

Combustion Model for Biodiesel-Fueled Engine Simulations using Realistic Chemistry and Physical Properties

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ABSTRACT

Biodiesel-fueled engine simulations were performed using the KIVA3v-Release 2 code coupled with Chemkin-II for detailed chemistry. The model incorporates a reduced mechanism that was created from a methyl decanoate/methyl-9-decenoate mechanism developed at the Lawrence Livermore National Laboratory. A combination of Directed Relation Graph, chemical lumping, and limited reaction rate tuning was used to reduce the detailed mechanism from 3299 species and 10806 reactions to 77 species and 209 reactions. The mechanism was validated against its detailed counterpart and predicted accurate ignition delay times over a range of relevant operating conditions. The mechanism was then combined with the ERC PRF mechanism to include n-heptane as an additional fuel component.

The biodiesel mechanism was applied in KIVA using a discrete multi-component model with accurate physical properties for the five common components of real biodiesel fuel. A mixture of methyl decanoate and methyl-9-decenoate was used as the biodiesel surrogate to account for both the saturated and unsaturated components found in real biodiesel fuels. Non-reacting biodiesel spray experiments were reproduced using the KIVA model, and the KH-RT spray model constants were adjusted to improve the liquid penetration trend under varying density and temperature conditions. The complete biodiesel engine model was shown to adequately reproduce the pressure and heat release rate predictions of diesel engine combustion experiments fueled with a soy methyl ester biodiesel. These results show that the

model gives accurate predictions of biofuel spray vaporization and combustion for these conditions. The current biodiesel model was also compared to a previous model and found to improve the magnitude of the NO_x prediction, as well as the trend of decreasing NO_x with increasing load.

INTRODUCTION

While biodiesel is not widely available for mainstream engines, interest in the fuel began to increase in the past decade motivated by the desire to reduce dependence on foreign oil imports and to address CO₂ emission/greenhouse gas concerns by adopting a renewable fuel source. This interest has led to several studies focusing on biodiesel combustion [1, 2, 3, 4] and spray behavior [5, 6], as well as its application in engines [7, 8, 9, 10]. These biodiesel studies highlight the need for engine models that can accurately predict effects due to the fuel characteristics. Such models offer the promise of reducing or even eliminating much of the time and expense associated with engine testing over wide operating conditions in the laboratory.

An accurate engine model requires that both the combustion chemistry and the physical processes (spray breakup, atomization, vaporization, etc.) are well represented. These two aspects of the model depend on the fuel's composition. Biodiesel is made from the transesterification of fatty acids with an alcohol [11]. A common alcohol used in the process is methanol, which results in a biodiesel fuel that is mainly composed of five methyl esters: 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 ($C_{19}H_{34}O_2$), methyl linolenate ($C_{19}H_{32}O_2$). As seen in [Figure 1](#), methyl palmitate and methyl stearate are saturated, while methyl oleate, methyl linoleate, and methyl linolenate contain one, two, and three double-bonds, respectively. A common short-hand notation for these methyl esters is simply $Cx:y$, where ‘x’ represents the number of carbon atoms in the alkyl chain and ‘y’ represents the number of carbon-carbon double-bonds (e.g., $C16:0$ for methyl palmitate).

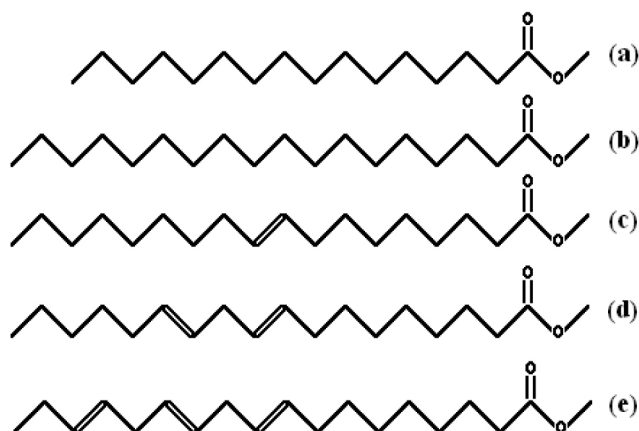


Figure 1. Five common components of biodiesel: (a) methyl palmitate, (b) methyl stearate, (c) methyl oleate, (d) methyl linoleate, and (e) methyl linolenate [12]

In order to adequately represent the combustion chemistry of biodiesel fuel, an accurate chemical kinetic mechanism must be available. Previous work has explored the use of methyl butanoate ($C_5H_{10}O_2$) as a biodiesel fuel surrogate [13], but studies have shown that this species does not adequately capture the ignition delay or the species history (e.g., CO_2) seen in biodiesel [1,2,14,15]. These results have been attributed to the insufficient length of the carbon chain in the surrogate. Others used a combination of methyl butanoate with *n*-heptane to represent biodiesel chemistry with some success [16, 17]. More recently, researchers at the Lawrence Livermore National Laboratory (LLNL) have proposed methyl decanoate ($C_{11}H_{22}O_2$) as a biodiesel fuel surrogate, arguing that its longer carbon chain would provide a better prediction of the ignition and species history [15]. The mechanism was tested against a limited number of ignition and jet-stirred reactor (JSR) experiments and it was seen that it does appear to be more representative of biodiesel fuel chemistry.

Studies have shown that the appearance and location of double-bonds can have a significant effect on the fuel chemistry [14,18]. Since biodiesel is typically composed of several unsaturated methyl esters, the methyl decanoate mechanism was expanded to include methyl-9-decenoate

($C_{11}H_{20}O_2$), which has a double-bond at the ninth position on the carbon chain [14]. [Figure 2](#) compares the chemical structure of the biodiesel fuel surrogates that have detailed chemistry mechanisms available to-date. The figure also depicts the numbering scheme applied to the carbons, as implemented in the LLNL mechanisms. Note that the species contain the similar methyl ester structure seen in [Figure 1](#), and the methyl-9-decenoate double-bond is in the same location as that of the first double-bond in the methyl oleate, methyl linoleate, and methyl linolenate components of real biodiesel fuels.

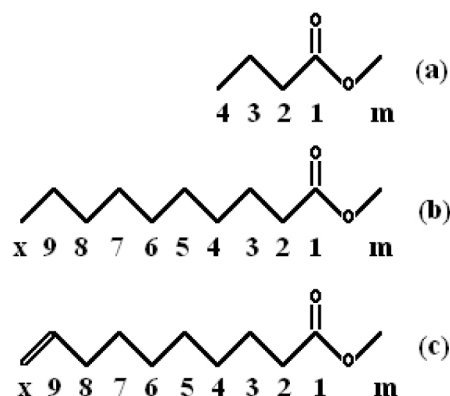


Figure 2. Chemical structure of three biodiesel surrogate species with available mechanisms: (a) methyl butanoate, (b) methyl decanoate, and (c) methyl-9-decenoate

The LLNL mechanism also included *n*-heptane for use as an alkane surrogate for biodiesel blending. As a result of their long carbon chains, the combined methyl decanoate (MD) and methyl-9-decenoate (MD9D) mechanism from LLNL contains 3299 species and 10806 reactions. While this mechanism was found to adequately represent biodiesel chemistry, it cannot be directly applied in engine computational fluid dynamics (CFD) models since computational time generally increases as the square of the number of species. Therefore, it is necessary to use a reduced mechanism for application in CFD models.

The general procedure for mechanism reduction involves identifying species and reactions that do not significantly contribute to the specific desired results (e.g., ignition delay time) of a given operating condition and removing them from the mechanism. For detailed mechanisms on the order of 100 species, it is possible to use a simple reaction flux analysis to identify which species are insignificant [16,19]. However, when mechanism sizes exceed 1000 species, it can be time consuming to manually evaluate every possible pathway. Several automated reduction techniques are available, which have been shown to drastically reduce the size of mechanisms, while maintaining much of the fidelity of their detailed counterparts.

Lu and Law [20] applied the theory of directed relation graph (DRG) to the process of mechanism reduction. This method identifies unimportant species by considering how they are coupled to other species in the mechanism. A normalized contribution parameter, r_{AB} , is calculated to quantify the contribution of species B to the production rate of species A. In Equation 1, I is the total number of reactions, $\nu_{A,i}$ is the overall stoichiometric coefficient for species A, ω_i is the production rate, and $\delta_{B,i}$ is a delta function that is unity if reaction i contains species B, and zero otherwise.

$$r_{AB} \equiv \frac{\sum_{i=1,I} |\nu_{A,i} \omega_i \delta_{B,i}|}{\sum_{i=1,I} |\nu_{A,i} \omega_i|} \quad (1)$$

The nodes in the directed relation graph are linked to individual species in the mechanism and an edge is formed between two species if r_{AB} is larger than some user-specified tolerance ε . Key species of interest (i.e., fuel and desired products) are identified and r_{AB} is calculated with respect to those species. The DRG can then be used to identify which species are strongly coupled to those key species and to eliminate the rest. Using a threshold value of $\varepsilon = 0.16$, the authors demonstrated that a detailed ethylene reaction mechanism of 70 species could be reduced to 33 species without a significant effect on performance. The reduced and detailed mechanisms were well matched in terms of auto-ignition and temperature profiles from perfectly stirred reactor simulations.

Perpiot-Desjardins and Pitsch [21] made several improvements to the DRG method. They noted that the original version considered production and consumption reactions of equal weight, but that a species that only consumes A would not have the same effect as one that produces and consumes it. This error-propagating (DRGEP) method considers the net contribution of species B to species A, giving a more appropriate indication of the strength of the relationship between the two species. Using this idea, Equation 1 was reformulated into Equation 2.

$$r_{AB,PDP} \equiv \frac{\sum_{i=1,I} |\nu_{A,i} \omega_i \delta_{B,i}|}{\max(P_A, C_A)} \quad (2)$$

where

$$P_A = \sum_{i=1,I} \max(0, \nu_{A,i} \omega_i)$$

$$C_A = \sum_{i=1,I} \max(0, -\nu_{A,i} \omega_i)$$

Other modifications have been made to the DRG reduction method and several studies have applied the method to reduce the methyl decanoate mechanism. Shi et al. [22,23]

developed an automatic reduction code based on the DRGEP method that used a Senkin-based model for single-zone HCCI engine simulation. The mechanism reduction procedure compared three performance parameters (CA50, peak pressure and peak heat release) of the reduced mechanism to those of the detailed mechanism. Additional details of this model are included in following section. Using this code, the original MD mechanism (no MD9D) was reduced from 3036 species and 8555 reactions to 435 species and 1098 reactions with validation against the detailed mechanism in single-zone HCCI simulations.

Seshadri et al. [4] reduced the MD mechanism to 125 species and 713 reactions with validation against the detailed mechanism in perfectly stirred reactor (PSR) simulations and against extinction experiments in a counterflow reactor. Luo et al. [24] focused on the high-temperature chemistry and used a combination of DRG and chemical lumping to reduce the MD+MD9D+n-heptane mechanism to 118 species and 837 reactions. The results were well matched to the detailed mechanism in PSR simulations and to jet stirred reactor experiments with rape seed oil methyl ester. DRG has shown promise as a means of significantly reducing the methyl decanoate mechanism. However, current computational resources still require mechanisms to be less than 100 species to ensure efficient computational times for use with multi-dimensional engine models.

The following section describes the single-zone model used in this work for mechanism reduction, as well as relevant aspects of the CFD code used for constant volume spray and biodiesel-fueled engine simulations. This is followed by a description of the procedure used in this work to create and validate an efficient reduced biodiesel surrogate mechanism from the detailed MD/MD9D mechanism [14]. The next section contains a description of the fuel property database required to accurately represent the five main components of soy-based biodiesel fuel. Finally the complete model is tested against constant volume spray experiments and biodiesel-fueled engine experiments performed at Sandia National Laboratories [5,9].

METHODOLOGY

SIMULATION MODELS

Two simulation models were used in this study. The first is the single-zone, Senkin-based DRGEP model mentioned previously [22]. For the current work, the code was modified to include a constant volume reactor model to test the mechanism's performance over a wider range of conditions. The code calculates the contribution index ($r_{AB,PDP}$ in Equation 2) for each species in the mechanism and compares the value to a given contribution tolerance, ε . Species with indices below ε are deemed to have an insignificant effect on the key species and can be reliably removed from the

mechanism. A reduced mechanism is generated and a second simulation is run to compare the performance parameters (ignition delay, peak pressure, and peak key species concentration) predicted by the reduced mechanism to those of the detailed mechanism at given conditions. If the reduced mechanism results do not exceed a specified error tolerance, DRG is repeated with an increased (less stringent) ϵ value. The process continues until either the error tolerance is exceeded or the mechanism size no longer changes. Following each reduction set, the single-zone simulations were repeated over 13 initial temperature conditions and compared to the detailed mechanism's results.

Multi-component engine simulations were conducted using KIVA3 V-Release 2 coupled with the Chemkin II library for chemistry [25, 26, 27, 28]. The IVC temperature, pressure and species concentrations are supplied to the chemistry model, which considers each cell as a well-stirred reactor. In subsequent time-steps, species concentrations and thermodynamic conditions are passed to the chemistry solver and the rate of change of each species is calculated based on the mass fraction, density, production rate and molecular mass of each species. Turbulence chemistry interactions are not considered in this work. Previous researchers [29, 30, 31] have found that energy release is dominated by chemistry effects and not by sub grid-scale turbulent transport. In addition, Kokjohn et al. [29] found that when flame propagation was considered, the flame structure is well predicted without the use of sub-grid scale turbulence-chemistry interactions (i.e., LES).

Ra and Reitz [32,33] expanded the KIVA3v-Release 2 package to include discrete multi-component (DMC) fuel considerations. Unlike a single-component model, the DMC code allows preferential evaporation based on the specific properties of each component. In addition, these individual components can be coupled with representative species in the reaction mechanism to account for component-specific chemistry. For this work, property information was obtained for each of the five main components of soy biodiesel and added to the KIVA-DMC fuel library. In terms of chemistry, the two saturated species (methyl palmitate and methyl stearate) are represented by MD and the unsaturated species (methyl oleate, methyl linoleate, and methyl linolenate) are represented by MD9D. NO_x formation is modeled with the addition of four species and 12 reactions to the mechanism [34,35] and soot is not considered in this work.

Spray break-up is modeled using the hybrid Kelvin-Helmholtz (KH)/Rayleigh-Taylor (RT) spray model [36]. The KH model predicts the primary break-up stage by evaluating the break-up time, τ_{KH} , using Equation 3, in which B_1 is an adjustable constant, and Ω_{KH} and Λ_{KH} are the calculated frequency and wavelength of the fastest growing wave, respectively (in KIVA, B_1 is termed “cnst22” and given a

value 40). As seen in the equation, a larger B_1 results in a longer break-up time and larger droplets.

$$\tau_{KH} = \frac{3.726 B_1 r}{\Omega_{KH} \Lambda_{KH}} \quad (3)$$

The radius of a child droplet in the KH model is calculated using Equation 4, where B_0 is an adjustable constant (in the KIVA model, B_0 is termed “balpha” and is assigned a value of 0.6).

$$r_c = B_0 \Lambda_{KH} r \quad (4)$$

A break-up length, L_b , is calculated using Equation 5,

$$L_b = C_b d_0 \sqrt{\frac{\rho_f}{\rho_a}} \quad (5)$$

where ρ_f and ρ_a are the fluid and air densities, respectively, and d_0 is the parent droplet diameter. C_b (known as “distant” in KIVA) is an adjustable constant with a value of 1.9. Beyond this break-up length, the RT model is utilized in modeling secondary break-up of the individual drops. When the wavelength of the fastest growing wave on a given droplet is smaller than the droplet diameter, RT waves grow on the droplet surface. When the waves grow for a time greater than the break-up time, the droplet breaks up into child droplets. The radius of each child droplet is given in Equation 6, where C_{RT} is an adjustable constant (“cnst3rt” in KIVA with a value of 0.10) and K_{RT} is the calculated wave number. In general, a smaller C_{RT} value will produce smaller child droplets.

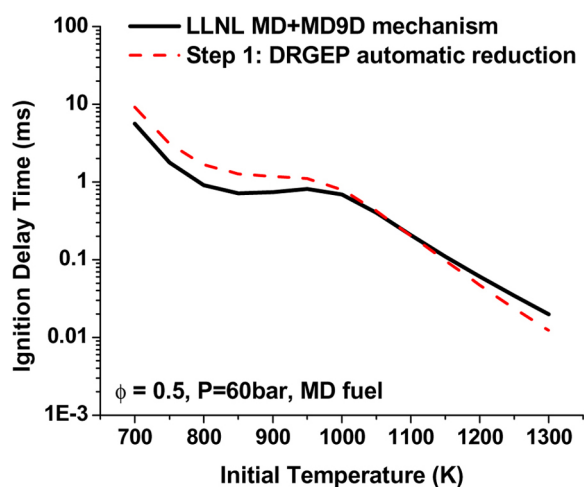
$$r_c = \frac{\pi C_{RT}}{K_{RT}} \quad (6)$$

The DRGEP mechanism reduction process was completed on a 2.40 GHz Intel® Core™ 2 desktop computer. The initial single-zone simulations, using the 3299-species detailed mechanism at a single operating condition, took about 10 hours to complete. The results from these simulations were used in the DRGEP reduction process, which repeated the single-zone simulations with consecutively reduced mechanisms. These reduction sets were completed in less than 5 hours. The single-zone initial temperature sweeps (to test the reduced mechanisms) and the spray and engine simulations were run on a computer cluster that consists of an array of Intel® Pentium™4 and Core™2 processors. The single-zone initial temperature sweeps were run on a single

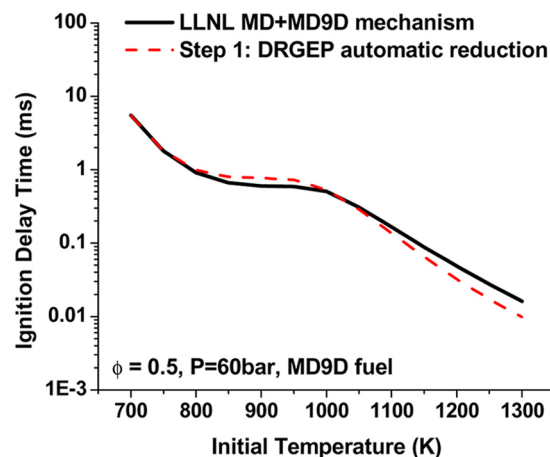
processor and the 13 conditions were completed in less than 5 minutes. The spray simulations finished in about 15 minutes on a single processor. The engine simulations were run in parallel and took about 40 hours on two processors (about 80 CPU hours total).

MECHANISM REDUCTION

Mechanism reduction was performed in four main steps. In the first step, DRGEP was applied to the detailed mechanism using the MD fuel and MD9D fuels separately, which was done to ensure that each fuel is properly modeled. A lean equivalence ratio ($\phi=0.5$) and low temperature ($T=800\text{K}$) condition was chosen for the DRG reduction, because these conditions require the greatest number of reactions. The initial DRGEP contribution tolerance was set to 1.0e^{-4} as recommended by Ref. [22]. The key species to track were the fuel, CO and HO_2 to ensure that the fuel decomposition, CO oxidation and $\text{H}_2\text{-O}_2$ chemistry were well represented. The error tolerance for comparison to the detailed mechanism's ignition delay time was set to 50% for this step in order to obtain a very small mechanism. This step resulted in two separate intermediate mechanisms, with 359 species (1228 reactions) for MD fuel and 270 species (1052 reactions) for MD9D fuel. Figure 3 shows ignition delay time calculations for the two fuels.



(a)



(b)

Figure 3. Ignition delay time predicted for step 1: (a) methyl decanoate and (b) methyl-9-methyl decenoate fueling with intermediate reduced mechanism.

Agreement is seen to be better between the intermediate MD9D mechanism and the detailed mechanism, because the error tolerance never exceeded 15% and the DRG simply failed to find any further species with low contribution indices to remove. The MD intermediate mechanism was limited by the error tolerance. The general trend of the ignition delay time curves remains intact and discrepancies between the intermediate and detailed mechanisms are accounted for in the second step, as described next.

In the second step, isomer species in each mechanism were identified and lumped into a single, representative species and slight adjustments to the rate constant were applied, if necessary. These isomers tend to have common thermodynamic data and often share the same reaction rates in reactions. Figure 4 shows one of the many sets of isomers created when MD is the fuel. The “j” represents a radical site on the carbon numbered according to the convention shown in Figure 2. In this case, md6j had the largest reaction flux and was chosen to represent the remaining isomers, hence removing nine species. Once the isomers were lumped, the DRG procedure was repeated to remove species that lost pathways connecting them to the key species.

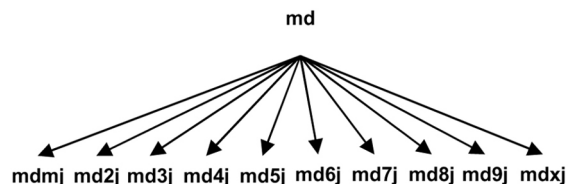
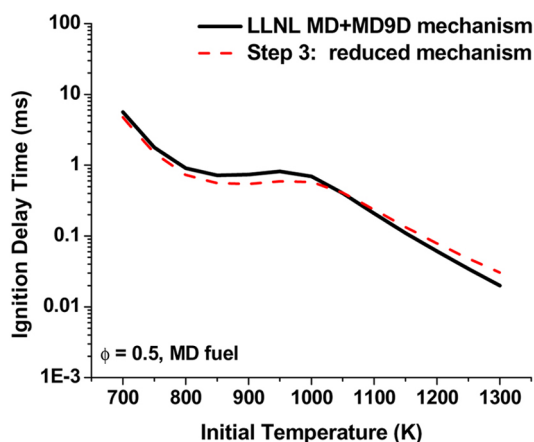


Figure 4. Example of one of the many sets of isomers formed from oxidation of the MD fuel species. Only md6j was retained in the second reduction step.

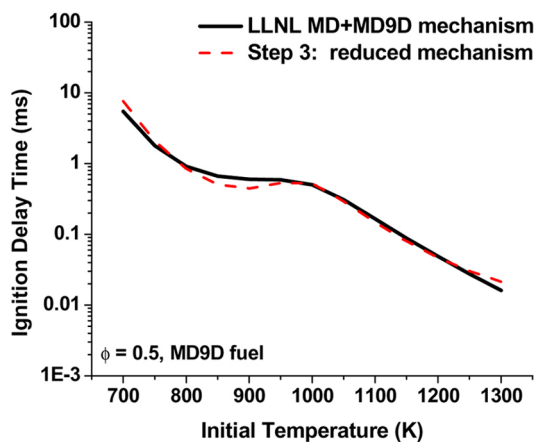
The third step combined the two reduced mechanisms into a single mechanism and tested each fuel over a range of conditions with the new reduced mechanism. The ultimate goal of this mechanism was to apply it in engine simulations. The conditions shown in [Table 1](#) are representative of those seen in engines and were used to validate the mechanism. [Figure 5](#) shows the resulting improved ignition delay predictions that should be compared to those in [Figure 3](#). This reduced mechanism contains 85 species and 280 reactions; a reduction of over 98%.

Table 1. Constant volume operating conditions used to test the performance of the reduced mechanism.

Parameter	Range Considered
Equivalence ratio, ϕ	0.5, 1.0, 2.0
Initial Temperature (K)	700-1300 (50K increments)
Initial Pressure (bar)	40, 60, 80



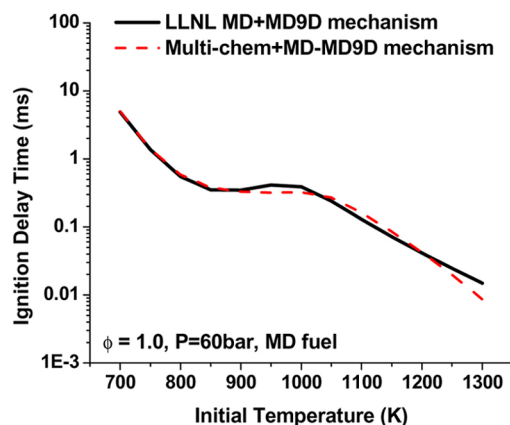
(a)



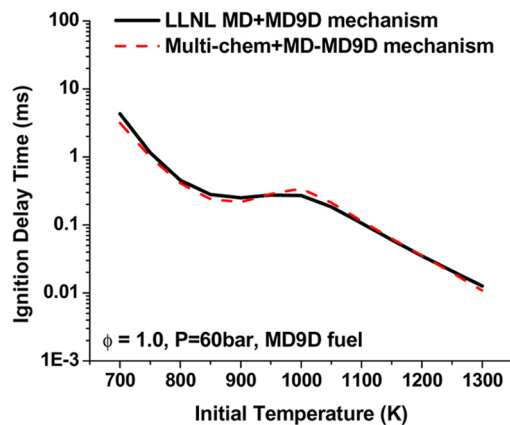
(b)

Figure 5. Ignition delay time predicted for (a) methyl decanoate and (b) methyl-9-methyl decenoate fueling after combining the two intermediate mechanisms from steps 1 and 2 into a single mechanism.

Finally, the MD-MD9D reduced mechanism was combined with a multi-chemistry mechanism that contains oxidation reactions for a variety of fuel species [33]. This was done anticipating that the present reduced biofuel mechanisms will be used to model biodiesel fuel blends in the future. The lower-level reaction pathways of the multi-chemistry mechanism were used to maintain consistency. Once the mechanisms were combined it was necessary to repeat the validation process. It was found that several lower-level carbon species could be removed from the MD-MD9D portion of the mechanism and the resulting model contained 77 species and 216 reactions (including those for n-heptane oxidation). [Figure A1](#) in the [Appendix](#) shows the key pathways identified in the mechanism reduction process. [Figure 6](#) shows the ignition delay predictions under stoichiometric conditions. Similar agreement was seen over the wide range of conditions shown in [Table 1](#).



(a)



(b)

Figure 6. Ignition delay time predicted for (a) methyl decanoate and (b) methyl-9-methyl decenoate fueling under stoichiometric conditions after combining intermediate mechanism from step 3 into a the multi-chemistry mechanism.