

SKELETAL MECHANISM CONSTRUCTION FOR METHYL OLEATE IN REAL BIODIESEL FUELS

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ABSTRACT

A skeletal mechanism with 133 species and 877 reactions for MOD9D (one of the main unsaturated methyl esters in biodiesel fuels) is constructed by using decoupling methodology. The obtained skeletal mechanism consists of four parts: high temperature decomposition, low temperature oxidation, ester group reactions and detailed chemistry of small species. Extensive validations are firstly performed against available experimental data in shock-tube for auto-ignition delay. The predicted results by the skeletal mechanism matches well with the experiment results. The comparison has been conducted between the detailed mechanism and a semi-detailed mechanism. Good agreement or even better predictions at some initial conditions has been observed. Further validations are conducted against the experimental data of fuel species' conversion rate and species concentration in PSR at varying initial temperatures. The results indicate that the developed skeletal mechanism is capable of predicting the combustion characteristics of MOD9D.

Keywords: biodiesel, unsaturated methyl esters, mechanism reduction, decoupling methodology

NONMENCLATURE

Abbreviations

MHD	Methyl palmitate
MOD	Methyl stearate
MOD9D	Methyl oleate
MOD9D12D	Methyl linoleate
MOD9D12D15D	Methyl linolenate
MD	Methyl decanoate
MD9D	Methyl-9-decenoate
PSR	Perfectly stirred reactor

DRGEPISA	Directed relation graph with error propagation and sensitivity analysis
PFA	Path flux analysis
<i>Symbols</i>	
Φ	Equivalence ratio

1. INTRODUCTION

Conventional fossil fuels are depleting fast and severe air pollution threatens the life of our generation, bringing out a strong demand on the exploring of alternative fuel which is renewable and clean [1-3]. Among various alternative fuels, biodiesel stands at the forefront as a significant substitute to conventional fossil fuel. The combustion characteristics of biodiesel fuel has been widely explored in the past few decades [4, 5]. Direct use of biodiesel has been realized in diesel engine with little modification due to the similar physico-chemical properties with conventional diesel fuel.

As a complement or even a replacement of tradition experimental test, numerical simulation is playing an important role in the study of biodiesel combustion. Due to complicated composition of biodiesel, a combination of a small amount of hydrocarbon and oxygenated hydrocarbon species is taken as the surrogate for real biodiesel. The detailed mechanism of such surrogate is developed and validated against available experimental data. In the past few years, detailed mechanisms for two widely used surrogates for biodiesel fuel has been proposed. In 2010, Herbinet et al. [6] used a combination of n-heptane/MD/MD9D as the biodiesel surrogate and developed a detailed mechanism consisting of 3299 species and 10,806 reactions. However, the species in the surrogate are not the real components in biodiesel

fuel which have much longer chain length. To more accurately represent biodiesel fuel, Westbrook et al. [7] proposed a detailed mechanism for a new surrogate which is a combination of the five main methyl esters in real biodiesel, i.e. saturated MHD and MOD, and unsaturated MOD9D, MOD9D12D and MOD9D12D15D. Consisting of about 5000 species and more than 20,000 reactions, the detailed mechanism is not suitable for complex combustion modelling. Reduction on the detailed mechanism is needed. The large size of the detailed mechanism also makes the reduction by using other methods such as DRGEPISA and PFA very difficult. In this study, a decoupling methodology is employed to reduce the detailed mechanism for one of the main unsaturated methyl ester MOD9D in real biodiesel.

2. METHODOLOGY AND MODEL DEVELOPMENT

The prototype of decoupling methodology was first brought out by You et al [8] where they mentioned that a detailed description of the pyrolysis process may not be necessary as long as the major cracking product distribution is well predicted. In Ref. [9], Chang et al. further illustrated the concept of decoupling methodology. To prove the validity of this method, extensive validations have been performed in various combustion apparatus including shock-tube, PSR, burner and 3-D diesel engines.

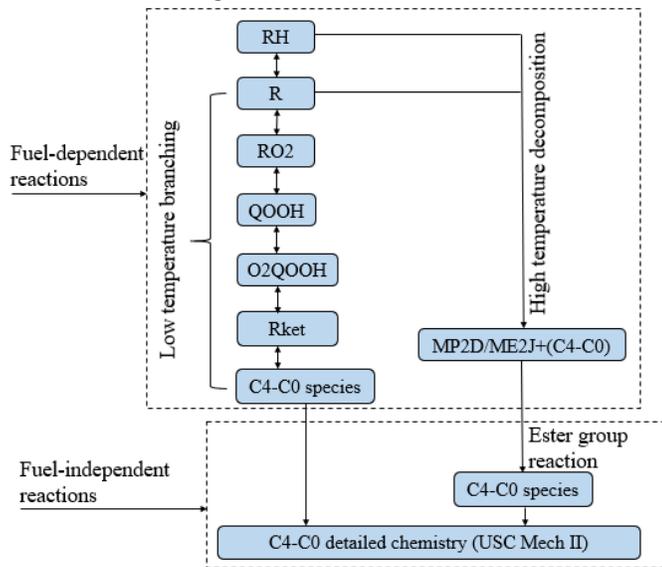


Fig. 1 Simplified schematic oxidation pathway for heavy unsaturated methyl esters.

In this study, the decoupling methodology divides reactions into four parts. The first one is high temperature decomposition. At high temperature, the fuel species are assumed to directly decomposed into small species through β -scission. The second one is low temperature oxidation: $RH \rightarrow R \rightarrow RO_2 \rightarrow QOOH \rightarrow$

$O_2QOOH \rightarrow Rket$ (ketohydroperoxide) \rightarrow small species, following the classical autoignition rules proposed by Cox et al. [10]. The third one is ester group reactions, which are directly taken from the biodiesel detailed mechanism [7]. And the fourth one is reactions of small species, i.e. the USC mech II [11] adopted in this study, which are fuel-independent and serve as fundamental chemistry. Fig. 1 shows the simplified four-part oxidation scheme of MOD9D for this study. More details of the use of decoupling methodology and model development method can refer to our previous publication [12].

3. MODEL VALIDATION

In this part, the developed mechanism is validated against available experimental data including auto-ignition delay at high temperature in shock-tube and species concentration in PSR. The predicted results of the detailed mechanism [7] and semi-detailed mechanism developed by Rodriguez et al. [13] are also included from the literatures as a comparison.

3.1 0-D ignition delay validation for MOD9D

The predicted results of ignition delay by our model is first compared with those of the detailed mechanism and the semi-detailed mechanism. The initial pressure is set to be 13.5 bar for stoichiometric MOD9D/air mixture. From Fig. 2, it can be observed that the results of our model match well with that of the detailed mechanism especially at high temperature region. An obvious NTC region has been well captured. At low temperature, the predictions of our model are even better than the predictions of the semi-detailed mechanism.

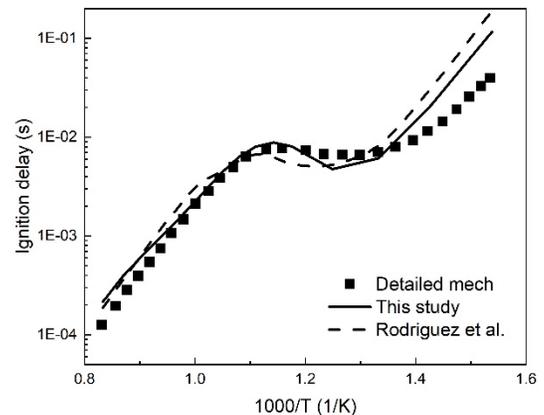


Fig. 2 Ignition delay comparison for MOD9D/air mixture at 13.5 bar and stoichiometric condition.

Further validation is performed against two available experiments by Wang et al. [14] and Campbell et al. [15] as shown in Fig. 3 and Fig. 4 respectively. As can be seen, the dependence of ignition delay times on pressure, temperature and equivalence ratio is well predicted. At

some temperatures, the prediction of our model is even better than the detailed mechanism and semi-detailed mechanism. From the above observation, our model shows a satisfactory performance on predicting the ignition delay behaviour of MOD9D.

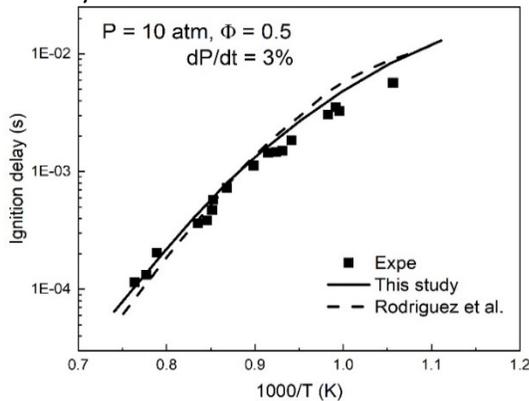


Fig. 3 Ignition delay comparison between experiment [14], model in this study and model by Rodriguez et al for MOD9D/air mixture: $P = 10 \text{ atm}$, $\Phi = 0.5$.

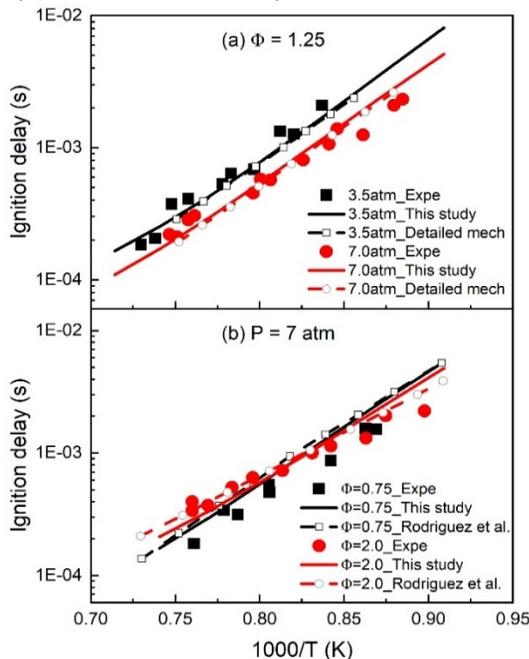


Fig. 4 Ignition delay comparison between experiment [15], model in this study and the detailed mechanism for MOD9D, (a) $\Phi = 1.25$; (b) $P = 7 \text{ atm}$, in 4% oxygen/argon mixtures.

3.2 PSR experiment validation for MOD9D

Due to the lack of PSR experiment for pure MOD9D, the existing PSR experiment [16] for MOD9D/NC10H22 mixture is utilized to further validation the performance of our model regarding the fuel species' conversion rate and species concentration. Fig. 5 shows the comparison of conversion rate of MOD9D and NC10H22 in PSR between experimental data and available prediction data of the detailed mechanism and the semi-detailed

mechanism from the literature. As can be seen, the overall performance of our model is satisfactory and even better than that of the detailed mechanism and semi-detailed mechanism at NTC region. Fig. 6 shows the comparison of the species concentration between our model and experiment. The concentration profile of small important species (CH_4 , O_2 , CO and CO_2) has been well reproduced by our model.

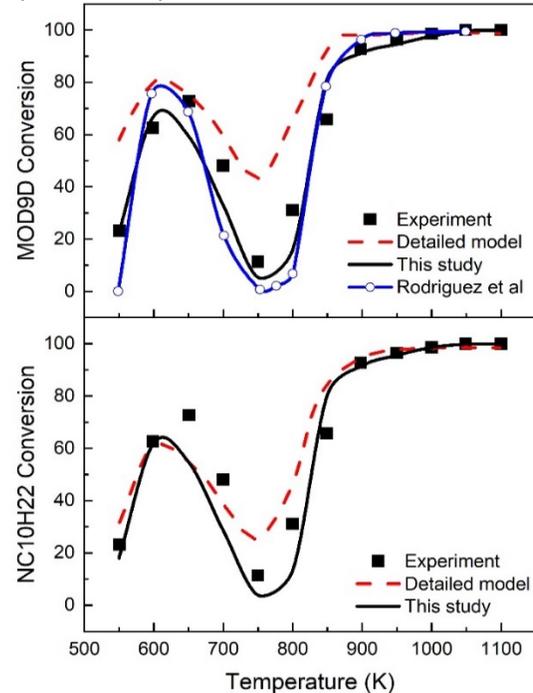


Fig. 5 Comparison of conversion rate of MOD9D and NC10H22 in PSR between experiment [16], the detailed model, model in this study and Rodriguez's model for n-decane/MOD9D fuel mixture at 1 atm, 1.5s, 0.2% fuel (0.26 MOD9D/0.74 n-decane) at $\Phi = 1.0$ with He diluent.

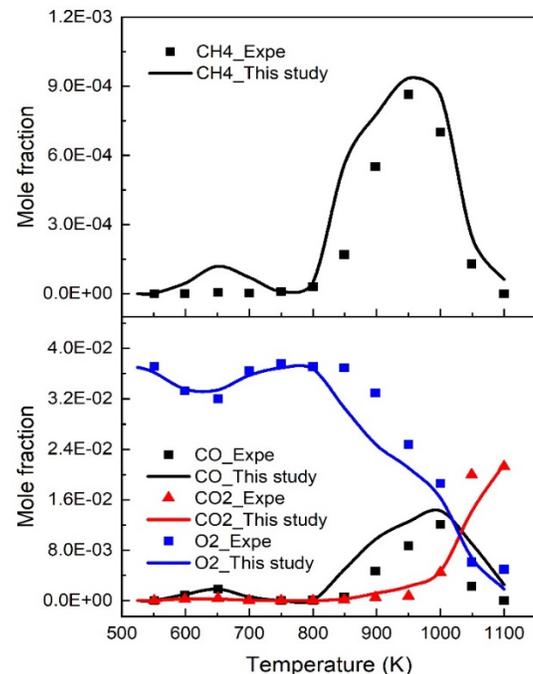


Fig. 6 Comparison of species mole fraction in PSR between model in study and experiment.

4. CONCLUSION

To more accurately simulate the combustion of biodiesel, one of the major approaches is to adopt the main components in real biodiesel as surrogate. In this study, a skeletal mechanism for MOD9D (one of the main methyl esters in real biodiesel) is constructed by using a decoupling methodology. The obtained mechanism has a compact size with 133 species and 877 reactions of which only 7 species and 13 reactions are fuel-dependent. And it shares the same fuel-independent species and reactions with the skeletal mechanisms of saturated methyl esters developed in our previous work [12], making it easy for them to be coupled to model biodiesel-fueled engine combustion. To show the reliability of the skeletal mechanism, extensive validations have been conducted against the available experimental data including ignition delay in shock-tube and fuel conversion rate and species concentration in PSR. Good agreement has been observed. The overall performance of our mechanism is satisfactory and able to provide an effective prediction of the combustion characteristics of MOD9D.

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REFERENCE

[1] Lai JYW, Lin KC, Violi A. Biodiesel combustion: Advances in chemical kinetic modeling. *Progress in Energy and Combustion Science* 2011;37(1):1-14.
[2] Li H, Yang W, Zhou D, Yu W. Numerical study of the effects of biodiesel unsaturation on combustion and emission characteristics in diesel engine. *Applied Thermal Engineering* 2018;137:310-8.
[3] Luo Z, Plomer M, Lu T, Som S, Longman DE, Sarathy SM, et al. A reduced mechanism for biodiesel surrogates for compression ignition engine applications. *Fuel* 2012;99:143-53.
[4] An H, Yang WM, Chou SK, Chua KJ. Combustion and emissions characteristics of diesel engine fueled by biodiesel at partial load conditions. *Applied Energy* 2012;99:363-71.
[5] Lele AD, Anand K, Narayanaswamy K. Surrogates for Biodiesel: Review and Challenges. 2017:177-99.
[6] Herbinet O, Pitz WJ, Westbrook CK. Detailed chemical kinetic mechanism for the oxidation of biodiesel fuels

blend surrogate. *Combustion and Flame* 2010;157(5):893-908.

[7] Westbrook CK, Naik CV, Herbinet O, Pitz WJ, Mehl M, Sarathy SM, et al. Detailed chemical kinetic reaction mechanisms for soy and rapeseed biodiesel fuels. *Combustion and Flame* 2011;158(4):742-55.
[8] You X, Egolfopoulos FN, Wang H. Detailed and simplified kinetic models of n-dodecane oxidation: The role of fuel cracking in aliphatic hydrocarbon combustion. *Proceedings of the Combustion Institute* 2009;32(1):403-10.
[9] Chang Y, Jia M, Liu Y, Li Y, Xie M. Development of a new skeletal mechanism for n-decane oxidation under engine-relevant conditions based on a decoupling methodology. *Combustion and Flame* 2013;160(8):1315-32.
[10] COX RA, COLE JA. Chemical Aspects of the Autoignition of Hydrocarbon-Air Mixtures. *COMBUSTION AND FLAME* 1985;60:109-23.
[11] Wang H, You X, Joshi AV, Davis SG, Laskin A, Egolfopoulos F, et al. USC Mech Version II. High-Temperature Combustion Reaction Model of H₂/CO/C₁-C₄ Compounds; May 2007.
[12] Li H, Yang W, Zhou D, Yu W. Skeletal mechanism construction for heavy saturated methyl esters in real biodiesel fuels. *Fuel* 2019;239:263-71.
[13] Rodriguez A, Herbinet O, Battin-Leclerc F, Frassoldati A, Faravelli T, Ranzi E. Experimental and modeling investigation of the effect of the unsaturation degree on the gas-phase oxidation of fatty acid methyl esters found in biodiesel fuels. *Combustion and Flame* 2016;164:346-62.
[14] Wang W, Gowdagiri S, Oehlschlaeger MA. The high-temperature autoignition of biodiesels and biodiesel components. *Combustion and Flame* 2014;161(12):3014-21.
[15] Campbell MF, Davidson DF, Hanson RK, Westbrook CK. Ignition delay times of methyl oleate and methyl linoleate behind reflected shock waves. *Proceedings of the Combustion Institute* 2013;34(1):419-25.
[16] Bax S, Hakka MH, Glaude PA, Herbinet O, Battin-Leclerc F. Experimental study of the oxidation of methyl oleate in a jet-stirred reactor. *Combust Flame* 2010;157(6):1220-9.