

Development and Validation of Chemical Kinetic Mechanism Reduction Scheme for Large-Scale Mechanisms

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ABSTRACT

This work is an extension to a previously reported work on chemical kinetic mechanism reduction scheme for large-scale mechanisms. Here, Perfectly Stirred Reactor (PSR) was added as a criterion of data source for mechanism reduction instead of using only auto-ignition condition. As a result, a reduced n-hexadecane mechanism with 79 species for diesel fuel surrogate was successfully derived from the detailed mechanism. Following that, the reduced n-hexadecane mechanism was validated under auto-ignition and PSR conditions using zero-dimensional (0-D) closed homogeneous batch reactor in CHEMKIN-PRO software. Agreement was achieved between the reduced and detailed mechanisms in ignition timing predictions and the reduced n-hexadecane mechanism was able to reproduce species concentration profiles with a maximum error of 40%. Accordingly, two-dimensional (2-D) Computational Fluid Dynamic (CFD) simulations were performed to study the spray combustion phenomena within a constant volume bomb. Both non-reacting and reacting conditions were applied in this study. Liquid and vapor penetration lengths were replicated for non-reacting diesel spray. For reacting diesel spray, both ignition delay and lift-off length were simulated. The simulation results were then compared to the experimental data of Sandia National Laboratories and No. 2 Diesel Fuel (D2) was designated as the reference fuel. Both liquid and vapor penetrations for non-reacting condition were well-matched, while ignition delay was advanced by 17.95% with 7.18% longer lift-off length for the reacting condition.

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INTRODUCTION

Of late, there is growing interest to better understand the combustion of large hydrocarbons especially n-hexadecane. It is the primary reference fuel for diesel combustion with cetane number of 100, allowing this value to be varied over a wide range when blended with other fuels. Besides, it is also a large n-alkane fuel which plays an important role in low temperature reactivity and early ignition kinetics. According to the research carried out by Westbrook et al. [1], the combustion characteristics of the large n-alkanes such as n-octane to n-hexadecane (nC_8 - nC_{16}) are remarkably comparable. Although their ignition and oxidation are not identical, they are adequately similar such that the n-alkanes are interchangeable and can be used in simulations for a wide range of applications. While n-heptane [2] has been successfully implemented as a single-component diesel fuel surrogate in many application simulations, effort is now focused on n-hexadecane which is a better representative of large n-alkane component in the real diesel fuels especially in terms of the ignition rate and physical properties [3]. The boiling point of n-hexadecane extends to a wide range of the distillation

curve of the D2 fuel and it is also able to model the vaporization characteristics of the D2 fuel. n-Hexadecane is a less volatile fuel and its volatilities extend a substantial portion of the D2 fuel volatility range [4]. Moreover, it possesses longer liquid penetration length as compared to short-chain hydrocarbons such as the n-heptane. It is evident that the liquid penetration of diesel fuel jet is significant in enhancing in-cylinder processes of diesel engines [5]. The liquid-phase penetration is essential in promoting air/fuel mixing and consequently affects the levels of engine-out emissions. Based on these arguments, n-hexadecane is deemed as a good diesel surrogate model.

However, it is common to assume that better agreement can be achieved if fuel compositions and cetane number of the surrogate fuel match that of the real diesel fuel at a typical range of 40 - 56 [6,7]. For this reason, n-heptane which has a cetane number of ~55 is frequently employed as a single component diesel surrogate. Nevertheless, the ignition characteristics of n-heptane might not be similar to the commercial diesel fuels throughout a wide range of speed/load

conditions as reported in some studies [8]. Additionally, n-heptane is a more volatile fuel and this gives rise to significant variances in liquid spray penetration and vaporization, which subsequently affect the local air/fuel ratio. Therefore, cetane number is not the only consideration when proposing a diesel fuel surrogate model for engine applications. Based on this, it is reasonable to appraise n-hexadecane as a possible diesel surrogate model for diesel engine applications in spite of its high cetane number.

Based on the aforementioned discussions, n-hexadecane is chosen as a single component diesel surrogate in this study to examine its performance in multi-dimensional CFD simulations. In the previous work [9], a reduced n-hexadecane mechanism with 49 species for diesel surrogate was derived using an integrated mechanism reduction scheme. Validation of the reduced mechanism was performed by comparing the ignition delay timing predictions with those of the detailed mechanism. Although ignition delay timing predictions were well-matched, species concentration profiles of the major species were not reproduced accurately. Set against this background, improvement and validation of the mechanism reduction scheme are carried out here, followed by 2-D spray combustion modeling studies.

IMPROVEMENT OF MECHANISM REDUCTION SCHEME

In the previous work, a five-stage mechanism reduction scheme was introduced for large-scale mechanism reduction. The reduction procedure is shown in [Figure 1](#).

By implementing the mechanism reduction scheme in [Figure 1](#), a reduced n-hexadecane mechanism with 49 species and 97 elementary reactions was successfully derived in the previous work. Nonetheless, validation effort of the surrogate model was insufficient to evaluate the robustness and applicability of the reduced mechanism generated from the implemented reduction scheme. Thus, investigation was conducted and it was perceived that species concentration profiles of the reduced mechanism did not agree well with those of the detailed mechanism. Consequently, in this reported work, the mechanism reduction scheme was improved by including PSR condition as an additional data source for mechanism reduction aside auto-ignition condition during the first stage of DRGEP reduction.

The detailed n-hexadecane mechanism [1] comprising 2116 species and 8130 elementary reactions was applied in the first stage of mechanism reduction. Operating conditions such as equivalence ratio of 0.5 - 2, initial pressure of 40 - 80 bar and initial temperature of 650 - 1350 K were sampled for auto-ignition. On the other hand, initial temperature of 300 K as well as residence time covering the ignition and extinction ranges

were sampled for PSR. Similar to the former exercise, the pressure range applied here was chosen based on the in-cylinder pressure values during the main fuel injection event for light-duty direct-injection diesel engines.

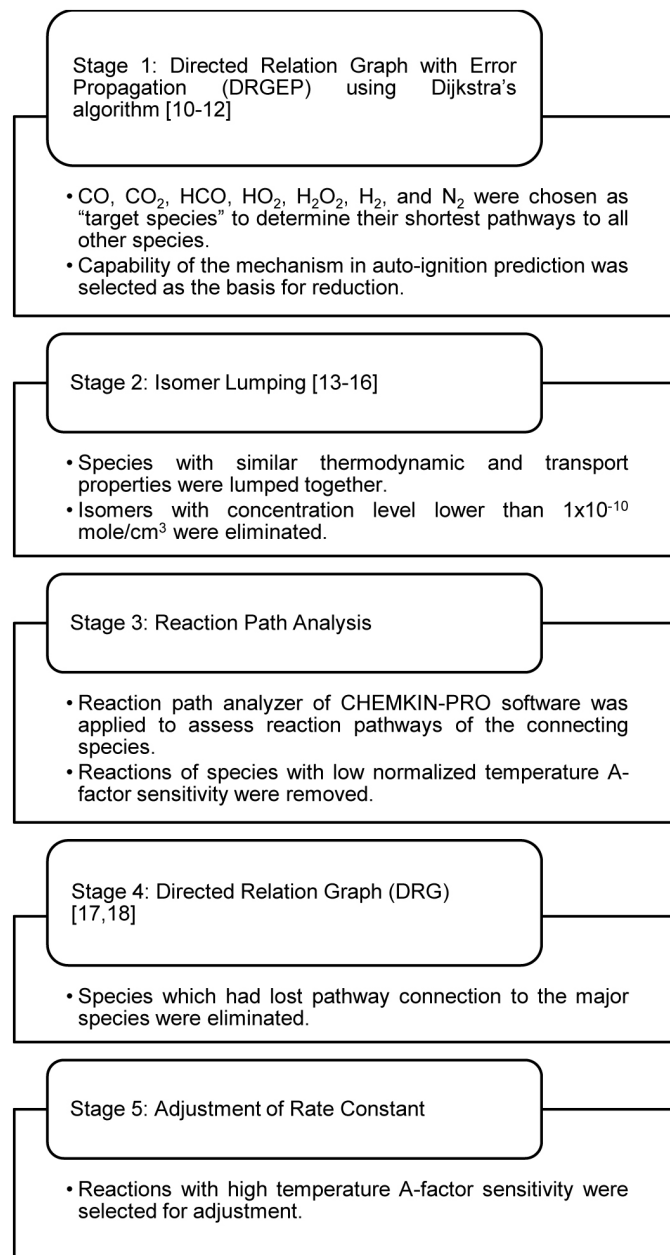


Figure 1. Flow chart of the five-stage mechanism reduction scheme.

During the DRGEP reduction, a reduced mechanism with 447 species was produced. In comparison to the previous reduction work, difference in the resulting mechanism size was relatively minor in which reduced mechanism with 425 species was obtained in the previous work.

Once the detailed mechanism was reduced using DRGEP approach, isomers which were maintained in the reduced mechanism were grouped together according to their thermodynamic and transport properties. Some of the significant isomer groups are demonstrated in Table 1.

Table 1. Isomer lumping.

Isomer Group	Isomers
$C_{16}H_{33}$	$C_{16}H_{33-2}$, $C_{16}H_{33-3}$, $C_{16}H_{33-4}$, $C_{16}H_{33-5}$, $C_{16}H_{33-6}$, $C_{16}H_{33-7}$, $C_{16}H_{33-8}$
$C_{16}H_{33}O$	$C_{16}H_{33}O-2$, $C_{16}H_{33}O-3$, $C_{16}H_{33}O-4$, $C_{16}H_{33}O-5$, $C_{16}H_{33}O-6$, $C_{16}H_{33}O-7$, $C_{16}H_{33}O-8$
C_8H_{17}	C_8H_{17-1} , C_8H_{17-2} , C_8H_{17-3} , C_8H_{17-4}

Accordingly, major reaction pathways during the fuel ($C_{16}H_{34}$) oxidation process were analyzed using the reaction path analyzer of CHEMKIN-PRO software and they are illustrated in Figure 2. The reaction pathways were assessed based on the auto-ignition and PSR criterions. The reaction pathway on the left in Figure 2 had been included in this newly developed mechanism as this pathway was not considered in the previous work. It is found that predictions of ignition delays as well as species concentration profiles have been improved. However, this also causes a dramatic increment in mechanism size.

Moreover, based on the reaction pathway analysis, it is observed that H-atom abstractions on the fuel ($C_{16}H_{34}$) by OH, H and O radicals are more dominant as compared to thermal decompositions of the fuel for fuel-lean conditions throughout the temperature range. This importance also increases with temperature. In contrast, for fuel-rich conditions, thermal decompositions of the fuel are more prevalent especially in high temperature. On the other hand, for stoichiometric conditions, H-atom abstractions are prevailing for low temperature whereas thermal decompositions are more significant when temperature is high. It is observed that reaction such as ' $C_9H_{19-1} + C_7H_{15-1} = C_{16}H_{34}$ ' is not incorporated in the 49-species mechanism and this reaction plays an important role during thermal decomposition. Therefore, by including reactions from this class, ignition delay predictions for high temperature have been improved in this work.

Next, tuning of the reaction rate constants was required since species lumping as well as species elimination processes would affect the ignition delay timings and species concentrations throughout the combustion process. The adjusted A-factor values for the reduced n-hexadecane mechanism are shown in Table 2.

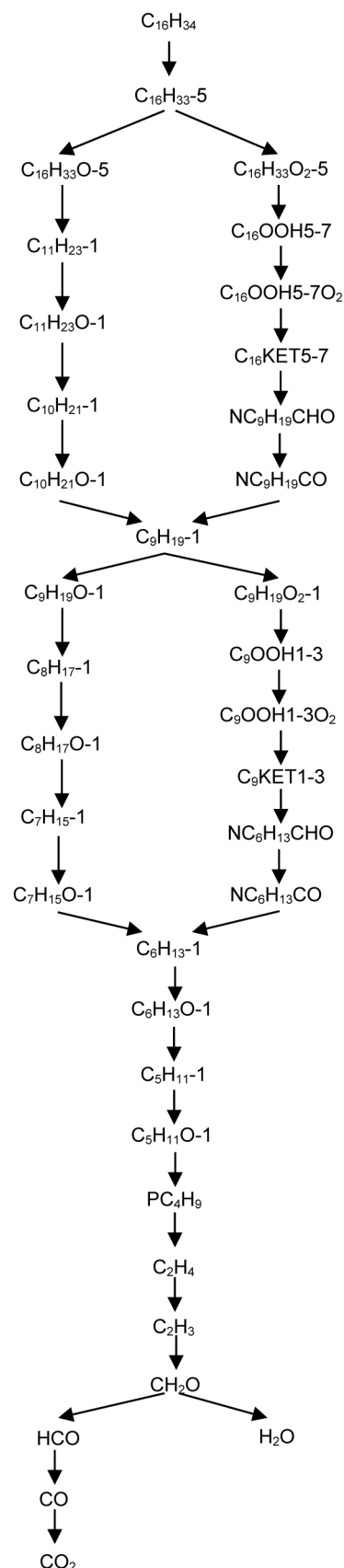


Figure 2. Main reaction pathways of $C_{16}H_{34}$ oxidation.