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A skeletal mechanism for biodiesel blend surrogates combustion

H. An, W.M. Yang *, A. Maghbouli, J. Li, K.J. Chua

Department of Mechanical Engineering, Faculty of Engineering, National University of Singapore, Singapore

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ABSTRACT

A tri-component skeletal reaction mechanism consisting of methyl decanoate, methyl-9-decenoate, and n-heptane was developed for biodiesel combustion in diesel engine. It comprises 112 species participating in 498 reactions with the CO, NO_x and soot formation mechanisms embedded. In this study, a detailed tri-component biodiesel mechanism was used as the start of mechanism reduction and the reduced mechanism was combined with a previously developed skeletal reaction mechanism for n-heptane to integrate the soot formation kinetics. A combined mechanism reduction strategy including the directed relation graph with error propagation and sensitivity analysis (DRGEPSA), peak concentration analysis, isomer lumping, unimportant reactions elimination and reaction rate adjustment methods was employed. The reduction process for biodiesel was performed over a range of initial conditions covering the pressures from 1 to 100 atm, equivalence ratios from 0.5 to 2.0 and temperatures from 700 to 1800 K, whereas for n-heptane, ignition delay predictions were compared against 17 shock tube experimental conditions. Extensive validations were performed for the developed skeletal reaction mechanism with 0-D ignition delay testing and 3-D engine simulations. The results indicated that the developed mechanism was able to accurately predict the ignition delay timings of n-heptane and biodiesel, and it could be integrated into 3-D engine simulations to predict the combustion characteristics of biodiesel. As such, the developed 112-species skeletal mechanism can accurately mimic the significant reaction pathways of the detailed reaction mechanism, and it is suitable to be used for diesel engine combustion simulations fueled by biodiesel, diesel and their blend fuels.

1. Introduction

Biodiesel can be derived from vegetable oil or animal fats via trans-esterification process. The major components of biodiesel are the fatty acid methyl esters which feature the ester functional group and long carbon chains [1]. For example, typical soy or rapeseed derived biodiesel consists of five major methyl esters having the molecular structure of R—(C=O)—O—R', where R and R' are chains of alkyl and alkenyl groups. These methyl esters have similar molecular structures, but differ from each other based on the carbon chain length as well as the number of double bonds presence in the chain (see Fig. 1). Compared to typical diesel surrogate fuels such as n-heptane, the carbon chain of biodiesel is much longer and more complex, which results in significant differences on the combustion and emission characteristics.

Many experimental studies have been carried out to characterize the effects of biodiesel addition to fossil diesel on the emissions of a diesel engine. It has been shown that the use of biodiesel can substantially lower the unburned hydro-carbon (HC), particular matter (PM) and carbon monoxide (CO) emissions [2–5]. However, a slight increase in the nitrogen oxides (NO_x) emission is reported by most researchers [6,7]. Despite experimental investigations, numerical simulation also plays an important role in engine research. Accurate computational fluid dynamics (CFD) simulations can provide better insights on fuel oxidation and emission formation processes, for which experimental studies could not easily obtain. However, to ensure an accurate prediction, a comprehensive and reliable reaction mechanism is of critical importance.

There have been many studies on the development of detailed chemical kinetics for biodiesel combustion simulations. One of the earliest attempts was done on methyl butanoate (MB) by Fisher et al. [8] because MB possesses the essential chemical structural feature of the ester functional group. However, the carbon length of MB is much shorter than typical biodiesel methyl esters with chains of 16–18 carbon atoms, leading to a poor reproduction of the kinetic features of biodiesel fuels. Considering that, a detailed reaction mechanism for a larger methyl ester:methyl decanoate (MD) was developed by Herbinet et al. [9]. The model was constructed based on the same systematic rules established by Curran and co-workers for the oxidation of n-heptane and iso-octane

* Corresponding author. Tel.: +65 6516 6481; fax: +65 6779 1459.
E-mail address: mpeywm@nus.edu.sg (W.M. Yang).

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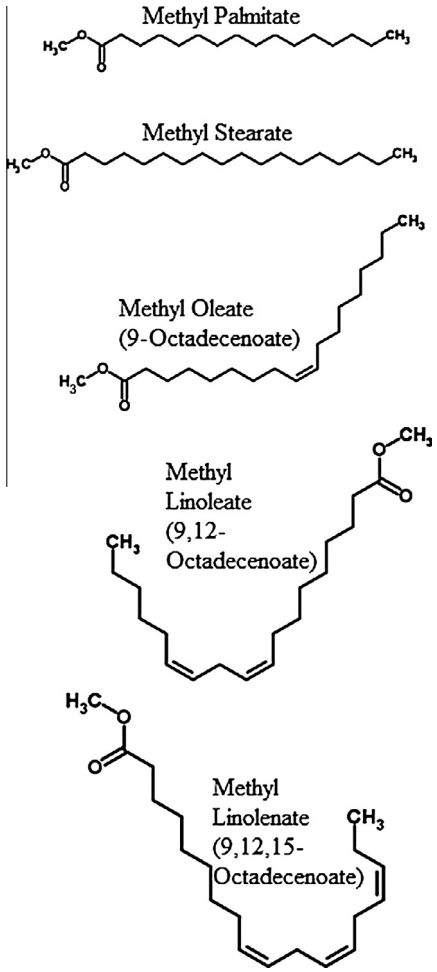

Fig. 1. Molecular structure of the five major components of soy/rapeseed biodiesel.

[10,11], and the developed mechanism was able to mimic the earlier formation of carbon dioxide due to the presence of ester group in biodiesel fuels. Unlike MD which is a saturated methyl ester, most biodiesel methyl ester components are unsaturated with one, two or three double bonds. The earlier study has concluded that the presence of C=C double bond in the biodiesel methyl ester components is responsible for the reduced rate of low temperature reactivity, and the amount of reduction compared to those saturated methyl esters is roughly proportional to the number of double bonds [12]. Hence, to take into account the effect of double bonds, a blend surrogate mechanism was developed to be more representative of biodiesel fuels [13]. Methyl-9-decenoate (MD9D) was chosen to represent the unsaturated methyl ester because its double bond is located at the same position as the one in methyl oleate and at the same position as the first double bond in methyl linoleate and methyl linolenate. Besides the detailed reaction mechanisms discussed above, some detailed chemical kinetics were also developed for real biodiesel components: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate [14,15]. The resulting reaction mechanisms include approximately 3500 species and more than 17,000 chemical reactions.

Although these comprehensive reaction mechanisms are very useful, it is generally unaffordable to integrate them into three dimensional CFD applications due to the extraordinary computational time, huge memory requirement and high stiffness. As such, it is often necessary to develop skeletal reaction mechanisms by eliminating unimportant species and reactions. There exist some skeletal reaction mechanisms in the literature. Brakora et al. [16] built a two component biodiesel reaction mechanism (MB and n-heptane) to simulate the oxidation of biodiesel. A reduced mechanism for MB was first developed from its detailed reaction mechanism. The reduction process included peak concentration analysis, reaction pathway analysis, sensitivity analysis, and reaction rate adjustment. The reduced MB mechanism was then combined with another skeletal mechanism for n-heptane, and it was assumed that the hypothetical fuel was a mixture consisting of one mole of MB and two moles of n-heptane. Based on a similar approach, Ng et al. [1] developed a compact biodiesel–diesel reaction mechanism comprising the reaction mechanisms of methyl crotonate (MC), MB and n-heptane which represent the unsaturated methyl ester, saturated methyl ester and straight chain hydrocarbons, respectively. It was claimed that the compact reaction mechanism was generally able to accurately predict the oxidation, ignition and combustion of biodiesel derived from different feedstocks, diesel and their blend fuels. The same objective was also achieved by the reduced chemical kinetics developed by Ismail et al. [17]. The mechanism was first constructed by reducing a detailed MB/MB2D mechanism, which was then combined with a skeletal n-heptane mechanism. Two global reactions were also introduced to cater for the change in the ratio between saturated and unsaturated methyl esters in the fuels. To simulate the combustion of real biodiesel methyl esters with long carbon chains, Golovitchev and Yang [18] proposed a single surrogate fuel ($C_{19}H_{34}O_2$) oxidation mechanism consisting of 309 species and 1472 reactions. A global reaction was introduced to decompose the surrogate fuel into three constitutive components of n-heptane, toluene (C_7H_8O) and MB. One feature of this mechanism is its ability to predict soot production. However, taking a closer look at the above studies, the highest carbon lengths of the reduced reaction mechanisms (exclusive of the global reactions) are all remained at C_7, which is much shorter as compared to real biodiesel components. Recently, Luo et al. [19] developed a tri-component (MD, MD9D and n-heptane) skeletal biodiesel reaction mechanism based on the detailed biodiesel reaction mechanism from [13]. The reduction process involved direct relation graph (DRG), isomer lumping, and DRG-aided sensitivity analysis (DRGASA) methods. The final mechanism consists of 115 species and 460 reactions. However, in their reaction mechanism, the soot prediction model was not included, and the ignition delay calculations for diesel surrogate (n-heptane) fuel were not monitored during the reduction process.

The objective of this study is to develop a skeletal reaction mechanism which is able to simulate the combustion and emission formation processes of biodiesel, diesel and their blend fuels with CO, NO_x and soot formation mechanisms embedded. An updated tri-component (MD, MD9D and n-heptane) biodiesel reaction mechanism comprising 3299 species and 10,806 reactions is used as the starting mechanism for reduction. After the first reduction, the resulting mechanism is combined with a comprehensive n-heptane skeletal reaction mechanism with the soot formation kinetics embedded. A second reduction process is then performed to achieve a more compact mechanism which is feasible for 3D engine simulations. Extensive validations are performed by comparing the ignition delay predictions for n-heptane against the experimental results and biodiesel against the detailed mechanism under various conditions, as well as 3D engine experiments.

2. Methodology

2.1. Mechanism reduction strategies

Many mechanism reduction methods have been successfully developed and demonstrated in the literature. Manual removal