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Development and validation of a reduced combined biodiesel–diesel reaction mechanism

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HIGHLIGHTS

- ▶ A compact combined biodiesel–diesel reaction mechanism is proposed.
- ▶ The mechanism is able to emulate any diesel–biodiesel blends and feedstock type.
- ▶ Combination of mechanisms follows a chemical class-based approach.
- ▶ Reaction mechanisms of methyl crotonate and methyl butanoate are reduced.
- ▶ The mechanism accurately predicts the ignition delay timing under 234 conditions.

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ABSTRACT

In this study, a compact combined biodiesel–diesel (CBD) reaction mechanism for diesel engine simulations is proposed through the combination of three component mechanisms using a chemical class-based approach. The proposed mechanism comprises the reaction mechanisms of methyl crotonate (MC), methyl butanoate (MB) and *n*-heptane which are the surrogate fuel models of unsaturated fatty acid methyl ester, saturated fatty acid methyl ester and straight chain hydrocarbon (HC), respectively. The MC and MB mechanisms are adopted to represent biodiesel fuels, while *n*-heptane is utilised to characterise the combustion of fossil diesel. Here, the MC and MB mechanisms are reduced before integrating with a compact *n*-heptane mechanism. CHEMKIN-PRO is used as the solver for the zero-dimensional, closed homogenous reactor with a constant volume in this study. In the first phase, the mechanisms of MC and MB are methodologically reduced. The MC mechanism by Gail et al. with 301 species and 1516 reactions is reduced to 47 species and 210 reactions, while the MB mechanism by Brakora et al. with 41 species and 150 reactions is reduced to 33 species and 105 reactions. The mechanisms are reduced from a combination of methods, including peak molar concentration analysis, reaction flux analysis and the removal of individual species. In the second phase, the reduced MC and MB mechanisms are combined with the *n*-heptane mechanism by Pang et al. with 46 species and 112 reactions. Upon the combination of the component mechanisms, parametric adjustments to the Arrhenius rate constants of pertinent chemical reactions are performed for better ignition delay (ID) prediction. The final mechanism developed comprises 80 species and 299 reactions. The compact-sized CBD mechanism is validated against 234 test conditions ranging from initial temperatures of 750–1350 K, pressures of 40–60 bar and equivalence ratios of 0.4–1.5. The mechanism is generally found to accurately predict the timing and duration of ID for the combustion of each surrogate fuel. This model is also shown to be feasible for use with multidimensional computational fluid dynamics studies involving a light-duty diesel engine fuelled with biodiesel of different feedstock types, diesel as well as their blends.

1. Introduction

Biodiesel has emerged as a promising alternative fuel due to its lower cost as compared to other alternative fuels, its availability of current production technology and its compatibility with existing infrastructure of conventional diesel applications. Most importantly, the use of biodiesel in diesel engines has been associated with reduced tailpipe emissions such as carbon dioxide (CO_2), particulate matter and unburned hydrocarbons [1,2]. However, several unresolved issues associated with biodiesel usage remain. For example, the long-term effects of physico-chemical properties

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of the fuel on engine performance/durability, as well as the fundamental in-cylinder physics governing the observed emissions trend such as the increase in the level of engine-out nitrogen oxides (NO_x).

In order to understand these, in-cylinder phenomena such as fuel oxidation, ignition, combustion and emissions formation processes must be examined. Chemical kinetic mechanisms are commonly used in conjunction with multidimensional computational fluid dynamics (CFD) in diesel engine simulations [3–14] to elucidate these events. Prior to 2008, most research efforts had focussed on the development of reduced chemical kinetic mechanisms for combustion modelling of fossil diesel. The most comprehensive *n*-heptane reaction mechanism to date which covers both the low and high temperature oxidation of *n*-heptane is the detailed mechanism with 570 species and 2520 reactions proposed by Curran et al. [15] in 1998. Based on this detailed model, Golovitchev [16] constructed a reduced mechanism in 2000 which consists of 40 species and 165 reactions. Patel et al. [5] further reduced Golovitchev's model in 2004 to a skeletal mechanism of 29 species and 52 reactions. However, this skeletal mechanism does not possess species and reactions which are involved in the main ramification pathways for *n*-heptane. The skeletal mechanism developed by Maroteaux and Noel [17] in 2006 however, meets the requirement of representing the main ramification pathways and it comprises only 25 species and 26 reactions. In a more recent work, an *n*-heptane diesel surrogate fuel model with sub-mechanism of soot precursor formation predicting capabilities is proposed by Pang et al. [11]. This mechanism, which contains 44 species and 109 reactions, is reduced from the mechanism employed by Tao et al. [4] in diesel spray simulations which has 65 species and 273 reactions.

The development of chemical kinetic mechanisms for surrogate biodiesel fuels is identical to that for surrogate diesel fuel. The first few chemical models are usually comprehensive and large. These detailed mechanisms normally serve as the base mechanisms for reduction in order to lower computational costs. Criteria and scales of reduction strongly depend on the intended applications. The surrogates for biodiesel fuel can be categorised into two groups, with long carbon chains and short carbon chains. These models are discussed in the subsequent sub-sections.

1.1. Biodiesel surrogate

1.1.1. Biodiesel surrogate with long carbon chains

The major component of biodiesel is fatty acid methyl esters which feature the ester functional group and long carbon chains. For instance, rapeseed and soybean derived biodiesel mainly consists of five components which are methyl palmitate ($C_{17}H_{34}O_2$), methyl stearate ($C_{19}H_{38}O_2$), methyl oleate ($C_{19}H_{36}O_2$), methyl linoleate ($C_{19}H_{34}O_2$) and methyl linolenate ($C_{17}H_{32}O_2$) [18]. These esters have the characteristic R—(C=O)—O—R′ structure, where the R and R′ are the chains of alkyl and alkenyl groups having as many as 17–19 carbon atoms. In one of the most recent work, Westbrook et al. [19] developed detailed chemical kinetic reaction mechanisms for the aforementioned five components. Capabilities and limitations of the model are examined through the biodiesel oxidation in the jet-stirred reactor (JSR), as well as intermediate shock tube ignition/oxidation conditions where the temperature ranges from 700 to 1100 K. It is highlighted that further refinement is required on this mechanism [19].

Alternatively, Herbinet et al. [18] developed a detailed mechanism by following the rules established by Curran and co-workers [15]. This was implemented to study the oxidation of methyl decanoate (MD), a representative of the saturated ester [18]. Without reliable experimental data at the time of the study, this mechanism was compared to rapeseed methyl ester (RME) experiments in a JSR. The predicted mole fraction profiles of most combustion products generally match the experimental data satisfactorily. Most importantly, the MD mechanism provides better prediction of CO_2 than the *n*-cetane mechanism. The MD mechanism is also capable of capturing the early formation of CO_2 from biodiesel fuels, although the corresponding mole fraction is slightly underpredicted.

Based on the above MD mechanism, the same group of researchers subsequently constructed detailed models for unsaturated esters, methyl-5-decenoate (MD5D) and methyl-9-decenoate (MD9D) to investigate the influences of double bonds in the alkyl chain [20]. By validating against the RME experiments in a JSR, the MD9D model is concluded as a better representation. This is attributed to its greater length of the continuously-saturated carbon chain in the reactant, which leads to a higher possibility of RO_2 isomerisations and hence a higher overall reactivity. The MD9D model is also combined with the mechanisms of MD and *n*-heptane, and this integrated mechanism is validated against RME and methyl palmitate/*n*-decane experiments in a JSR. The calculated mole fraction profiles of most combustion products agree with the experimental data satisfactorily. As longer chain methyl esters produce larger permutation of species during combustion, the reaction mechanism is normally complex and the associated chemistry size is inevitably large. This model consists of 3299 species and 10,806 species.

The use of detailed chemical kinetic reaction mechanisms coupled with multidimensional CFD simulations is prohibitively expensive even with the most advanced, state-of-art computing capabilities at present. As such, a delicate trade-off is often necessary to reduce the complexity of the chemical kinetic mechanism without removing the ability to accurately describe the effects of chemistry on the combustion process. Luo et al. [21] utilised an improved directed relation graph (DRG) method, coupled with isomer lumping and DRG-aided sensitivity analysis (DRGASA) to obtain a skeletal mechanism with 118 species and 837 reactions from the MD/MD9D/*n*-heptane mechanism developed Herbinet et al. [20]. Ignition delay (ID) times under constant pressure autoignition as calculated by the skeletal model are compared with those of the base mechanism. This includes a wide range of parameters, where the pressure and equivalence ratio (ER) values are varied from 1 to 100 atm and 0.5–2.0, respectively at temperatures of above 1000 K. It is also validated for various fuel composition in JSR simulations, as well as experimental measurements in literature for RME in JSR and counterflow diffusion flames of pure MD. It is shown to be applicable for both extinction and ignition for a range of temperature, pressure and ER values.

A limitation of this model lies in its applicability to simulations involving low-temperature ignition, particularly those in the negative temperature coefficient (NTC) regions. This is addressed in their subsequent work [12]. The former validation exercise is implemented, but with an extended temperature range down to 700 K. The revised mechanism is even smaller, comprising only 115 species with 460 reactions. This model, coupled with CFD solver, is validated using three dimensional (3-D) turbulent spray combustion under compression ignition engine conditions carried out at the Sandia National Laboratories. ID time, flame lift-off length as well as concentration profiles of hydroxyl (OH) and soot under different conditions are reasonably well predicted, proving the model's versatility and robustness [12].

Parallel to this, Brakora et al. [10] implemented a similar reduction methodology on the same detailed mechanism. A combination of DRG, chemical lumping and limited reaction rate tuning was employed to reduce the detailed mechanism. Integrating the multi-chemistry mechanism developed by Ra et al. [22], a final mechanism with 77 species and 216 reactions is produced. Brakora et al. [10] implemented their chemical model with 3-D CFD solver