical kinetic mechanism for actual fuel, and the engine geometry. The output of the model is crank angle resolution, species concentration, cylinder pressure and temperature. Agreement in temperature and pressure profiles (before autoignition occurrence) can be improved by varying the initial conditions of cylinder temperature and pressure and also the air-fuel ratio.

The calculated data from the ignition code is validated against the experimental data, which was provided by Christensen et al., at Lund Institute of Technology [3]. The engine experiments were performed in a Volvo TD100 engine modified to run on one cylinder and with a secondary piston in the cylinder head giving the opportunity to vary the compression ratio. Iso-octane and n-heptane were mixed to achieve various octane numbers. The fuel was supplied via port injection. The charge temperature was varied between 30 and 130 °C. The compression ratio was adjusted between 21.4 and 10.8 in order to have an optimal point of ignition in each case. The validation of the detailed mechanism was performed for different cases of RON. Air-fuel equivalence ratio (λ) was set to 3.0 for all the cases and the engine speed were 1000 rpm. The initial pressure at inlet valve closing (IVC) for the calculations was consequently set to the measured cylinder pressure minus 0.1 bar, the wall temperature was chosen to be 490 K and EGR (5% residual gas) for all the cases. The calculated and the measured cylinder pressure for the two different cases are shown in figures 4 and 5. As we can see in the figure 4 for the RON 100 case at initial temperature of 330 K (at IVC), there is

a good agreement between the detailed mechanism and the experiments; it can be seen in cylinder pressure trace. Ignition occurs a bit early but altogether it follows the experimental data quite well especially in the low temperature region. This pattern of good agreement can be seen in other cases as well such as the case of RON 83 at initial temperature 359 K which is shown in the figure 5.
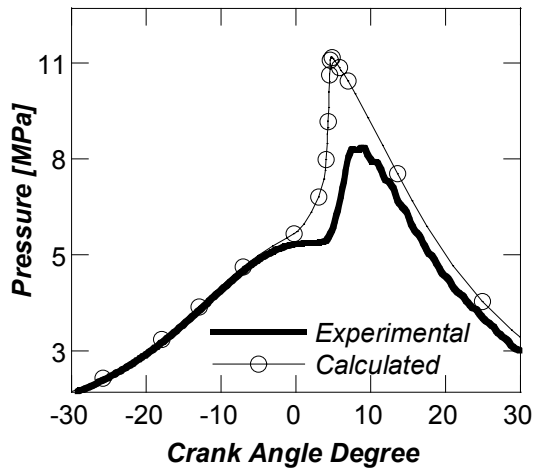

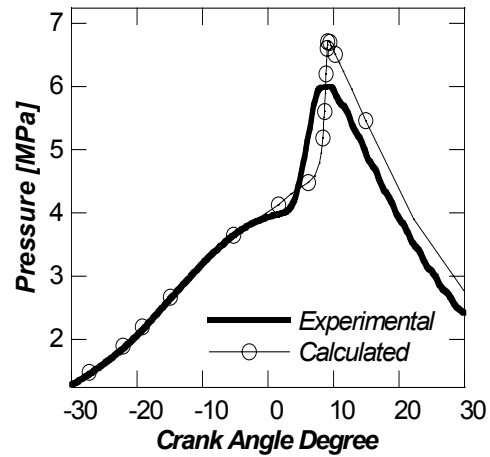*Figure4: Cylinder pressure for RON100 at initial temperature of 330K*

Figure5: Cylinder pressure for RON83 at initial temperature of 359K

CONCLUSION

A detailed reaction mechanism of n-heptane/iso-octane oxidation with special focus on optimising it to the HCCI engine conditions has been presented. The mechanism was constructed using a reaction type concept as used for automatic mechanism generation. The size of the mechanism is limited by making use of species lumping. The developed mechanism has been validated against the experimental data from shock tube and HCCI engine experiments. The ignition delay is well predicted for the shock tube experiments, at low and high temperatures and at low and high octane numbers. In the negative temperature regime the occurrence of low temperature oxidation reactions is well predicted. For the HCCI engine experiments there has been a significantly good agreement between model predictions and experimental data. This work provides a detailed kinetic mechanism for mixture of n-heptane and iso-octane containing a reasonable low number of the species and reactions. This item of the mechanism provides a good basis for further reduction of the mechanism, using sensitivity, reaction flow, and lifetime analysis.

REFERENCES

1. Blumenthal R., Fieweger K. and Adomeit G. Self-ignition of SI. engine model fuels: A shock tube investigation at high pressures. *Combustion and Flame*, **109**:599-619 (1997).

2. Ciezki K. and Adomeit G. Shock-tube investigation of self-ignition of n-heptane-air mixtures under engine relevant conditions. *Combustion and Flame*, **93**:421-433 (1993).

3. Christensen M., Hultqvist A. and Johansson B. Demonstrating the Multi Fuel Capability of a Homogeneous Charge Compression Ignition Engine with Variable Compression Ratio. *SAE* 1999-01-3679 (1999).

4. Curran H.J., Gaffuri P., Pitz W.J., and Westbrook C.K. A comprehensive modelling study of n-heptane oxidation. *Combustion and Flame*, **114**:149-177(1998).

5. Warnatz J., Maas U. and Dibble R.W. *Combustion*, Springer Verlag publications, Berlin (1996).