Kinetic modelling study of cyclo-alkane oxidation for transportation fuels

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Abstract. Cyclo-alkanes are the major constituents of hydrocarbons in market fuels such as petrol, diesel, and aviation fuels. Diesel fuels derived from bituminous sands have up to 30% of cyclo-alkanes. Besides that, cyclo-alkanes play a vital role in soot formation as they yield aromatic compounds through dehydrogenation. Thus, it is crucial to include cyclo-alkanes in the formulation of multi-component diesel surrogate fuel models. As a consequence, better prediction in the combustion and emission simulations can be achieved. In this study, a reduced cyclo-alkane kinetic model, namely methyl-cyclohexane (MCH) is developed for diesel engine applications. Here, the detailed MCH model with 1,540 species is served as the base model. The reduced MCH model is derived by performing mechanism reduction using five-stage reduction scheme. Accordingly, a reduced MCH model with 86 species is obtained after the reduction procedures. A 94% reduction in the mechanism size has been successfully achieved. Next, the reduced MCH model is validated against the detailed model with respect to ignition delay (ID) timings in zero-dimensional (0-D) simulations. Computed results by the reduced MCH model are in close agreement with the detailed model, with maximum deviation recorded at 33%. The reduced MCH model developed is ready to be used to represent cyclo-alkanes in multi-component diesel surrogate fuel models.

1. Introduction

Diesel engines are widely used in the industrial sector and transportation sector owing to their superior thermal efficiency. However, the main concern about the use of diesel engines is the production of exhaust emissions such as carbon dioxide (CO2), unburned hydrocarbon (UHC), particulate matter (PM), carbon monoxide (CO) and nitrogen oxides (NOx). Diesel exhaust has harmful impacts on the environment and human health. For instance, CO2 and NOx are greenhouse gases that accelerate global warming [4]. In addition, PM is a poisonous particulate that is highly inhalable owing to its small particle size (<2.5 μm). In order to meet the complex needs of society and strict emission regulations set by the government, it is necessary to continuously improve the combustion and emission performance of diesel engines.

Numerical modelling especially computational fluid dynamics (CFD) simulation is a favourable approach for the investigation studies of the complex combustion and pollutant formation of the engines. In the past decades, detailed chemical kinetic models are often incorporated into CFD simulation to explore the microscopic chemical processes and the macroscopic physical processes [9]. However, detailed models recently developed are not feasible to be used due to large number of species which require high computational expenses and would eliminate the cost-effective advantages of CFD simulation. Therefore, mechanism reduction techniques are introduced to eliminate the
unimportant species from detailed models while retaining adequate detail and accuracy. With advances in these techniques, the reduced models produced are able to achieve consistency between simulation and experimental results as well as minimise computational time.

Generally, actual diesel fuels contain ~ 30 % of cyclo-alkanes. The presence of cyclo-alkane in fuel combustion plays an important role in soot formation process as it produces aromatic compounds which are important for the formation of soot precursor [1-2]. It is noted that the reduced cyclo-alkane model is scarce to date. Thus, this study aims to develop a reduced cyclo-alkane surrogate fuel model.

2. Methodology

2.1 Detailed MCH Model

Here, methyl cyclohexane (MCH) is employed here as its fuel representative. An outline of the reduced MCH model development plan is shown in Figure 1. Here, an integrated five-stage kinetic reduction scheme introduced by Poon, et al. [3-5] is applied to construct a reduced MCH model based on the detailed model developed by Weber, et al. [6] which contains 1,540 species with 6,498 reactions. The detailed model was well validated against experimental measurements for ID timings in rapid compression machine and shock tube conditions under an extensive range of conditions [7-9]. Further details of the numerical settings and operating conditions applied in this study can be obtained in [10].

![Figure 1. Overall flow of the reduced MCH model development.](image)

2.2 Chemistry and Thermodynamic Data Inputs

The input data file for the chemical kinetic models consist of all the elementary reactions and key chemical species which involve in the gas-phase chemistry systems, along with their important thermodynamic properties. On the other hand, the thermodynamic data files consist of all the physical properties of each chemical species and they are used to calculate the specific heats, enthalpies, and entropies of each species.

3. Construction of Reduced MCH Chemical Kinetic Model

Firstly, the Directed Relation Graph (DRG) method with Error Propagation using Dijkstra’s algorithm is applied as the first reduction phase. The selected target species for the reduction procedure are the typical key emission species as well as intermediate species which are vital in chain branching reactions.

Subsequently, isomer lumping is carried out in order to group all the isomers with same transport and thermodynamic properties together to form a single pseudo species. Apart from this, isomers which have very low production rate are eliminated as well.

Next, the reaction pathways during fuel oxidation are assessed and reactions with very low normalised sensitivity are removed as their effects on the production of connecting species are insignificant. Also, this reduction phase would further reduce the size of the reduced kinetic model too. Besides, DRG is performed to eliminate species which have off tracked the reaction paths due to isomer lumping and reaction path analysis.

Finally, adjustment of the A-factor reaction rate constants is carried out to optimise the reduced model in order to improve the ignition delay (ID) timing predictions. A final reduced MCH model which comprises only 86 species is successfully developed using the integrated kinetic reduction scheme.
4. Model Validations

The reliability of the reduced model is examined by performing 0-D simulations in CHEMKIN-PRO software using closed homogeneous batch reactor model. Simulated results by the reduced model are compared with those of detailed model. Typically, the maximum tolerable deviation, $D_{MAX}$ for large-scale mechanism reduction is around 30\% - 50\% [11-14]. Here, $D_{MAX}$ is set to 40\%.

Results for ID timing predictions under auto-ignition conditions are shown in Figure 2. It is observed that the reduced model can reproduce the ID timing predictions of the detailed model with reasonably good accuracy in spite of its 94\% reduction in number of species. The computed results of the reduced model and detailed model exhibit close agreement across a wide range of operating conditions. The maximum deviation in ID timings is recorded at 33\%.

![Computed ID timings by the detailed model (lines) and the reduced models (symbols) at pressure of 60 bar and $\phi$ of (a) 0.5, (b) 1.0, (c) 2.0.](image-url)
5. Conclusion

In this study, a reduced MCH model with 86 species is successfully formulated from the detailed MCH model with 1,540 species. A 94% reduction in mechanism size is achieved. The reduced model developed is well validated against detailed model in 0-D simulations using the closed homogeneous batch reactor model. Computed results by the reduced model are in good agreement with the detailed model. The maximum deviation in ID timings is maintained to within 33%. The five-stage reduction scheme has shown to be efficient to perform large-scale mechanism reduction. Besides, the compact reduced model developed here is able to provide satisfactory results despite simplified chemistry.

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