

Development and Validation of a Reduced Reaction Mechanism for Biodiesel-Fueled Engine Simulations

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ABSTRACT

In the present study a reduced chemical reaction mechanism for biodiesel surrogate fuel was developed and validated for multi-dimensional engine combustion simulations. An existing detailed methyl butanoate mechanism that contained 264 species and 1219 reactions was chosen to represent the oxygenated portion of the fuel. The reduction process included flux analysis, ignition sensitivity analysis, and optimization of reaction rate constants under constant volume conditions. The current reduced mechanism consists of 41 species and 150 reactions and gives predictions in excellent agreement with those of the comprehensive mechanism.

In order to validate the mechanism under biodiesel-fueled engine conditions, it was combined with another skeletal mechanism for n-heptane oxidation. This combined reaction mechanism can be used to adjust the energy content of the fuel, and account for diesel/biodiesel blend engine simulations. The combined mechanism, ERC-bio, contains 53 species and 156 reactions. Biodiesel-fueled engine operation was successfully simulated using the ERC-bio mechanism.

INTRODUCTION

In recent years, increasingly stringent emissions standards and the high price of petroleum-based fuels have renewed an interest in fuels from alternative sources. Biodiesel, an oxygenated fuel composed of mono-alkyl esters [1], is seen as a promising alternative to conventional diesel for use in compression-ignition (CI) engines. In terms of emissions, biodiesel has been shown to reduce unburned hydrocarbons, carbon monoxide, and particulate matter compared to its petroleum counterpart. In addition, biodiesel contains no sulfur, and therefore produces no sulfur oxides or sulfates. As a plant-based fuel, it can be produced domestically and is a renewable energy source [2].

Unfortunately, some disadvantages of biodiesel are limiting widespread use of the fuel. On a volumetric basis, there is less energy per gallon of biodiesel compared to conventional diesel, which results in an estimated 11% decrease in fuel economy. Additionally, biodiesel's higher cloud and pour points can cause flow problems in cold temperatures [3]. The most notable disadvantage is that biodiesel-fueled engines have been shown to increase oxides of nitrogen (NO_x) emissions. Several studies suggest increases of 10% or more for neat (100%) biodiesel [4]. The increase lessens if blends of biodiesel and diesel fuel are used, but in light of current and future regulations, any increase in emissions is undesirable.

The NO_x increase associated with the use of biodiesel is not completely understood and is the subject of many studies [4-7]. It is difficult to identify the main factor in the increase, because biodiesel and conventional diesel differ in both chemical and physical properties. As an oxygenated fuel, biodiesel combustion produces intermediate species that are not found in conventional diesel combustion. These intermediates and their reactions may cause the increased in-cylinder temperatures or reaction pathways responsible for NO_x production. In terms of physical properties, the density, kinematic viscosity and surface tension of biodiesel are much higher [8,9]. These properties can greatly affect spray penetration, break-up, and atomization, which may impact the start of combustion.

Multidimensional engine simulations have been used extensively to provide a better understanding of processes occurring inside the combustion chamber. Detailed kinetics models have been coupled with these simulations to improve predictions of the ignition and combustion processes [10-12]. These models require accurate reaction mechanisms to represent the species, pathways, and reaction rates that describe the fuel chemistry.

The objective of this work is to develop a practical reaction mechanism that will effectively predict biodiesel combustion in a multi-dimensional diesel engine simulation. Methyl butanoate (MB) has been suggested as a surrogate for the large methyl esters found in biodiesel. A detailed kinetic mechanism for MB was developed by Lawrence Livermore National Laboratory (LLNL) [13].

For this study, the LLNL detailed mechanism was reduced and combined with a skeletal n-heptane mechanism. Ignition delay times of the reduced MB and combined MB/n-heptane mechanisms were validated against the detailed mechanism. For further validation the mechanism was applied to engine simulations and the results were compared to biodiesel experiments performed at the Sandia National Laboratories' Combustion Research Facility in their SCORE engine.

MODEL FORMULATION

KINETIC MECHANISMS

A suitable model of ignition and combustion begins with a chemical kinetic mechanism. Mechanisms vary in size and complexity depending on the molecule of interest. Large molecules oxidize and decompose into hundreds of smaller species and can require thousands of reactions to describe the process. Alternately, smaller molecules generate less species and require significantly smaller mechanisms.

The detail and accuracy of kinetic mechanisms vary as well. Comprehensive mechanisms contain the most complete reaction information available and, as a result, are generally very large and unsuitable for multidimensional engine simulations. Skeletal mechanisms, which only include significant elementary reactions, are much smaller in size; yet maintain the key features of comprehensive mechanisms.

Surrogate Fuels

Typical hydrocarbon fuels are not pure substances. Diesel and gasoline, for example, consist of many, high molecular weight components. In addition, the exact composition of these fuels varies based on the source, distributor, and intended region of use. To model these fuels, each component would require its own set of species and reactions and the resulting mechanism could be computationally prohibitive. In response to this issue, it is common practice to represent complex fuels with a single, relatively simple, surrogate species that exhibits similar combustion characteristics.

Diesel fuel has been adequately represented by n-heptane ($\text{n-C}_7\text{H}_{16}$) in many combustion models. Curran *et al.* [14] developed a comprehensive mechanism for n-heptane oxidation that involved 550 species and 2450 reactions. Several modeling studies were used to determine the species and reactions

responsible for both high and low temperature kinetics. Numerical results from tests with initial pressures from 1-42 atm, temperatures from 550-1700 K, equivalence ratios from 0.3-1.5, and nitrogen-argon dilution from 70-99% were validated against experimental measurements from jet-stirred reactors, plug flow reactors, rapid compression machines, and shock tubes.

Although comprehensive mechanisms are very useful, they are much too large to apply with CFD models for practical simulations. When detailed chemistry is applied, computational run times on a single processor are found to be proportional to the square of the number of species, and the square of the number of computational grid points [15]. As a result, several reduced n-heptane mechanisms have been developed that are more appropriate for modeling use.

Seiser *et al.* [16] created a reduced n-heptane mechanism using a sensitivity analysis based on ignition delay. Constant pressure, homogeneous reactor simulations were performed using the detailed mechanism under several conditions. Species and all reactions in which the species appeared were systematically removed and the ignition delay time was measured. If the ignition delay did not deviate from that of the detailed mechanism by more than 0.84%, that species and its corresponding reactions were removed from the mechanism. This process resulted in an intermediate mechanism of 282 species and 1282 reactions. The mechanism was reduced further by assessing the chemical pathways related to the fuel breakdown and oxidation. Species were neglected if they only appeared in pathways where the rate of fuel breakdown and oxidation were small. The final reduced mechanism had 160 species and 770 reactions.

Golovitchev [17] created a skeletal n-heptane mechanism containing 40 species and 165 reactions. This method utilized sensitivity analysis and atom conservation. The resulting mechanism was validated against experimental shock tube data for 13.5 bar and 41 bar pressures.

The Golovitchev skeletal mechanism was further reduced by Patel *et al.* [12]. In a similar method to that of Seiser, a sensitivity analysis was performed on species over a range of operating conditions. Species and reactions were removed based on ignition delay time comparisons. This method included application of a micro-genetic algorithm to optimize reaction rate constants in order to improve the agreement with more detailed mechanisms. The final reduced mechanism included 29 species and 52 reactions and was successfully applied to diesel engine simulations over a wide range of operating conditions.

Unlike diesel, which consists of many components, soy-based biodiesel fuel is assumed to be composed of just five methyl esters: methyl palmitate ($\text{C}_{17}\text{H}_{34}\text{O}_2$), methyl stearate ($\text{C}_{19}\text{H}_{38}\text{O}_2$), methyl oleate ($\text{C}_{19}\text{H}_{36}\text{O}_2$), methyl linoleate ($\text{C}_{19}\text{H}_{34}\text{O}_2$) and methyl linolenate ($\text{C}_{19}\text{H}_{32}\text{O}_2$).

would seem relatively easy to create a representative biodiesel fuel from such a small number of components. Unfortunately, these long-chain methyl esters require large mechanisms to describe their oxidation, and the combination of the mechanisms for each ester would be even larger.

This dilemma illustrates the need for a biodiesel surrogate as well. Though biodiesel fuel has been available for many years, no widely accepted surrogate has been adopted. Recently, methyl butanoate (MB) was proposed as a surrogate for the large methyl esters found in biodiesel. Researchers at the Lawrence Livermore National Laboratory (LLNL) developed a detailed kinetic reaction mechanism for MB that contained 264 species and 1219 reactions [13]. This mechanism was validated using a limited number of low-temperature, sub-atmospheric experiments.

MB, a C_5 species, is of manageable size and features the similar $RC(=O)OCH_3$ chemical structure of biodiesel. Table 1 shows a comparison of MB with the average characteristics of the soy-based biodiesel typically used in the United States. Also included in the table is a hypothetical fuel mixture of 1 mole of MB and 2 moles of n-heptane.

Table 1: Comparison of soy-based biodiesel and methyl butanoate, a proposed surrogate for biodiesel fuel

	Soy-based Biodiesel	Methyl Butanoate	1 mole MB + 2 moles n-heptane
Chemical Structure	$RC(=O)OCH_3$	$R'C(=O)OCH_3$	$R'C(=O)OCH_3 + 2 C_7H_{16}$
Chemical Formula	$\sim C_{19}H_{34}O_2$	$C_5H_{10}O_2$	$C_{19}H_{42}O_2$
Lower H.V. (MJ/kg)	36-38	27	39
Molec. Mass (kg/kmol)	292	102	302
% Oxygen (by mass)	$\sim 11\%$	$\sim 30\%$	$\sim 11\%$

MECHANISM REDUCTION METHODOLOGY

The purpose of this study was to identify a kinetic mechanism that will allow accurate simulations of biodiesel-fueled engine operation using multi-dimensional CFD codes. The detailed MB mechanism, hereafter referred to as the "LLNL mechanism", is much too large for practical CFD modeling. As mentioned previously, computational time for CFD models that include detailed chemistry are strongly dependent on the number of species. Therefore it was necessary to reduce the 264-species LLNL mechanism before applying it to engine simulations.

Due to limited available experiments related to MB, validation for the reduced mechanism was simply based upon comparisons with the LLNL mechanism. Though several automated reduction processes have been proposed, the process was not automated in the present

study. Instead, it followed similar methods to those of Seiser [16] and Patel [12] with the goal of maintaining the same ignition delay timing as that of the LLNL mechanism. For this analysis, ignition was defined as the time at which the simulation experienced a temperature rise of 400K above the initial unburned gas temperature.

The reduction process used in this study consisted of the following steps:

1. Perform constant volume SENKIN analysis for a range of initial pressures, initial temperatures, and equivalence ratios (ϕ).
2. Identify significant species based on their peak concentrations. Remove insignificant species and reactions from mechanism.
3. Identify significant reaction pathways based on reaction path fluxes. Remove insignificant species and reactions from mechanism.
4. Adjust reaction rate constants slightly in order to match the ignition time of the detailed mechanism
5. Combine the resulting reduced MB mechanism with the reduced n-heptane mechanism of Patel [12], allowing one to adjust the oxygen content of the fuel by blending MB with n-heptane, as shown in Table 1.

At each step, ignition delay for the reduced mechanism was calculated and compared to the LLNL mechanism over the range of initial conditions. Figure 1 illustrates the definition of ignition delay time for one set of initial conditions.

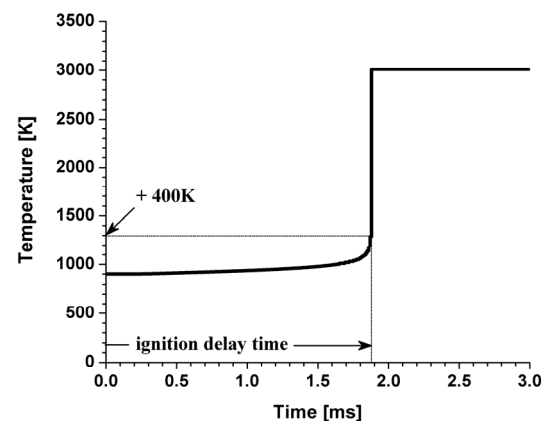


Figure 1: Ignition delay time at an initial temperature of 900K, initial pressure of 40 bar, and equivalence ratio of 1.0

SENKIN Analysis

SENKIN is a FORTRAN program used to analyze homogeneous gas mixtures in closed systems [18]. Six systems are available for analysis: adiabatic constant pressure, adiabatic constant volume, adiabatic time-dependant volume, constant pressure and temperature, constant volume and temperature, and time-dependant pressure and temperature. Once the problem is specified, SENKIN uses the same differential equations

as those in the CHEMKIN-II solver [19] to provide species and temperature histories of the mixture based on the given mechanism. In addition, SENKIN can evaluate sensitivity based on the reaction rates.

A constant volume adiabatic system was chosen for this study. Analysis began with a homogeneous mixture of air (20.95% O₂ and 79.05% N₂) and fuel (MB). The ratio of these components varied based on the desired equivalence ratio. Since EGR was not considered, no additional species were included in the initial mixture.

Initial conditions were varied to cover a range of pressures, temperatures, and equivalence ratios. In total, 90 conditions were evaluated in the SENKIN analysis. Table 2 summarizes these conditions.

Table 2: Operating conditions for adiabatic, constant volume SENKIN analysis

Condition	Range Evaluated
Initial Pressure [bar]	40, 60
Initial Temperature [K]	650-1350 (50 K increments)
Equivalence Ratio	0.4, 1.0, 1.5

Peak Concentration Analysis

XSENKPLOT is an interactive graphics postprocessor that displays species and reaction information provided from SENKIN [20]. The program presents molar concentrations, steady-state analysis, reaction rates, reaction equilibrium, and temperature/time histories of the species as graphs that can be manipulated by the user.

The initial analysis utilized the display of molar concentrations to identify thresholds below which species could be labeled insignificant. Four peak mole fraction thresholds were chosen (10⁻¹⁰, 10⁻⁹, 10⁻⁸ and 10⁻⁷). SENKIN constant volume results for φ=1.0 at 40 bar initial pressure were chosen for the concentration threshold analysis.

Starting with the 10⁻¹⁰ concentration (Threshold 1), species that never exceeded the specified threshold were removed. Ignition delay was recalculated to ensure that it was not significantly affected by the species removal. If ignition time did not vary from the detailed mechanism by more than 25% over the range of initial temperatures, the missing species were considered insignificant and remained out of the mechanism. The process was repeated for the three remaining threshold values.

Figure 2 shows the results of removing species with each of the four thresholds. It can be seen that removal of all species with concentrations less than 10⁻¹⁰ resulted in a considerable change in ignition time at low temperatures (Threshold 1). However, by retaining species with the methyl ester structure, the ignition time

was improved (Threshold 1*). Also, removal of species below 10⁻⁷ (Threshold 4) caused a delay in ignition. The species CH₂CHO, which is a reactive intermediate involved in several primary decomposition reactions of MB, was responsible for the delay. This species was replaced in the mechanism, which improved the ignition delay prediction (Threshold 4**). The peak concentration analysis thus eliminated 111 species from the LLNL mechanism without significantly changing the ignition time.

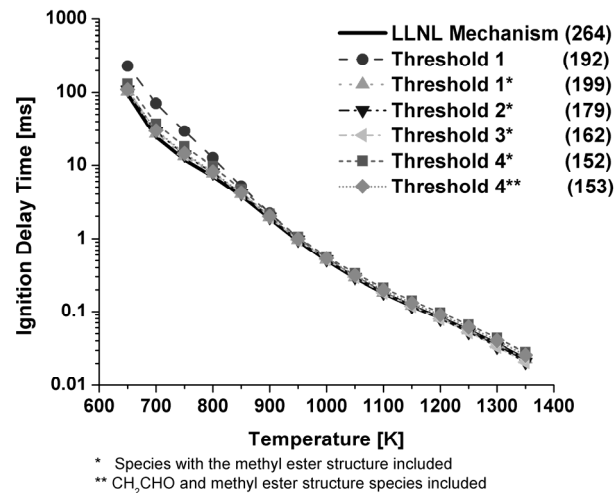


Figure 2: Sensitivity of ignition due to species removal based on peak molar concentration

Reaction Flux Analysis

Reaction pathway analysis was used to further reduce the mechanism. By assessing the relative flux of each species, it was possible to identify the most significant pathways. Flux is defined as the integral of the reaction rate over time.

XSENKPLOT offers another interactive feature that displays species and reaction pathways in a flowchart arrangement. This feature uses arrows of various widths to signify the importance of the flux of one species to the next. Users can view the reaction paths connecting each species in the mechanism and thus determine which pathways are important. The arrows connecting each species are separated into two sections: a base and a point. The width of the base section quantifies the destruction of the reactant species. The width of the point section quantifies the formation of the product species.

The first step in the flux analysis involved the pathways related to the breakdown of MB. Figure 3 illustrates an example of six pathways displayed by XSENKPLOT. The base width of the arrows suggests that the flux of MB to 'mb2j' is relatively high and this pathway is likely to be significant. The species 'mb2j' is simply methyl butanoate (the fuel) with a radical site (j) on the second carbon. The species notation used in the MB mechanism is described in Appendix A.

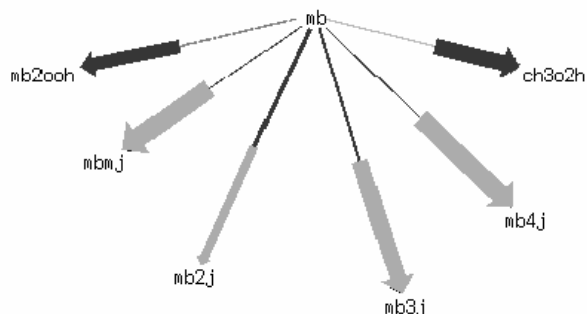


Figure 3: XSENKPLLOT's reaction pathway display showing the breakdown of MB fuel

Figure 4 shows that when the 'mb2j' species (and hence all connecting pathways that are not shown) was removed from the mechanism, ignition became significantly delayed. Removal of species 'mb2ooh' and 'ch3o2h' also caused large changes in ignition time. These three pathways were deemed to be important and were retained in the mechanism. However, 'mb3j', 'mb4j', and 'mbmj' had relatively small effects and these species, along with their corresponding reactions, were removed from the mechanism.

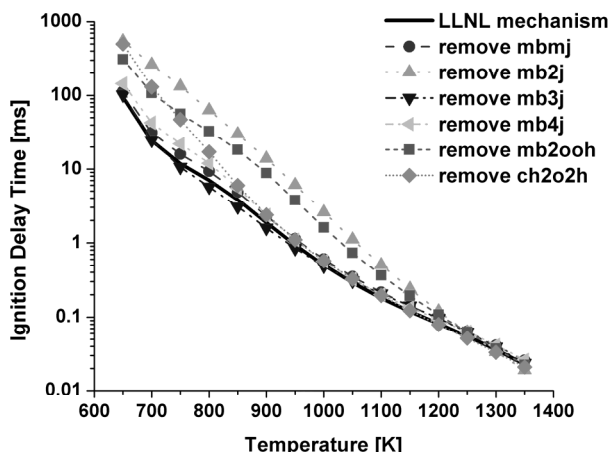


Figure 4: Sensitivity of ignition due to removal of pathways related to the breakdown of MB fuel

The reaction pathway analysis was repeated for the remaining pathways. The resulting significant pathways of the ERC-mb mechanism are shown in Figure 5. Several lower level species are shown in parentheses. SENKIN tests were repeated over the range of initial conditions of Table 2 to ensure that the new mechanism did not display significant discrepancies with the other equivalence ratios or pressures.

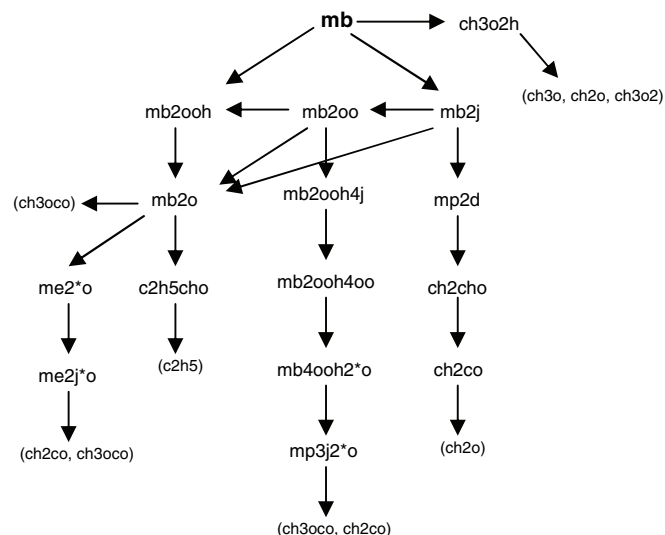


Figure 5: Significant pathways included in the reduced MB mechanism. Lower-level species are in parentheses

The final mechanism, "ERC-mb", contained just 41 species and 150 reactions. Twenty-two of these species are lower-level species that can be found in skeletal hydrocarbon mechanisms (e.g., CO_2 , O_2) and seven larger intermediates are included that may be represented in more comprehensive hydrocarbon mechanisms. The remaining 12 species contain the methyl ester structure, which make them unique to mechanisms for this type of oxygenated fuel.

Reaction Rate Adjustment

When species were removed from the mechanism, slight ignition delay changes were unavoidable. Figure 6 shows the ignition delay time predictions for the stoichiometric case at an initial pressure of 40 bar. The ignition delay times were in excellent agreement at high temperatures. However, at temperatures below 750 K, the ERC-mb mechanism over-predicted ignition delay times by as much as 40 ms.

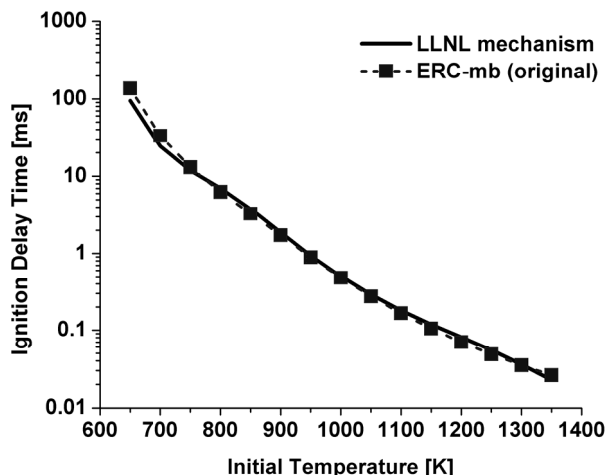


Figure 6: Initial ignition delay comparison for the ERC-mb mechanism at an initial pressure of 40 bar and equivalence ratio of 1.0.

In order to improve the ignition time predictions without increasing the number of reactions, it was necessary to adjust the reaction rate of certain reactions to compensate for species and pathways that were removed. The reaction rates are described by the Arrhenius rate expression:

$$k = A T^b \exp(-E / R T)$$

where “A” is the pre-exponential factor, “b” is the temperature exponent, and “E” is the activation energy. Kinetic reaction mechanisms include these three rate parameters.

Several reactions have been identified as significant in the ignition process of hydrocarbon fuels: [14,21-24]

1. high temperatures (>1200K)
 $H + O_2 \rightarrow O + OH$
2. intermediate temperatures (850K - 1200K)
 $H + O_2 + M \rightarrow HO_2 + M$
 $RH + HO_2 \rightarrow R + H_2O_2$
 $H_2O_2 + M \rightarrow OH + OH + M$
3. low temperatures (< 850K)
 $R + O_2 + M \rightarrow RO_2 + M$
 $RO_2 \rightarrow QOOH$

In the above steps, ‘R’ is an alkyl radical, ‘M’ is a third body, and ‘QOOH’ is the hydroperoxyalkyl radical. For the ERC-mb mechanism, it was necessary to adjust reactions that affect low temperature ignition. Reactions from the ERC-mb mechanism that had similar characteristics to those listed above were considered for reaction rate adjustment.

The following reactions were chosen for the ignition sensitivity analysis:

1. $mb2j + O_2 = mb2oo$
2. $mb2oo = mb2ooh4j$
3. $mb + O_2 = HO_2 + mb2j$
4. $mb + HO_2 = H_2O_2 + mb2j$
5. $mb + OH = H_2O + mb2j$

Reactions 1 and 2 are analogous to the reactions deemed important for low temperature ignition processes. The species ‘mb2oo’ has replaced the radical site of ‘mb2j’ with oxygen atoms, and ‘mb2ooh4j’ is an isomerization of ‘mb2oo’ (see Appendix A).

Additionally, several reactions were included that produced the ‘mb2j’ radical. In removal of the species and pathways in the initial fuel breakup (see Figure 3 and Figure 4), it was believed that the number of radicals available for the ignition process was reduced. By enhancing the remaining radical pathway (mb2j) the formation of those radicals could better approximate the detailed mechanism.

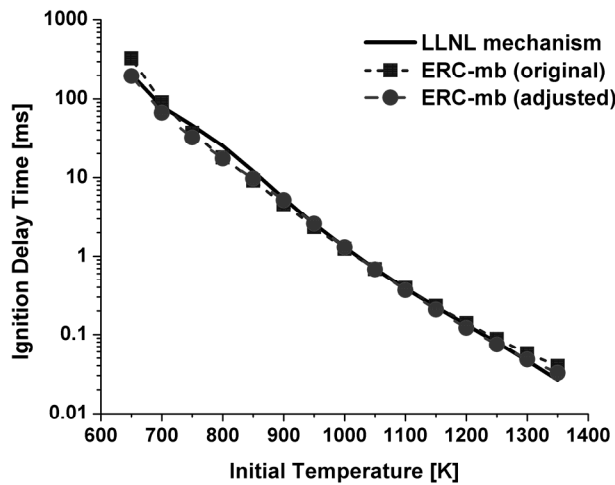
A sensitivity analysis was performed on the above reactions, wherein the pre-exponential factor and activation energy were systematically changed to assess their effect on ignition times. Additional details related to this process can be found in Ref [25].

Based on this study, two reactions were chosen for adjustments. Table 3 shows the reactions, their initial Arrhenius parameters, and the adjusted parameters (in *italics*).

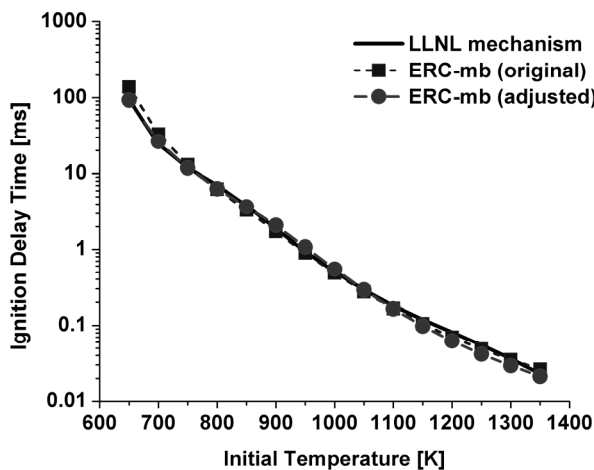
Table 3: Adjusted Arrhenius rate constants for the ERC-mb mechanism (in *italics*)

Reaction	A	b	E
mb2oo=mb2ooh4j	6.097e+10	0.000	25076
	<i>2.622e+10</i>	0.000	<i>22067</i>
mb+o2=ho2+mb2j	4.000e+13	0.000	41300
	<i>1.000e+14</i>	0.000	41300

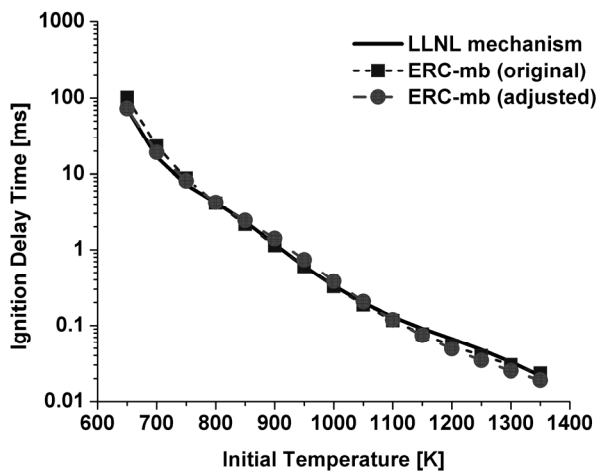
An increase in the reaction rate of the first reaction resulted in faster ignition at low temperatures. The second reaction, which alternately affected the low and high temperature ignition, was used to fine-tune the ignition delay prediction. Adjustments to these reactions significantly improved the predicted ignition times at low temperatures when compared to the LLNL mechanism. Figure 7 shows the resulting ignition delay comparisons over the range of equivalence ratios tested for an initial pressure of 40 bar. The results for the 60 bar pressure had similar agreement and can be found in Appendix B.



(a) $\phi = 0.4$



(b) $\phi = 1.0$



(c) $\phi = 1.5$

Figure 7: Ignition delay comparisons of the ERC-mb and detailed LLNL mechanisms for an initial pressure of 40 bar and three equivalence ratios

Combination of Mechanisms

The reduced MB mechanism was combined with the previously developed skeletal n-heptane mechanism to address the differences in structure and energy content described in Table 1. The n-heptane mechanism, “ERC n-heptane”, is an updated version of the reduced mechanism developed by Patel [12]. It contains 34 species and 77 reactions, including NO_x related species and reactions taken from the GRI-Mech [26].

The ERC n-heptane mechanism was considered the base of the combined mechanism. MB species and the corresponding reactions that were unique to the MB mechanism were added to the base mechanism. For instance, all species with the methoxy group (species in the mechanism that include an “m” in their name) were not previously found in the ERC n-heptane mechanism. Those species and all related reactions were included. However, many of the lower-level carbon species (e.g., CO₂, C₂H₂, CO) were common in both mechanisms. Only the ERC n-heptane reactions related to those species were used, and no other reactions were added to the combined mechanism.

Nineteen species were unique to MB and added to the base ERC mechanism. The resulting mechanism, called “ERC-bio”, contained 53 species and 142 reactions. Initial SENKIN analysis for $\phi = 1.0$ and an initial pressure of 40 bar revealed that the ignition delay curve drastically changed shape when the mechanisms were combined, as seen in Figure 8. This was found to be partially due to differences in the H₂/O₂ chemistry between the two mechanisms. Accordingly, fourteen HO₂ and H₂O₂ reactions from the ERC-mb mechanism were also included in the combined mechanism and this removed some of the observed negative temperature coefficient dependence. The final mechanism included 53 species and 156 reactions.

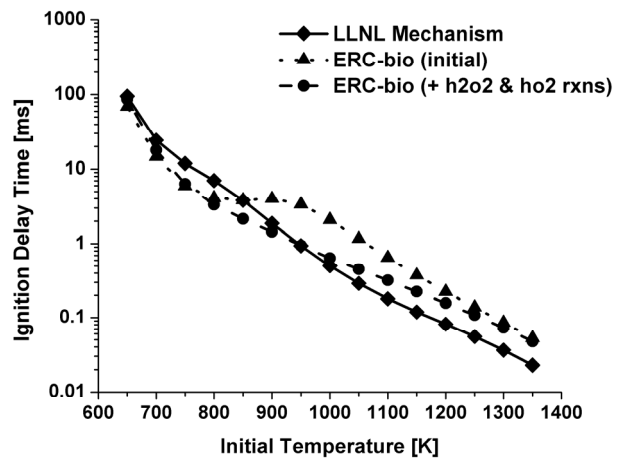


Figure 8: Initial ignition delay predictions for the ERC-bio mechanism

The rate constants for two reactions in the ERC-bio mechanism required additional tuning from their ERC-mb values. The reactions and their adjusted parameters can be seen in Table 4. These two reactions were taken from the sensitivity analysis performed for the ERC-mb mechanism.

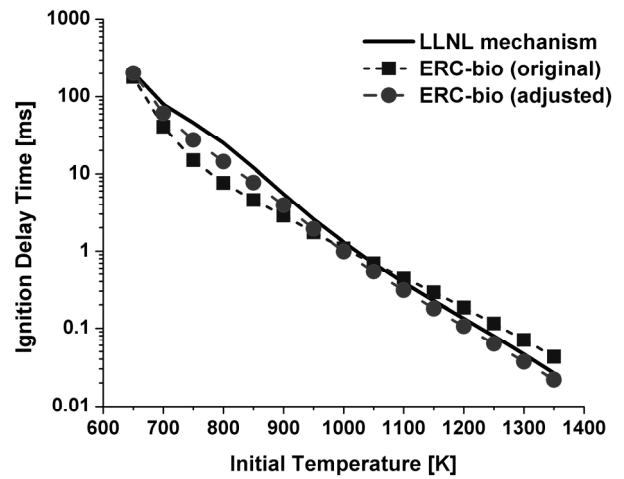
Table 4: Adjusted Arrhenius rate constants for the ERC-bio mechanism (in *italics*)

Reaction	A	b	E
mb+o2=ho2+mb2j	1.000e+14	0.000	41300
	<i>4.000e+14</i>	0.000	41300
mb+ho2=h2o2+mb2j	4.320e+12	0.000	14400
	<i>5.616e+12</i>	0.000	14400

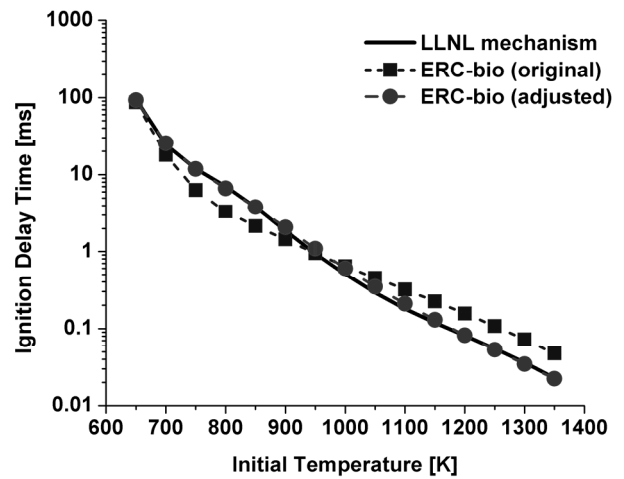
The reaction rate of the first reaction, which was previously adjusted, was further increased to delay ignition at low temperatures, while enhancing ignition at high temperatures. The second reaction affects the intermediate temperature ignition processes, and is analogous to the $\text{RH} + \text{HO}_2 \rightarrow \text{R} + \text{H}_2\text{O}_2$ reaction mentioned previously. It had the effect of shifting the entire ignition delay curve.

Figure 9 shows the resulting ignition delay comparisons over the range of equivalence ratios for the initial pressure of 40 bar. The ERC-bio results for initial pressures of 60 bar are also available in Appendix B. It was concluded that the final reduced mechanism is adequate for the present CFD engine modeling purposes.

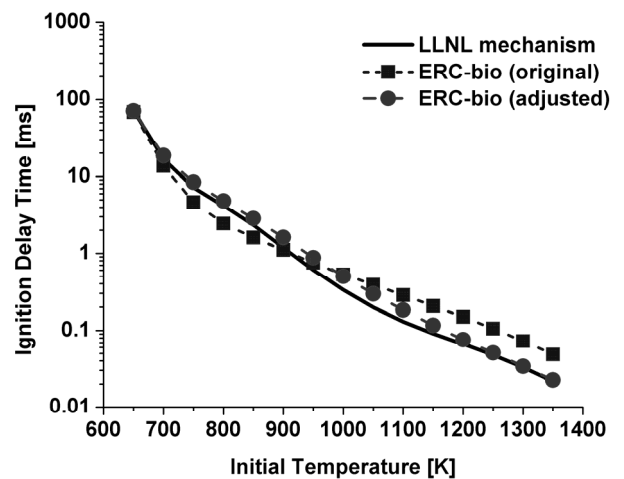
The species, reaction steps, and rates for the ERC-mb and ERC-bio mechanisms can be found in Appendix C and D, respectively. Further details of both mechanisms are given by Brakora [25].



(a) $\phi = 0.4$



(b) $\phi = 1.0$



(c) $\phi = 1.5$

Figure 9: Ignition delay comparison of the ERC-bio and detailed LLNL mechanisms for an initial pressure of 40 bar and three equivalence ratios

ENGINE VALIDATION

Once developed and validated against the detailed mechanism, it was of interest to test the applicability the ERC-bio mechanism for engine simulations. The combined mechanism was applied to diesel engine simulations using the KIVA3V-Release 2 CFD code coupled with CHEMKIN-II [10-12,19,27]. Numerical results were compared to biodiesel engine experiments performed at Sandia National Laboratories. Comparisons of combustion behavior and NO_x emissions were made.

EXPERIMENTS FOR VALIDATION

Cheng et al. [5] performed carefully controlled experiments in which neat (100%) biodiesel fuel was compared to several primary reference fuel (PRF) blends. The start of combustion timing and premixed burn fractions were matched between the fuels in order to isolate the cause of the increased NO_x typically seen in biodiesel combustion studies.

Experimental Engine/Operating Conditions

The experiments were performed on the Sandia compression-ignition optical research engine (SCORE), which is a modified version of the Caterpillar 3176 heavy-duty engine. The single-cylinder SCORE has a flat bottom piston bowl to provide optical access from underneath the combustion chamber.

The piston rings are lower than on the production engine to prevent contact with the windows on the cylinder walls. The lowered piston rings result in an increased clearance volume and decreased compression ratio compared to the production engine. However, the temperature and pressure of the intake air were increased in the SCORE to match the motored top dead center conditions of the production engine. The engine specifications can be seen in Table 5. The values in parentheses indicate those of the production engine, which were simulated by the experimental engine by adjusting the temperature and pressure as mentioned previously. A hydraulically actuated, electronically-controlled unit injector (HEUI) was used for the fuel injection. The injection system specifications are shown in Table 6.

Table 5: Specifications for the Sandia compression-ignition optical research engine (SCORE)

Engine type	Single-cylinder CAT 3176
Cycle	Four-stroke CIDI
Bore x Stroke	125 mm x 140 mm
IVO	-32° aTDC
IVC	-153° aTDC
EVO	116° aTDC
EVC	11° aTDC
Connecting rod length	225 mm
Piston bowl diameter	90 mm
Piston bowl depth	16.4 mm
Swirl ratio	0.59
Displacement	1.72 L
Compression ratio	11.3:1 (16.0:1)

Table 6: Fuel injection system specifications

Injector type	CAT HEUI A
Injector model	HIA-450
Nozzle style	Single-guided VCO
Number of orifices	6
Orifice diameter (nom.)	0.163 mm
Hydro-erosion	13%
Orifice L/D	8.0
Included spray angle	140°
Oil rail pressure	20.8 MPa
Max. fuel injection pressure	142 MPa
Pressure intensification ratio	6.85:1
Valve opening pressure	31 MPa

The engine was operated in a skip-fired mode in which the fuel injector was only fired once every eight engine cycles. This was done to limit the amount of window cleaning needed and reduce the risk of window failure in the optical engine. Skip-firing also removed exhaust gas residual (EGR) from the combustion chamber.

The engine was operated at low speed and higher load conditions in order to increase the potential for NO_x. NO_x concentrations were measured using a Thermoelectron Model 10 chemiluminescence analyzer. Start of Injection (SOI) timing was varied for each fuel in order to achieve a Start of Combustion (SOC) timing between TDC and 0.5 CAD aTDC. Operating conditions for the experiments are provided in Table 7.