AJChE 2015, Vol. 15, No. 1, 52 – 61

A Skeletal Kinetic Model For Biodiesel Fuels Surrogate Blend Under Diesel-Engine Conditions

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The biodiesel surrogate fuels are realistic kinetic tools to study the combustion of actual biodiesel fuels in diesel engines. The knowledge of fuel chemistry aids in the development of combustion modeling. In order to numerically simulate the diesel combustion, it is necessary to construct a compact reaction model for describing the chemical reaction. This study developed a skeletal kinetic model of methyl decanoate (MD) and n-heptane as a biodiesel surrogate blend for the chemical combustion reactions. The skeletal kinetic model is simply composed of 45 chemical species and 74 reactions based on the full kinetic models which have been developed by Lawrance Livermore National Laboratory (LLNL) and Knowledge-basing Utilities for Complex Reaction Systems (KUCRS) under the diesel like engine conditions. The model in this study is generated by using CHEMKIN and then it is used to produce the ignition delay data and the related chemical species. The model predicted good reasonable agreement for the ignition delays and most of the reaction products at various conditions. The chemical species are well reproduced by this skeletal kinetic model while the good temperature dependency is found under constant pressure conditions 2MPa and 4MPa. The ignition delay time of present model is slightly shorter than the full kinetic model near negative temperature coefficient (NTC) regime. This skeletal model can provide the chemical kinetics to apply in the simulation codes for diesel-engine combustion.

Keywords : Kinetic mechanism, Surrogate fuel, Ignition delay, Methyl Decanoate, n-Heptane.

INTRODUCTION

The combustion chemistry of biodiesel fuels has on-going challenges because of the complexity of molecular structure and different physical and chemical properties depending on the feedstock. Biodiesel fuels are mainly composed of mixtures of hydrocarbons, with bonds between hydrogen and carbon atoms. During combustion, these bonds are broken and new bonds are formed combining with oxygen atoms. For instance, soybean derived biodiesels mainly composed of the same five components: methyl palmitate, methyl stearate, methyl oleate, methyl linoleate and methyl linolenate (Dagaut *et al*. 2007). Biodiesel profoundly has large oxygen content which can lead to the complete combustion processes (Naik and Westbrook 2009).

There has been a strong interest in studying the oxidation of large hydrocarbon fuels depending on the various operating engines conditions. Because of the larger molecular structure of methyl esters, the combustion study of biodiesel causes the impractical reaction mechanism in the calculation time (Naik and Westbrook 2009). Therefore, the surrogate fuels instead of biodiesels have been used to compare the experiment and calculated results. The surrogate fuels are structurally similar to actual biodiesel fatty acid methyl ester (FAME). In most cases, methyl butanoate, methyl decanoate and n-alkanes namely n-octane and n-hexadecane have been investigated to predict their reduced chemical kinetic mechanisms (Herbinet *et al*. 2008, Westbrook *et al*. 2009, Herbinet *et al*. 2010). A binary mixture of n-alkanes and methyl esters can be used to simulate the experimental results obtained from a jet stirred reactor (Herbinet *et al*. 2008, Herbinet *et al*. 2010).

The chemical combustion process of fuel oxidation can be studied using the detailed and the reduced chemical kinetic mechanisms. In particular, it is necessary to justify how the reduced kinetics model can reproduce the full kinetics. Using the elementary reaction, the rate constants have to build for each class of reaction. Based on these concepts, the most important reaction paths during combustion have to be interpreted to capture the whole fuel combustion process at indicated temperatures and pressures.

The reduced chemical kinetic mechanisms, which are composed of small alkanes, have been developed in some research areas. Herbinet *et al*. (2008) developed full kinetics of the oxidation for the methyl decanoate ($C_{11}H_{22}O_2$), the medium size saturated methyl ester. Meanwhile, the large n-alkanes are good surrogates for the prediction of overall reactivity of large methyl esters and biodiesel fuels. However, a detailed kinetic mechanism for a real methyl ester can be only predicted in some kinetic detail parts. The detailed mechanisms of methyl decanote and n-heptane have been developed in Lawrence Livermore National Laboratory (Dagaut *et al*. 2007, Herbinet *et al*. 2008, Westbrook *et al*. 2009, Herbinet *et al*. 2010). A reduced kinetic model for methyl decanoate (MD) and n-heptane, also called biodiesel surrogate fuel blend is developed in this study. Methyl decanoate ($C_{11}H_{22}O_2$) has larger molecular structure compared to methyl butanoate ($C_5H_{10}O_2$) which is the basic chemical feature of methyl ester, also very popular in the study of biodiesel surrogate fuel. A detailed chemical kinetic mechanism of methyl butanoate was developed by Fisher *et al*. (2000). The reaction mechanisms of n-heptane and iso-octane have been developed by Curran *et al*. (1998, 2002). There was a complete reaction mechanism of iso-octane oxidation including 3600 elementary reactions and 860 species predicted by Curran et. al. (2002).The ignition delay times have been determined for a homogenous fuel-air mixture under high temperature and pressure, and then the results are compared with the full kinetic models.

Kawanabe and Ishiyama (2012) predicted the domination of fuel component with shorter ignition delay captures the ignition process of the fuel blend. The ignition delay (τ) of their reduced model including 59 chemical species and 96 reactions is longer than the full kinetic model. To capture the ignition quality of fuel, the ignition delay is one of the best representative parameters for the fuels. The purpose of this study is to establish the skeletal kinetic model to compare the full kinetics developed by Lawrence Livermore National Laboratory (LLNL) group (Herbinet *et al.* 2008, Herbinet *et al.* 2010) and Knowledge-basing Utilities for Complex Reaction Systems (KUCRS) (Tsurushima 2009). The ignition delay times of present model were calculated under different temperature and pressure conditions and compared it with the full kinetics.

DESCRIPTION OF CHEMICAL KINETIC MECHANISM

The chemical kinetic calculations are performed by using CHEMKIN in which thermodynamic and kinetic data are needed as input. The detailed chemical kinetic mechanism for the oxidation of MD has been developed by Herbinet *et al.* (2008) using the same systematic rules of Curran *et al.* (1998, 2002) for n-heptane and iso-octane. They noticed an error in the activation energy for H-atoms abstraction reaction. There was no significant difference even though they changed this erroneous value in relevant reactions (Herbinet *et al.* 2010). In the present work, the updated kinetic parameters and the thermochemical properties were used in this mechanism. The skeletal model which contains 45 chemical species and 74 reactions was developed based on LLNL and KUCRS. The results indicate that the mixture of methyl decanoate and n-heptane is consumed via the abstraction of hydrogen atoms to produce fuel radicals which ultimately lead to the production of alkenes.

The main reaction paths are the abstraction of H atom to produce MDJ ($C_{11}H_{21}O_2$) and the decomposition and partial oxidation reactions from MD to C_3 hydrocarbons and the oxidation reactions of C_3 hydrocarbons. The high temperature reaction oxidation was determined by approving the concepts of engine research center (ERC) mechanism (https://www.erc.wisc.edu/chemicalreaction). For the low temperature oxidation, the first addition of an alkyl radical to O_2 is the most predominant reaction. Herbinet *et al.* (2010) considered the rate constants used for their reactions depending on the number of atoms in the cyclic transition state and on the type of H-atoms. The first reaction step is the addition of O_2 to the methyl ester radical at the low temperature part of the mechanism. In this study, the low temperature reaction oxidation was calculated based on Tsurushima (2009). The degradation of low temperature chain oxidation was taken place when the formation of small olefins and aldehydes was not considered as intermediates at low temperature oxidation.

The reactions of additions of H-atoms, HO_2 and OH to the C-C double bond of the reactant fuel have already been included in the methyl decanoate (MD) mechanism (Herbinet *et al.* 2008, Herbinet *et al.* 2010). At the high temperature mechanism, the reaction sets for these two fuels are built by including C_3 oxidation reactions which are derived from Patel's model (Patel *et al.* 2004) and Kawanabe's model (Kawanabe and Ishiyama 2012) to the reaction system. The low temperature oxidation reactions are described in Table 1 which includes the decomposition and partial oxidation reactions of the fuel. "KET" represents a ketohydroperoxide. The initial model was unable to predict the auto-ignition delay, even if the frequency factor of each reaction was adjusted.

Reaction Rate Adjustment

The adjustments of frequency factors (A) in each reaction are used to catch the full kinetic models in this study. In particular, the reactions R8 and R13, which can be seen in Table 1, captured the good reasonable agreement among these reactions. The calculation was based under the condition of *p=2, 4MPa, ∅=1.0.* All of the reactions in skeletal model generally

Table 1. Low temperature reactions for the skeletal kinetic model

Methyl Decanoate (MD)				
No.	Reaction	A	n	E
1	MD + O_2 = MDJ + HO_2	1.00E+16	0	4.60E+04
	Rev	1.00E+12	0	0.00E+00
2	MDJ + O_2 = MDO_2	6.00E+12	0	0.00E+00
	Rev	2.51E+13	0	2.74E+04
4	MDO_2 = MDOOHJ	1.51E+11	0	1.90E+04
	Rev	1.00E+11	0	1.10E+04
5	MDOOHJ + O_2 = $MDOOHO_2$	3.16E+11	0	0.00E+00
	Rev	2.51E+13	0	2.74E+04
6	$MDOOHO_2$ => MDKET +OH	8.91E+10	0	1.70E+04
7	MDKET => C9OOCO + CH_2O + OH	2.39E+15	0	4.30E+04
	!C_9OOCO+O_2 =>			
	C_3H_6+C_2H_4+C_2H_4+HCO+HCO+CO+HO_2	3.16E+13	0	1.00E+04
	C_9OOCO+O_2 => $C_7H_{14}R$+HCO+HCO+CO+HO_2	3.16E+13	0	1.00E+04
	$C_7H_{14}R$ => C_3H_6+C_2H_4+C_2H_4	3.16E+15	0	1.00E+04
8	MD + OH => MDJ + H2O	1.20E+14	0	3.00E+03
9	MDJ + O_2 = MDD + HO_2	1.26E+13	0	6.00E+03
	Rev	3.16E+11	0	1.95E+04
10	MDD + O_2 => MOJ + CH_2O + HCO	3.16E+13	0	1.00E+04
11	MD + HO_2 = MDJ + H_2O_2	1.00E+13	0	1.70E+04
12	MDJ => MOJ + C_2H_4	2.50E+13	0	2.88E+04
13	MOJ = C_3H_7+C_2H4+C_2H_3+HCO+CH_2O	1.14E+11	-0.42	2.70E+04

*k= $AT^n exp(-E/RT)$

predicted shorter ignition delays during calculation. It was found that the best estimation was occurred with the frequency factor of R8 which is 10 times larger than the original model and that of R13 which is 10^4 times smaller than the original model. In particular, the sensitivity of the present skeletal mechanism can be found during negative temperature coefficient (NTC) regime and low temperature oxidation

RESULTS AND DISCUSSION

The kinetic modeling of biodiesel combustion study is dependent on the use of surrogate fuels such as short chain alkyl esters and long chain alkyl esters (Jason *et al*. 2011). The surrogate fuels should be able to predict the combustion characteristics, ignition properties, flame properties, etc. The detailed kinetic mechanism has been generated to describe the oxidation of the surrogate fuels to obtain a reaction mechanism of manageable size and n-heptane at low and high temperature ranges. It is necessary to furnish that the compact skeletal kinetic model should reproduce the reasonable data to capture the full kinetic model based on various conditions.

Comparisons of Ignition Delay Times of Skeletal Model and Full Kinetics

In the present model, methyl decanoate and n-heptane are used as surrogate blend fuel, and a chemical reaction is calculated by a skeletal kinetic mechanism which is constructed based on the methyl decanoate model generated by LLNL and the n-heptane model developed by KUCRS. The skeletal model was assembled in order to better represent the oxidation of long methyl esters. Fisher *et al*. (2000) developed the kinetic mechanism for two oxygenated fuels: methyl butanoate and methyl formate. Because of the lack of any ignition data for some biodiesel surrogate fuel blends, we compared the ignition delay times of methyl decanoate (MD) and n-heptane to those of full kinetic models. Naik and Westbrook (2009) showed that the autoignition behavior of methyl stearate is similar to n-heptane and n-decane mechanism. They compared the auto-ignition characteristics of long chain methyl esters to those measured in shock tubes for n-heptane and n-decane at different pressure conditions. MD has no double bond and less reactive than n-decane in such case of n-alkane experiments at the lower temperature. Ignition delay predictions were also performed using LLNL mechanism. The fuel is thermally decomposed into the smaller hydrocarbons such as C_3H_6, C_2H_4 during the delay period (Kawanabe and Ishiyama 2012, Patel *et al*. 2004). Using the present model, the ignition processes at high temperature and pressure similar to those in diesel engine conditions are calculated for the fuels.

Figure 1 shows the change of the ignition delay times against the temperature under constant pressure conditions such as p = 4MPa and p= 2MPa. The thick and thin lines represent the results of full kinetics and the solid square and circle symbols show those of present model.

The ignition delay results by the present model are in good agreement with those

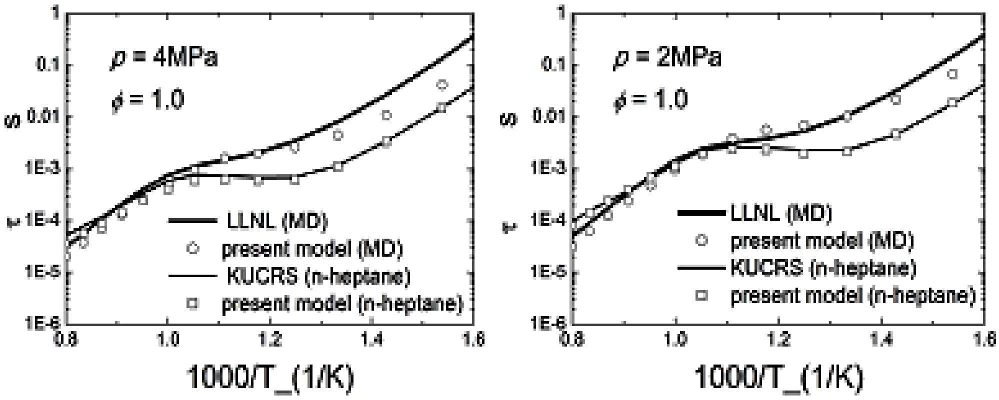

Fig. 1 : Comparison of ignition delay times of present model with full kinetics developed by LLNL and KUCRS

by the full kinetic models. In particular, the ignition delay times are well reproduced at temperature ranging from T_i= *800K* to *1200K* for both fuels while the slightly shorter ignition delay time is found for MD around 700K at 4MPa.

Comparisons of Ignition Process of Skeletal Model and Full Kinetics

The changes of chemical species during the combustion process are determined for both of full kinetics and present model. The ignition processes of the mixture under the high temperature and pressure conditions are discussed based on the changes of some chemical species. The changes of chemical species during combustion process are determined for both of full kinetics and present model. The temporal changes of the mole fractions for fuels, O_2, OH, CO, CO_2, HO_2, H_2O_2, H_2O and CH_3 with temperature T_i= 900K under constant pressure conditions are shown in figure 2. The concentration of CO and CO_2 of present model, which affect the heat release, are slightly larger than those of full kinetic model. The temporal changes for HO_2 are well reproduced in the low temperature to high temperature heat release. These species take significant parts during the ignition process. For n-heptane, all of the species have similar temporal changes except larger CO_2 concentration at 2MPa. We also found that the temperature change is well reproduced at both conditions. Based on this condition, further investigation would be necessary to catch this discrepancy which means the change of formation of chemical species between the present model and full kinetics.

Effects of Equivalence Ratios (∅)

The effect of equivalence ratios on the ignition process is also investigated. Figure 3 exhibits the comparison of ignition delay time τ against various equivalence ratios ∅. All of the black lines represent the results of full kinetic models and solid circles for 2MPa, solid triangles for 4MPa, respectively. The tendency of the ignition delay time change of the developed present skeletal kinetic model is similar to those of the full kinetic model. Then, τ at higher equivalence ratios is slightly longer compared with the results by the full

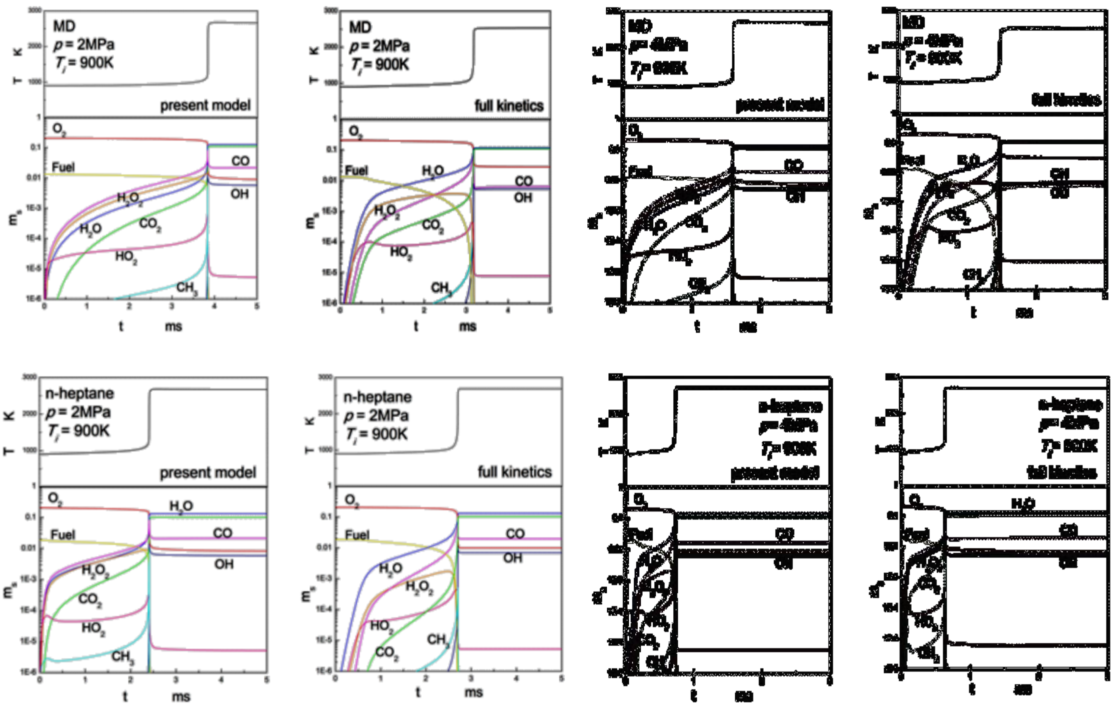

Fig. 2 : Course of temperature T and mole fraction for some chemical species for MD and n-heptane

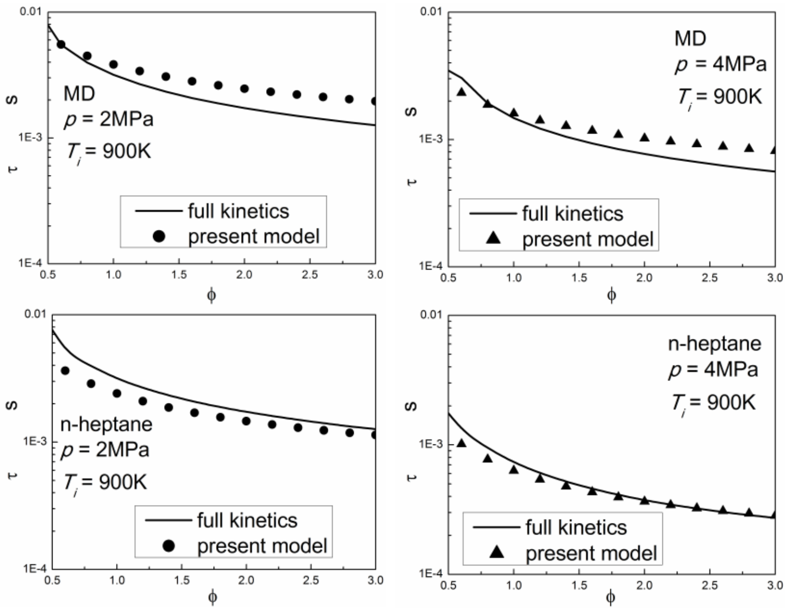

Fig. 3 : Change of ignition delay time τ against equivalence ratio for MD and n-heptane

kinetic models. It is profoundly compared the changes of τ against the equivalence ratios $\emptyset=1.0$(the color in black), $\emptyset=2.0$(the color in green) and $\emptyset=3.0$ (the color in red) as depicted in figure 4. MD gives slightly shorter ignition delays at 4MPa during negative temperature coefficient (NTC) region. The skeletal kinetic model is calculated based on the ignition processes of fuel mixture under an engine like high

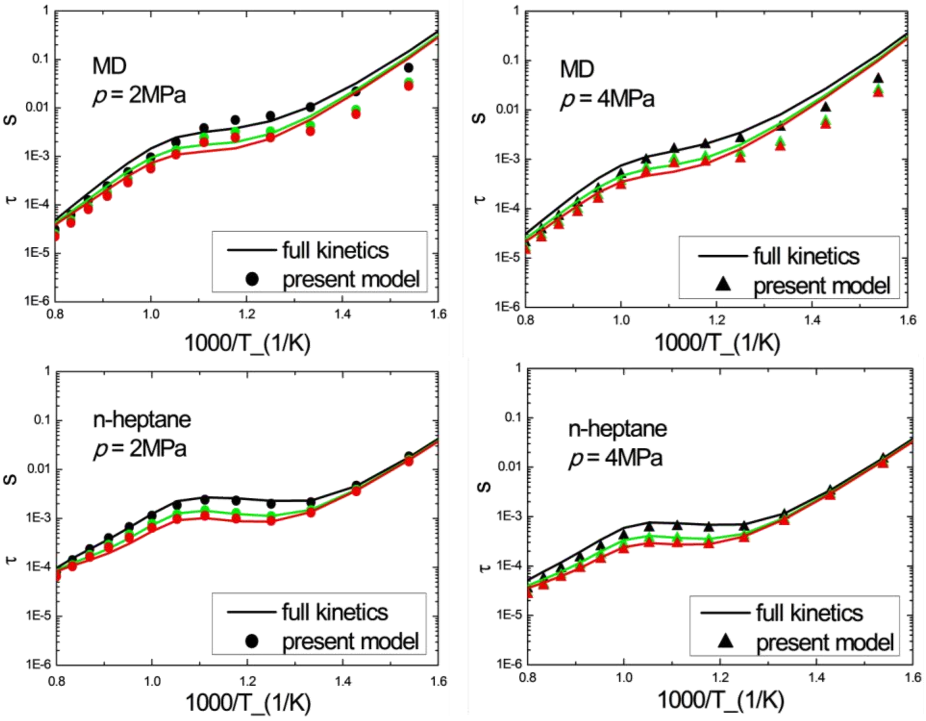

Fig. 4 : Comparison of changes of ignition delay times for present model with full kinetic models against various equivalence ratios

temperature and high pressure condition. It can be observed that the results are successfully compared with the full kinetic models. Negative temperature coefficient (NTC) phenomenon gave a strong effect to reproduce the good agreement during constructing of present model in this work.

Comparison with Some Experimental data

We also tried to compare the data of present skeletal model, full kinetics and some experimental data. It is significant to note in figure 5 that the lower ignition delays for full kinetics and present model are found in comparison with the experimental work. To capture the differences between the predictions of present model and experiment in more detail, it will be necessary to study the simulation of engine or some combustion devices using commercial computational fluid dynamics (CFD) code.

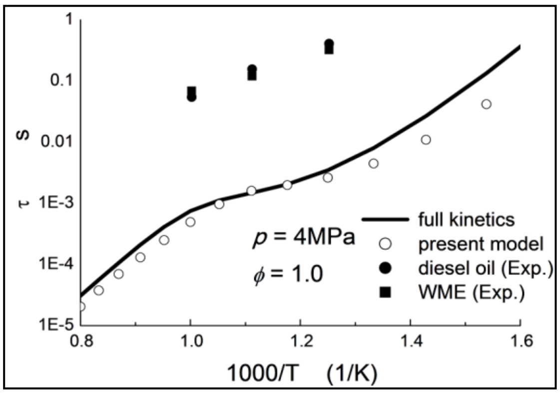

Fig.5 : Comparison of present model and experimental data of diesel oil and waste-cooking oil methyl ester

CONCLUSIONS

The skeletal kinetic mechanism including 45 chemical species and 74 chemical reactions was developed in this study. The temperature dependency of the ignition delay time of fuels for MD and n-heptane is well reproduced by the present skeletal model. The temporal changes of HO_2 are well reproduced by this model from the start from low temperature heat release to high temperature heat release. Therefore, the reasonable good agreement is exclusively found between the developed skeletal kinetic model and full kinetic models which are built by LLNL and KUCRS. The direct formation of oxygenated hydrocarbons warrants further investigation into the practical biodiesel combustion systems. Moreover, it is necessary to apply some commercial engine combustion simulation codes to validate this developed skeletal kinetic model in the near future.

ACKNOWLEDGMENT

The authors would like to thank Prof. Miyoshi for his kind helpful advices during the calculations.

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