

Evaluation and Development of Chemical Kinetic Mechanism Reduction Scheme for Biodiesel and Diesel Fuel Surrogates

Hiew Mun Poon, Hoon Kiat Ng, and Suyin Gan
University of Nottingham Malaysia Campus

Kar Mun Pang and Jesper Schramm
Technical Univ of Denmark

ABSTRACT

The aim of this study is to evaluate the existing chemical kinetic mechanism reduction techniques. From here, an appropriate reduction scheme was developed to create compact yet comprehensive surrogate models for both diesel and biodiesel fuels for diesel engine applications. The reduction techniques applied here were Directed Relation Graph (DRG), DRG with Error Propagation, DRG-aided Sensitivity Analysis, and DRG with Error Propagation and Sensitivity Analysis. Nonetheless, the reduced mechanisms generated via these techniques were not sufficiently small for application in multi-dimensional computational fluid dynamics (CFD) study. A new reduction scheme was therefore formulated. A 68-species mechanism for biodiesel surrogate and a 49-species mechanism for diesel surrogate were successfully derived from the respective detailed mechanisms. An overall 97% reduction in species number and computational runtime in zero-dimensional closed homogeneous batch reactor simulations was achieved for both reduced mechanisms. Accordingly, the reduced n-hexadecane mechanism was integrated into a CFD solver to simulate spray combustion in a constant volume bomb. However, the ignition delay was underestimated by 0.04 ms owing to its high cetane number. This corresponds with recent study which demonstrates that n-hexadecane alone is unsuitable as a single-component diesel surrogate. Thus, fuel blending is recommended here to match the diesel fuel kinetics and compositions. As such, the reduced n-hexadecane mechanism is expected to be a better representative of surrogate component for various transportation fuels such as biodiesel. Additionally, it can be applied to predict the reactivity of other n-alkane or interchange with one another for kinetic and CFD simulations.

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INTRODUCTION

With the advancement in fuel processing technology, biofuels have made considerable in-roads as a viable alternative to fossil fuel in order to alleviate growing concerns on environmental pollution and depleting oil reserves. Nevertheless, continued reliance on fossil fuels as the main energy source is expected in the foreseeable future although there are uncertainties surrounding their future availability [1,2]. For ground transportation purpose, there is an increasing trend of utilizing blends of diesel and different biofuels to power most of the compression ignition engines. As fuel composition is set to become more varied which will affect fuelling strategy and all engine technologies, research into in-cylinder combustion of these fuel blends offers many

untapped opportunities for further development. In line with this, there are considerable interests within the automotive industry to better understand the complex processes governing reacting spray jets of diesel-biodiesel fuel blends, which resulted in the observed engine-out measurements. For this reason, detailed insights into the combustion and pollutant formation events for both diesel and biodiesel fuels inside the combustion chamber are essential. Numerical modeling, particularly the Computational Fluid Dynamics (CFD) simulation has been shown as the more cost-effective approach than experimental measurements to facilitate the investigation into these complex in-cylinder processes. For successful simulation of dynamic reacting sprays with appropriate representation of key species and reactions, the size of chemical kinetic mechanism describing this are

typically large. Despite the outstanding capability in fuel reactivity prediction, employment of such massive mechanisms in CFD computation is certainly too computing intensive and can defeat the cost-effective benefit associated to CFD. Thus, numerous mechanism reduction techniques have been introduced in order to produce compact yet comprehensive reduced mechanisms to overcome the time-cost limitation. It is important that further improvement and refinement are made to the reduction techniques to cope with larger mechanisms in line with the current trend of development in this area for successful CFD simulations. Set against this background, the focus of this study is to appraise the different mechanism reduction techniques currently available. This is followed by the formulation a reduction scheme and its application on large surrogate models for both diesel and biodiesel fuels.

In the following sections, the methodology adopted in this work is first presented. Next, common mechanism reduction techniques are reviewed and then used to perform mechanism reduction for a biodiesel surrogate mechanism. A comprehensive validation exercise is carried out under shock tube conditions and performance of each technique is assessed accordingly. Following that, a new mechanism reduction scheme is designed and implemented to generate reduced mechanism for a diesel surrogate model. While both biodiesel and diesel surrogates selected here are considered as large-scale mechanisms, similar level of reduction is expected for both. Thus, reduction of diesel surrogate mechanism is performed using the new reduction scheme instead of repeating the same validation procedure for the biodiesel surrogate mechanism reduction using existing reduction techniques. After an appropriate validation study is completed, performance of the generated reduced mechanism for diesel surrogate with the CFD modeling is further evaluated through the combustion simulations.

METHODOLOGY

First and foremost, species and reaction elimination techniques are applied to perform mechanism reduction for the biodiesel surrogate. The prominent methods under this category are Directed Relation Graph (DRG) [3,4], DRG aided Sensitivity Analysis (DRGASA) [5,6], DRG with Error Propagation (DRGEP) [7] as well as DRG with Error Propagation and Sensitivity Analysis (DRGEP-SA) [8, 9, 10]. These reduction methods are commonly favored for huge mechanism reduction owing to its straightforward chemical analysis as well as its simple application to prevailing kinetic modeling codes (e.g. CHEMKIN-PRO code). As a consequence, MATLAB program is employed to execute numerical computation for each reduction algorithm and capability of the mechanism in predicting auto-ignition is designated as the basis for reduction. Following that, the reduced mechanism established from each reduction methodology is validated against the detailed mechanism with respect to ignition delay (ID) timings using zero-

dimensional (0-D) closed homogeneous batch reactor in CHEMKIN-PRO software. The maximum allowable induced error in ID timings, $V_{AL,MAX}$ applied here is 40%. Next, performance of each reduction technique is evaluated with respect to the efficiencies in reduction scale, computational runtime (T_C) and accuracy in ID timing predictions. In addition, a new reduction scheme is implemented for further reduction of biodiesel surrogate. Lumping method and reaction path analysis are integrated into the new reduction scheme. Subsequently, the newly developed reduction scheme is employed to perform mechanism reduction for n-hexadecane which is selected as the diesel surrogate in this work. Similar to the former exercise, ID timings of the reduced mechanism for diesel surrogate are compared with those of the detailed mechanism. Lastly, the validated reduced mechanism for diesel surrogate is applied to simulate spray combustion in a constant volume bomb using OpenFOAM software and simulation results are compared with the data from experimental study.

REVIEW OF CURRENT MECHANISM REDUCTION TECHNIQUES

According to the research carried out by Lu et al. [3,4], a systematic mechanism reduction algorithm namely DRG is developed. It is noted that determination of the unimportant elementary reactions that contribute to insignificant species production rate is fairly straightforward and simple. However, to identify and subsequently remove the unimportant species due to coupling of species is challenging. For instance, if there exist sturdy connections from a species to another two strongly coupled species respectively but they do not appear together in any reaction, they are considered to be strongly coupled to each other as well. With the existence of such couplings, elimination of a single species from the detailed mechanism may involve elimination of a group of species that possesses strong connection to it. Thus, on the contrary, if a species is required to be kept, then the entire group has to be retained too. The connectivity measure between two species, say species x and species y , is defined by the following equation:

$$r_{xy} = \frac{\sum_{i=1, N_R} |v_{x,i} \omega_i \delta_{yi}|}{\sum_{i=1, N_R} |v_{x,i} \omega_i|} \quad (1)$$

r_{xy} is the species coupling coefficient (normalized contribution of species y to the production rate of species x) while $v_{x,i}$ is the stoichiometric coefficient of species x . ω_i is the net production rate of i^{th} elementary reaction and N_R is the total number of elementary reactions in the mechanism. δ_{yi} denotes the participation of species y in i^{th} elementary reaction and it can be expressed as follow:

$$\delta_{yi} = \begin{cases} 1, & \text{if the } i^{\text{th}} \text{ elementary reaction involves species } y; \\ 0, & \text{otherwise;} \end{cases} \quad (2)$$

By applying Equation 1 and 2, a universally specifiable threshold value, E_t normalized between 0 and 1 is attained [3]. Species with r_{xy} smaller than the desired E_t are then removed. As such, the upper error bound for the reduced mechanism is stated simultaneously and these features enable the reduction algorithm to be applicable in wider range of parametric space. Other than that, one of the main benefits of DRG reduction is that it manages to identify all the candidate reduced mechanisms with the time linearly proportional to N_R in detailed mechanism. As compared to other species elimination methods such as reaction rate analysis and Jacobian analysis [11, 12, 13], DRG does not involve iterative process and thus it significantly reduces the time cost for the reduction process.

On the other hand, since DRG assumes upper-bound error propagation in the graph-searching procedure, reduced mechanisms developed by DRG are normally not nominal. Therefore, DRGASA is derived by Zheng et al. [5], which is an extended methodology of DRG to further reduce species set to the minimal size. As DRG retains species set with strong coupling, it is said that not every species in the species set is equally significant to the main species as well as global parameters. There is still a possibility to remove some of those species that have minor effects on other species. Therefore, brute-force sensitivity is introduced to identify the entire set of eliminable species. However, the reduction process is computationally expensive especially when greater total number of species, N_S is considered. For instance, if auto-ignition is selected as the basis of reduction, all the conditions for auto ignition are required to be tested in the sensitivity phase. Apart from that, DRGASA is unable to remove all the unimportant species in the reduced mechanism since it utilizes DRG as first stage reduction which does not take consideration of distance from targets.

Nonetheless, based on the studies carried out by Pepiot et al. [7], several drawbacks of DRG reduction method have been pointed out. Although DRG utilizes species coupling coefficient to resolve the error induced by removal of a single species to the production rate of another species, the value is yet not directly correlated to an error measure. Additionally, DRG assumes that every selected species is equally significant and hence the group of strongly coupled species has to be fully retained, which may not be necessary. Therefore, a new method namely DRGEP is proposed to overcome the weaknesses of DRG. DRGEP has modified the approach of DRG by introducing a generalized coupling coefficient based on error propagations. Attention is paid on the transmission of error from a species to the targets. The dependency of a species on another is based on its impact to

the total production or consumption rate and it is described by the Direct Interaction Coefficient (DIC) below:

$$r_{xy} = \frac{|\sum_{i=1}^{N_R} v_{x,i} \omega_i \delta_{yi}^t|}{\max(P_x, C_x)} \quad (3)$$

P_x is the overall production rate of species x whereas C_x is the overall consumption rate of species x and they are expressed as:

$$P_x = \sum_{i=1}^{N_R} \max(0, v_{x,i} \omega_i) \quad (4)$$

$$C_x = \sum_{i=1}^{N_R} \max(0, -v_{x,i} \omega_i) \quad (5)$$

On top of that, selected species are no longer equally imperative whereby interrelated species that are situated far from each other might be more important than those directly connected to the targets. An Overall Interaction Coefficient, R_{xy} , which is defined as the maximum of all dependency pathways for all species relative to the targets will eventually be taken into account in the reaction state:

$$R_{xy} = \max_{\text{all path } p} \left(\prod_{j=1}^{N_S-1} r_{s_j s_{j+1}} \right) \quad (6)$$

j refers to the j^{th} species of pathway p . S is defined as the placeholder for the intermediate species beginning at species x and finishing at species y . r here is similar to r_{xy} as introduced in Equation 3.

In comparison to DRG, DRGEP considers species further from targets to be less significant. Distance from targets is not important in DRG as long as the selection of “starting set” of species ensures that the directed graph is populated by all species. Moreover, similar to DRG, DRGEP has also adopted a set of E_t normalized between 0 and 1 to filter a subset of undesirable species. Therefore, optimal E_t is carefully selected in an iterative way so that greater reduction in DRGEP can be reached.

Besides that, Niemeyer et al. [8] has also presented a novel mechanism reduction technique, i.e. DRGEP-SA. The two formerly established methods are integrated in this new technique, i.e. DRGEP and DRGASA. According to the research, it is demonstrated that the combination of DRGEP and DRGASA methods allows DRGEP-SA approach to overcome the weaknesses of each, i.e. DRGEP is unable to detect all unimportant species and DRGASA shields unimportant species from removal. By merging these two methods, DRGEP-SA is capable to identify and eliminate more insignificant species than its precursors. In the DRGEP-SA methodology, DRGEP is firstly performed in an iterative manner and the reduced mechanism generated is compared with the detailed mechanism until the maximum allowable error is reached. In this way, a minimal reduced mechanism can be obtained with DRGEP. Subsequently,

sensitivity analysis is carried out on limbo species to further identify unimportant species. Limbo species refers to species with R_{xy} values that satisfy $\varepsilon_{EP} < R_{xy} < \varepsilon^*$ (ε_{EP} is E_t during EP phase while ε^* is a higher value). The unimportant species and elementary reactions that involved eliminable species are then removed until the user-specified limit is reached.

Aside from DRG-based reduction methods, lumping method [14, 15, 16, 17] is also another common technique to simplify a huge and complex chemical kinetic mechanism. Isomer lumping in huge chemical kinetic mechanisms involves the grouping of species with similar composition or functionalities into a single representative species. During the oxidation process of hydrocarbon, a huge amount of structurally similar isomer species with different chemical functionalities is formed. Isomer usually contains comparable thermal and transport properties. Therefore, the existence of large isomer groups may bring about great elimination in number of variables described in the differential equations. For example, the transport equation for a set of isomers K with mixture-averaged diffusion is described as:

$$\frac{\partial}{\partial t}(\rho Y_k) + \frac{\partial}{\partial x_i}(\rho u_i Y_k) = \nabla \cdot (\rho D_k \nabla Y_k) + \omega_k \quad (7)$$

where k is the isomer in isomer set K , D_k is the diffusion coefficient, Y_k is the mass fraction, ρ is the density, u_i is the velocity vector and ω_k is the production rate of the isomer. When isomers are lumped into a single lumped group, the transport equation is expressed as following:

$$\frac{\partial}{\partial t} \left(\rho \sum_{k \in K} Y_k \right) + \frac{\partial}{\partial x_i} (\rho u_i Y_K) = \nabla \cdot (\rho D_K \nabla Y_K) + \sum_{k \in K} \omega_k \quad (8)$$

and Y_k can be described by the following equation:

$$Y_k = Y_k(Y_K, Y_{other}, T, P, \dots), k \in K \quad (9)$$

Y_{other} is the concentration vector of other species excluding the isomers. As a consequence of isomer lumping, N_R in chemical kinetic mechanism is significantly reduced since lumping may result in repeated reactions as well as parallel reaction pathways.

MECHANISM REDUCTION FOR BIODIESEL SURROGATE

In this section, the biodiesel surrogate mechanism established by Herbinet et al. [18] was selected as the base mechanism. It was developed based on the detailed chemical kinetic mechanisms for n-heptane, methyl-decanoate (MD) as well as methyl-9-decanoate (MD9D). This detailed mechanism contains 3299 species and 10806 elementary reactions.

Successively, mechanism reduction for the biodiesel surrogate was performed via DRG, DRGASA, DRGEP and DRGEP-SA. Following that, the reduced chemical kinetic

mechanism generated from each reduction technique was validated against the detailed mechanism in term of accuracy in ID timing predictions as well as efficiency in reduction scale and T_C . The operating conditions applied in this study are shown in Table 1. The selected pressure range for this study covers the typical in-cylinder pressure values during the main fuel injection event for light-duty, direct-injection diesel engines. In this work, only results for initial pressure of 60 bar are demonstrated. Same trend was observed in the ID timing curves when the initial pressure were 40 bar and 80 bar. Subsequently, the results obtained were analyzed and evaluated.

Table 1. Operating conditions applied to evaluate the performance of each reduced mechanism.

Working Parameter	Range considered
Equivalence ratio, Φ	0.5, 1.0, 2.0
Initial Pressure (bar)	40, 60, 80
Initial Temperature (K)	650 – 1350 (with increments of 100K)

Directed Relation Graph (DRG) Method

The performance of DRG method was evaluated with respect to reduction time and accuracy as a function of number of stages. In comparison with a single-stage DRG, greater reduction with higher accuracy can be achieved through a two-stage DRG regardless of the huge variations in r_{xy} value for each pair of retained species during second stage of reduction. Generally, accuracy of the reduced mechanism diminishes as larger E_t is selected in order to maximize the reduction scale. Therefore, the implementation of two-stage DRG is able to preserve the species groups with strong coupling through first stage reduction which might have been eliminated by single-stage DRG. Nonetheless, there might be arguments claiming that more than two stages of DRG reduction is required to achieve a set of converged reduced species when dealing with large chemical kinetic mechanisms such as n-heptane [19], iso-octane [20] and the biodiesel surrogate mechanisms. The finding here agrees with the work carried out by Lu et al. [4] in which two-stage DRG is sufficient to produce reduced mechanism with minimal size. On the other hand, while size of the reduced mechanism generated from single-stage DRG is already much smaller than that of the detailed mechanism, the execution of two-stage or multi-stage DRG will only contribute to minor raise in reduction scale. As a consequence, increment in overall reduction time is insignificant with the presence of an additional DRG stage despite the remarkable difference in accuracy.

In the present study, 216 points were sampled to facilitate the analysis of every representative reaction condition and it is observed that the number of sampling points used is sufficient for the specified accuracy. Besides that, each stage

of DRG reduction process required less than a minute to accomplish on a 6-core PC with 16GB RAM and 3.4GHz processing speed.

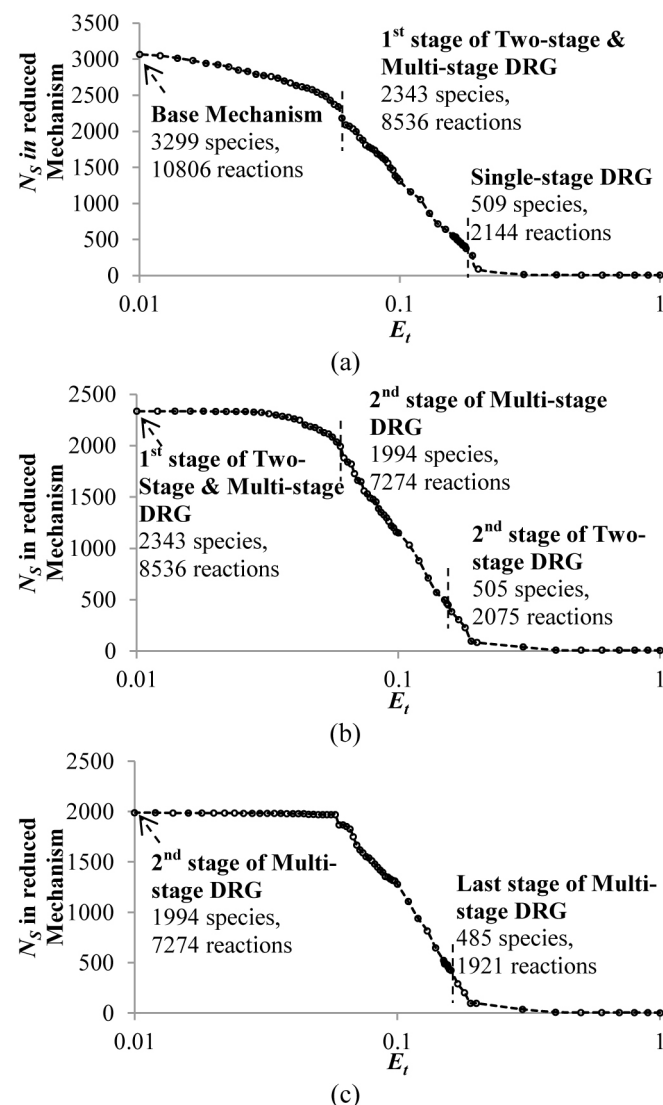


Figure 1. Dependency of N_S in the reduced mechanism of MD+MD9D on E_t for (a) single-stage, (b) two-stage and (c) multi-stage DRG reduction to truncate weak relations of the species.

During the reduction process, methyl-decanoate (MD), methyl-9-decanoate (MD9D) and n-heptane (nC_7H_{16}) were chosen as the “starting set” of species for every stage of DRG reduction. The dependency of N_S in reduced mechanism on the user-defined E_t for single-stage, two-stage as well as multi-stage DRG reduction is demonstrated in Figure 1. In this work, multi-stage DRG refers to a three-stage DRG reduction. It can be observed that N_S in reduced mechanism is very close to that of the detailed mechanism when E_t is very small. In contrast, only the “starting set” of species is retained as the E_t approaches unity. In addition, there are

“jumps” in N_S at certain values of E_t , such as $E_t = 0.058$ in Figure 1(a), $E_t = 0.06$ in Figure 1(b) and $E_t = 0.066$ in Figure 1(c). This can be explained by the existence of species groups with strong coupling at that particular E_t . As a consequence, they should either be kept or eliminated together. For that reason, the value of E_t should be selected either before or after the “jump”.

Table 2 shows the E_t selection for each stage of DRG reduction and the respective reduction scale achieved. E_t for the first stage of a two-stage DRG as well as the second stage of a multi-stage DRG were selected right before the “jump”. This is to ensure that the strongly coupled species are kept together since removal of the group will induce significant errors to the ignition timings. On the other hand, E_t of the final stage of each DRG reduction, including the single-stage DRG reduction, were selected based on the error induced on ignition timings, V_{ID} . Subsequently, ID timings computed by the reduced mechanisms were compared against those predicted by the detailed mechanism under a 0-D closed homogeneous batch reactor and the results are shown in Figure 2.

Table 2. Selection of E_t as well as the resulting N_S and N_R of the reduced mechanisms for each stage of DRG reduction.

Reduction Method		E_t	N_S	N_R
Single-stage DRG		0.165	509	2144
Two-stage DRG	1 st stage	0.058	2343	8536
	2 nd stage	0.15	505	2075
Multi-stage DRG	1 st stage	0.058	2343	8536
	2 nd stage	0.06	1994	7274
	3 rd stage	0.155	485	1921

Based on the results shown in Figure 2, it can be observed that ID timing predictions for reduced mechanisms generated from all stages of DRG reduction demonstrates good agreement with the ID timings of detailed mechanism for the entire parameter range. Nonetheless, it can still be perceived that the performance of two-stage and multi-stage DRG is superior as compared to the single-stage DRG since they are able to predict the ID timings in NTC region more accurately. For instance, referring to Figure 2, V_{ID} at temperature of 950K are 39.7% for single-stage DRG, 20.7% for two-stage DRG and 26.7% for multi-stage DRG. The reason is that species groups with strong coupling which have been eliminated by single-stage DRG are retained. Besides that, it is perceived that size of the reduced mechanism generated via multi-stage DRG is the smallest compared to the others. In