Efficient lumping technique for the automatic generation of n-heptane and iso-octane oxidation mechanism

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Introduction

The future demands of engine development are to have highly efficient engines with almost no emissions. It is a global trend for the automotive industry to look forward in this area, mainly due to fact that the demands of energy consumption are increasing more and more and almost 90% of this came from the fossil fuels, which are becoming obsolete from their natural resources. New sources of energy and highly fuel-efficient existing conventional engines with low emissions are the demands of future. Low fuel consumption and increased efficiency is desirable both due to considerations of pollutant emissions (CO_2 production is contributing to the greenhouse effect) and economy (cost effectiveness). This all leads to the continuation in developing a better understanding of the combustion process, specially the oxidation process of large hydrocarbon fuels such as n-heptane and iso-octane over a wide range of engine operating conditions. These primary reference fuels (PRF) oxidation mechanisms are quite complex and large in terms of species and reactions such as 1033 species and 8476 reactions for example. An urgent need is there to reduce the size and complexity of the mechanism in order to implement this mechanism in the three dimensional computational fluid dynamics codes which are used to study different engine parameters and combustion processes and yet having the same reliability and results as the detailed ones. This could be done by generating a semi-detailed mechanism first and then its simplification by lumping process and further on by necessity analysis. Some previous works have been done on lumping procedures by Ranzi et al.[1] and Fournet et al.[2]

Mechanism

This work has been done to generate a semi-detailed mechanism for n-heptane and iso-octane oxidation mixture. The construction of the mechanism is systematically in accordance with Curran et al.[3] using the reaction classes and rate constants suggested by the authors as a reference. Intermediate reactions, considered of low importance for the timing of ignition, are simplified substantially by optimizing it. The mechanism contains the pathways 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[4]). The detailed mechanism contains 241 species and 1905 reactions. Lumping procedure has been applied on n-heptane mechanism which reduces the mechanism size to 223 species and 1869 reactions including iso-octane sub-mechanism. In the present mechanism all the reaction paths which are known to be pertinent from both high and low temperatures are included in order to cover the full range of temperature and pressure. To reduce the mechanism size in order to make it faster and fewer complexes, its reduction has been done first by lumping technique and further on by necessity analysis. Lumping is the procedure of substituting different species of similar molecular structure into one species called "lumped species". The new lumped species is related not only to the original species concentrations but also on the important parameters. Necessity analysis is the process to calculate the contribution of reaction steps to the production rate of necessary species and hence eliminate the non-important reactions. The mechanism is used in study the effect of elevated pressure and temperature of the n-heptane and iso-octane oxidation mixture in engine for different operating conditions.

The calculations have been performed for the 1st and 2nd ignition delay times using the constant volume flow model and then also Homogenous Charge Compression Ignition (HCCI) engine model in- house ignition code,[5] for both detailed and lumped mechanisms.

Lumping Procedure. The species of similar molecular structure and position of H-abstraction from secondary sites are lumped together. This is because the rate parameters and thermodynamic data vary slightly between different structures of the similar ring size species. At first four species of similar ring size 5, are lumped together to form new lumped species. The rate constants were calculated for each lumped species reactions individually for both forward and backward reactions. The concentration of new lumped species is then balanced by dividing the backward rate constants as shown in equation (1) for each individual reaction with the number of species lumped together which is four in this case. Similar approach has been made to lump the other species of the same ring sizes and molecular structure and further on in other reaction types of the mechanism as well. **Figure 1** is showing the concentration profiles of the lumped species against the four added species. **Figure 2** is showing the product species before and after lumping.

$$\frac{d[5r-HEOOH]}{dt} = \sum\left([2-C_7H_{15}O_2]+2\times[3-C_7H_{15}O_2]\right)k_{1f} + [4-C_7H_{15}O_2]k_{2f} - \left([5r-HEOOH]\,k^*_{1b}/4 + [5r-HEOOH]\,k^*_{2b}/4\right) \quad \rightarrow eq(1)$$

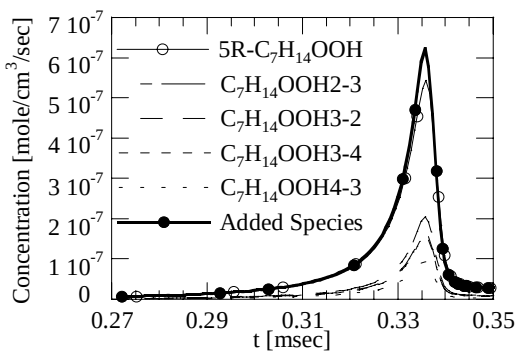

Figure 1 Concentration of new lumped species 5R-C7H14OOH is plotted by shifting the ignition delay time 0.034 sec to have better view against the added concentration of four species at initial pressure set to 40 bar, phi is 1.0 and initial temperature is 800 K.

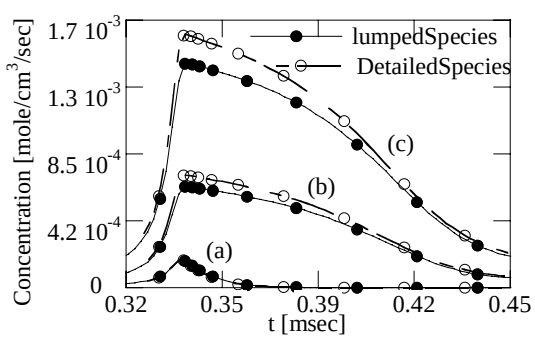

Figure 2 Concentration profile of a product species N-$C_4CH_9COCH_2$ (a), N-C_4H_9CHO (b) and N-C_3H_7CHO (c) before and after lumping at initial temperature of 800 K.

Validation

The lumped reaction model and the semi-detailed n-heptane and iso-octane mixture oxidation mechanism have been first validated against the shock tube experimental data from Fieweger et al.[6]and Ciezki et al.[7] 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. The initial temperature range from 700 to 1300 K is set for all the cases. Fuel-air equivalence ratio (ϕ) is equal to 0.5, 1.0 and 2.0, and Research Octane Number (RON) is 0, 20, 40, 60, 80, and 100. In general, there is a good agreement between the semi-detailed mechanism calculations and experimental ignition delay timings and then lump mechanism calculation fits well with the detailed one. Result for RON 0, ϕ=1 and P=40 atm is shown in the **Figure 3** as an example. This verifies the efficiency of the lumping technique.

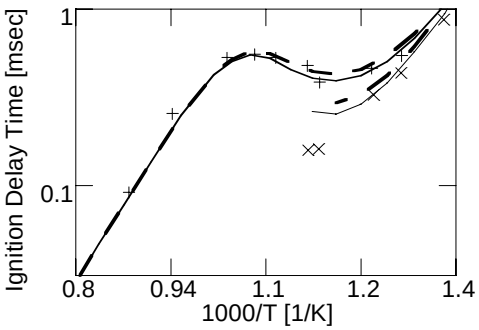

Figure 3 Ignition delay time for n-heptane at P=40 atm and ϕ=1.0. Experimental data (symbols). Calculated data (lines). 1st Ignition (×), 2nd Ignition (+). Detailed mechanism straight line. Lumped mechanism dashed lines.

The mechanism has been further validated against HCCI engine experiments using the same computer program[5], 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.

The calculated data from the ignition code is validated against the experimental data, which was provided by Christensen et al.[8] 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 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 semi-detailed mechanism calculation and the measured cylinder pressure for the RON 83 case is shown in **Figure 4**, 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 and then it is a good agreement between detailed and lumped mechanism calculations. Ignition occurs at the same Crack Angle Degree (CAD) as experiment. The maximum pressure from the calculation is a bit high as compared to the experiment due to the assumption of homogeneity of the model[5], but altogether it follows the experimental data quite well especially in the low temperature region.

Conclusions

A semi-detailed reaction mechanism of n-heptane and iso-octane oxidation with special focus on optimizing it to the ignition delay timings of the shock tube experimental data from Fieweger et al.[6] and HCCI engine conditions has been presented. The mechanism was constructed using a reaction type concept as used for the automatic generation of mechanism. The size of the mechanism is limited by making use of lumping. This is very simple and straight forward approach which works very efficiently to generate automatically lumped mechanism, which has the same, performance as the detailed mechanism. 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 reactions is well predicted. For the HCCI engine experiments there has been a significantly good agreement between model predictions and experimental data and in all the cases there is a good agreement between the lumped and detailed mechanism calculations. This work provides a detailed kinetic oxidation mechanism for mixture of n-heptane and iso-octane containing a reasonable low number of species and reactions, which provides a good base for further reduction of the mechanism, using sensitivity, reaction flow, lumping and necessity analysis.

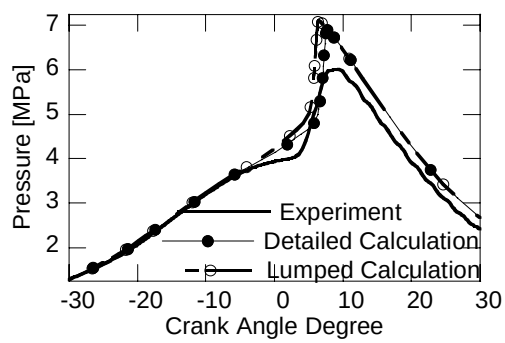

Figure 4 Cylinder pressure for RON83 at initial temperature of 359K

References

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