# LLNL Chemical Kinetics Modeling Group

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Abstract: The LLNL chemical kinetics modeling group has been responsible for much progress in the development of chemical kinetic models for practical fuels. The group began its work in the early 1970s, developing chemical kinetic models for methane, ethane, ethanol and halogenated inhibitors. Most recently, it has been developing chemical kinetic models for large n-alkanes, cycloalkanes, hexenes, and large methyl esters. These component models are needed to represent gasoline, diesel, jet, and oil-sand-derived fuels.

Key words : Detailed chemical kinetic models, Surrogate fuels

## 1.   Background and Brief History

The LLNL chemical kinetics group was formed in the late 1970's with pioneering work on chemical kinetics of methane, ethane, ethanol, and halogenated inhibitors [1-4]. The early work also included the application of detailed chemical kinetics to the field of detonations [5-7]. In 1981, Westbrook et al. published a landmark study that showed that the emission of unburned hydrocarbons from spark-ignition engines cannot be explained by wall-quenching on cold combustion chamber walls [8]. Instead, hydrocarbon emissions were later found to be due to unburned fuel and intermediate hydrocarbons emitted from crevices in engines. In 1984, Westbrook and Pitz published one of the first chemical kinetic mechanisms for a large hydrocarbon fuel, propane [9]. This was an important step forward, since propane has combustion properties more similar to practical hydrocarbon fuels than the previously considered fuel, methane. Subsequently, the chemical kinetic mechanism development work at LLNL moved quickly ahead in terms of molecular size, addressing

n-butane, iso-butane, n-octane and iso-octane [10-13]. During the development of chemical kinetic mechanisms, the LLNL chemical kinetics team devised a series of reaction rate rules for each class of reactions that are important for many hydrocarbon fuels. The team used these rules to rapidly assemble mechanisms for new fuels. In the 1990s and early 2000s, a detailed chemical kinetic mechanism for the primary reference fuels (n-heptane and iso-octane) for spark ignition engines was developed and validated [14, 15]. These mechanisms were widely used by the combustion community to represent gasoline in numerical modeling of engines. Also, the n-heptane mechanism has been popularly used to represent diesel fuel because n-heptane has a similar Cetane number compared to diesel. Both mechanisms are still in use today and are periodically updated and made available on the LLNL chemical kinetic mechanism website [16].

## 2.   Overview of Recent Advances
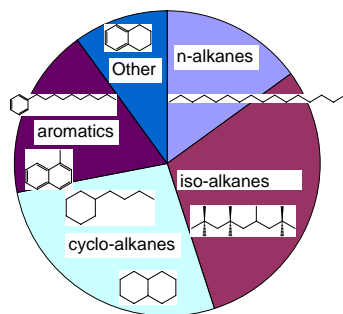
Recently, the LLNL chemical kinetics group has made

Fig. 1 Relative amounts of various chemical classes in diesel fuel.



Fig. 3 n-Decane ignition in a shock tube (stoichiometric, 80 bar). Model: filled symbols, Experiments [22]: open symbols.

significant progress in the development of detailed chemical kinetic models for fuel components in three areas: n-alkanes cycloalkanes, alkenes and methyl esters. N-alkanes, alkenes, and cyclo-alkanes are important components contained in gasoline [17]. N-alkanes and cycloalkanes are also important components in diesel (Fig. 1) [18] and in jet fuel [19]. Methyl esters are the principal components in soy bean and rapeseed based biodiesel [20]. Detailed chemical kinetic models for components can be combined to make surrogate models to represent gasoline, diesel, jet and biodiesel fuels. In this section, we discuss the development of these fuel component models by the LLNL chemical kinetics group.

### 3.1. Large n-Alkanes

There is a current need to extend chemical kinetic models to address large alkanes because they are included in recommendations for components in surrogates for diesel and jet fuels [18, 19]. The component recommendations for surrogates include n-hexadecane for diesel fuel and n-decane and n-dodecane for jet fuel [18, 19, 23]. Recently, the LLNL chemical kinetics team developed a chemical kinetic

model for all n-alkanes from n-octane to n-hexadecane [24]. This model allows the simulation of both low and high temperature chemistry of these n-alkanes. The inclusion of low temperature combustion in the model is important for simulation of new modes of combustion in engines such as homogeneous charge compression ignition (HCCI), premixed charge compression ignition (PCCI), and smokeless rich combustion [25-27]. Figure 2 shows comparison of results from the LLNL detailed chemical kinetic model for n-hexadecane [24] and measurements made in a stirred reactor [21]. The agreement between the modeling and the experimental results is good.

N-hexadecane is an important component for consideration for a diesel surrogate fuel because it is a primary reference fuel for diesel engines. There are little experimental data in the literature to provide for validation for a chemical kinetic model for n-hexadecane. However, there are experimental data (Fig. 3) on ignition of n-decane, a large n-alkane included in the LLNL n-hexadecane mechanism. The n-decane experiments were performed at engine-like conditions of 80 bar and at temperatures from 800 to 1100 K, including the negative temperature coefficient region [22]. Predictions of n-decane ignition by
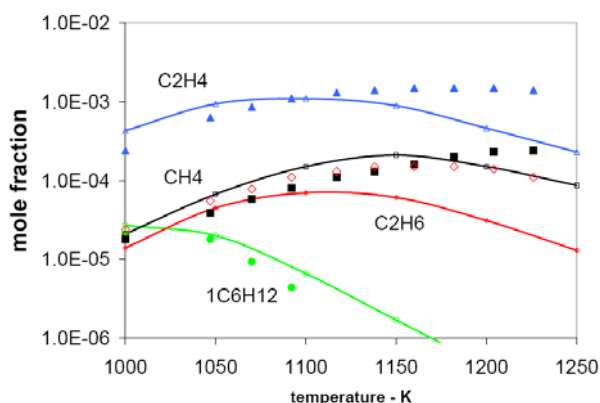


Fig. 2 Intermediate species for n-hexadecane oxidation in a stirred reactor [21]. Symbols are from the experiment and curves are from the model. (stoichiometric, 1 atm, 70 ms residence time)
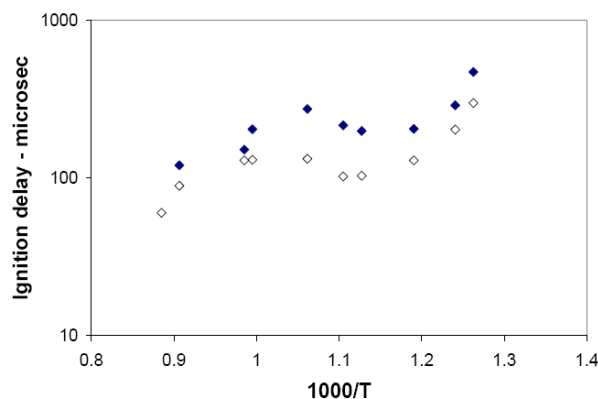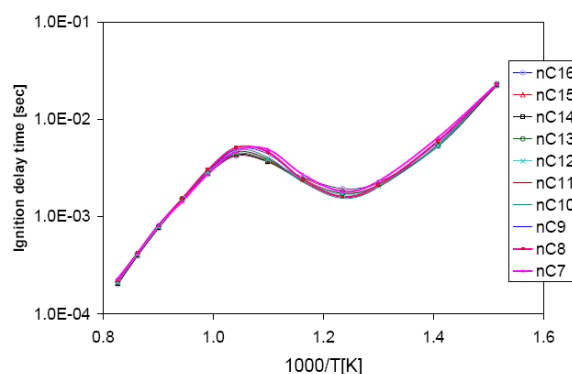


Fig. 4 Ignition behavior of a series of large n-alkanes (stoichiometric, fuel-air mixtures) [24].

the C8-C16 mechanism compared well with experimental measurements (Fig. 3). In order to assess the ignition behavior for all n-alkanes, the ignition of C8 to C16 alkanes were computed over the low to high temperature range at 13 bar, a pressure relevant in an internal combustion engine (Fig. 4). The calculations show that all the large n-alkanes exhibit nearly the same ignition behavior. Therefore, a small n-alkane like n-octane can be used to represent the ignition behavior of a much larger n-alkane like n-hexadecane. Using n-octane to represent the ignition of n-hexadecane would allow the use of a chemical kinetic model of much smaller size and require much less computer resources. Finally, the development of a chemical kinetic model for all n-alkanes up to n-hexadecane allows a broad choice of surrogate fuel components in the n-alkane chemical class for use in surrogate fuel models.

## 3.2. Cycloalkanes

Cycloalkanes are an important chemical class, particularly in diesel fuel (Fig. 1) [18] and jet fuel [19]. Methyl cyclohexane and cyclohexane have been recommended as components in gasoline fuel surrogates [17]. Methyl cyclohexane has also gained attention as a recommended component in jet fuel surrogates [23, 28].



Fig. 6 RO$_2$ isomerization in cyclohexane.

potential influence on soot emissions from the combustion of these fuels in engines [29].

Recently at LLNL, there has been much progress in the development of chemical kinetic models for cycloalkanes [31, 32]. These detailed chemical kinetic models are able to simulate the low and high temperature behavior of methyl cyclohexane and cyclohexane-air mixtures. Figure 5 gives an example of a comparison of the ignition delay times predicted by our cyclohexane model [31] to experimentally measured times in a rapid compression machine [30], which simulates temperature and pressure conditions at top dead center in an engine.

One of the key features of the chemical kinetic models that allow proper simulation of cycloalkane oxidation is the inclusion of the effect of the cycloalkane ring structure on reaction rate constants [32]. An important reaction sequence for predicting the correct reactivity is the addition of molecular oxygen to cycloalkyl radicals followed by an internal isomerization reaction. This sequence eventually leads to low temperature branching and heat release. Figure 6 shows the molecular structure of the transition state for the isomerization of a RO$_2$ radical. The cycloalkane ring is part of the structure of the transition state. The cyclic alkane ring structure increases the activation energy of the reaction compared to an acyclic alkane. This is due to the stiffness of the ring. However, the ring structure lowers the entropy change in the reaction so that the pre-exponential factor increases compared to the same reaction in an acyclic alkane. The comparison of the acyclic and cyclic RO$_2$ isomerization rate constants is shown in Table 1. The primary difference between the acyclic and cyclic reaction rate constants is that the RO$_2$ isomerization of the 6-membered ring is more favored in the cyclic case than in the non-cyclic case. The 6-membered ring leads preferentially to chain branching [13]. This means that cyclic alkanes have much more low temperature reactivity than would be expected, if its cyclic structure was not taken into account. The work at LLNL shows the importance of properly including the effect of molecular structure on reaction rates.
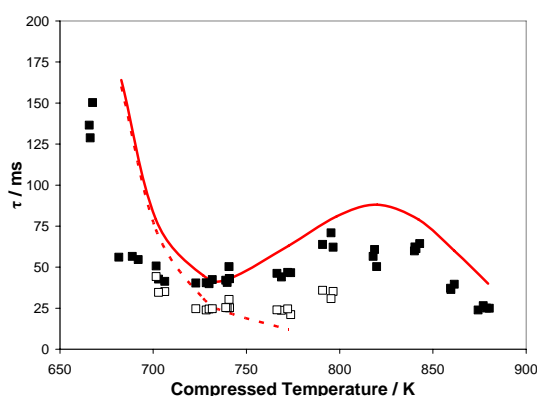


Fig. 5 Cyclohexane ignition in a rapid compression machine. End of compression pressures of 7 to 9 atm. Stoichiometric cyclohexane in simulated air mixtures. The diluent gas consisted of N$_2$/Ar/CO$_2$. The dashed line and open squares correspond to the first stage ignition. Solid lines and filled squares correspond to the total ignition time. Model: lines, Experiments [30]: symbols.

Additionally, cyclic alkanes are of interest because of their high concentration in oil-sand derived fuels and their
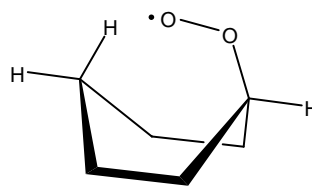
Table 1 Rate constants for RO$_2$ isomerization in acyclic alkanes and cyclic alkanes (cm-mole-sec units)

| Ring size | A | n | Ea | Rate, 750 K |
|---|---|---|---|---|
| **Curran et al. [15] non-cyclic RO$_2$:** | | | | |
| 5 | 1.0e+11 | 0 | 26850 | 6.0e+3 |
| 6 | 1.25e+10 | 0 | 20850 | 4.2e+4 |
| 7 | 1.56e+9 | 0 | 19050 | 8.8e+3 |
| **Modified for cyclic RO$_2$:** | | | | |
| 5 | 4.94e+11 | 0 | 31000 | 4.6e+2 |
| 6 | 1.86e+11 | 0 | 24080 | 1.8e+4 |
| 7 | 1.08e+10 | 0 | 24360 | 8.6e+2 |

### 3.4. Alkenes

Alkenes form another chemical class that is important to represent in gasoline. Alkenes comprise about 2 to 18% of gasoline by volume [17]. Most of the alkenes present in gasoline are C5 to C7 [17]. In collaboration with the chemical kinetics group in Milano, Italy, the LLNL kinetics team has developed a new detailed chemical kinetic model for a series of C6 alkenes: 1-hexene, 2-hexene and 3-hexene [33]. Figure 7 shows computed ignition behavior of 1-hexene, 2-hexene and 3-hexene in comparison to experimental data from the Lille rapid compression machine. The LLNL detailed chemical kinetic model well predicts the behavior observed in the experiments. The model and experiments show the effect of the position of the double bond on ignition, with the 1-hexene being the most ignitable, followed by 2-hexene and 3-hexene. When the double bound is located in the middle of the molecule, it is least ignitable. The chemical kinetic model shows that the possible RO$_2$ isomerizations are limited in this case compared to the case where the double bond is located on the end of the molecule.

### 3.5. Methyl esters

One important renewable fuel is biodiesel which is frequently derived from vegetable oils from soybeans, rapeseed (canola) and other plants. These vegetable oils are usually converted into methyl esters so that they can be easily blended with conventional diesel fuel. Methyl esters derived from soybean and rapeseed oils consist of primarily five components (Fig. 8), instead of the hundreds to thousands of components present in gasoline, Diesel and jet-fuel. As a starting point, the LLNL chemical kinetic
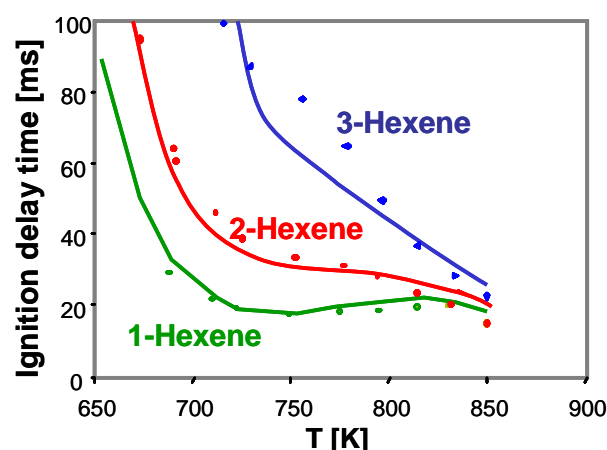
Fig. 7 Ignition behavior of 1-hexene, 2-hexene and 3-hexene in a rapid compression machine. (End of compression pressure: 0.86-1.09 MPa, stoichiometric mixtures): Curves: Computations. Symbols: experimental data [34].

group has used methyl decanoate, a large saturated methyl ester, as a surrogate fuel for the methyl esters found in soybean and rapeseed derived biodiesel. Methyl decanoate has a long n-alkane chain as in methyl palmitate found in soybean and rapeseed-derived methyl esters (Fig. 8). The n-alkane chain in methyl decanoate is shorter than methyl palmitate and may lead to a lower reactivity than biodiesel. However, this effect can be compensated for by adding a large n-alkane to the methyl decanoate, if needed, to increase the reactivity of the biodiesel surrogate.

Recently, the LLNL kinetics team developed a chemical kinetic mechanism for the low and high temperature oxidation of methyl decanoate [20, 35]. This development significantly enhances the capability for modeling biodiesel fuels. The results of the methyl decanoate model [20] are
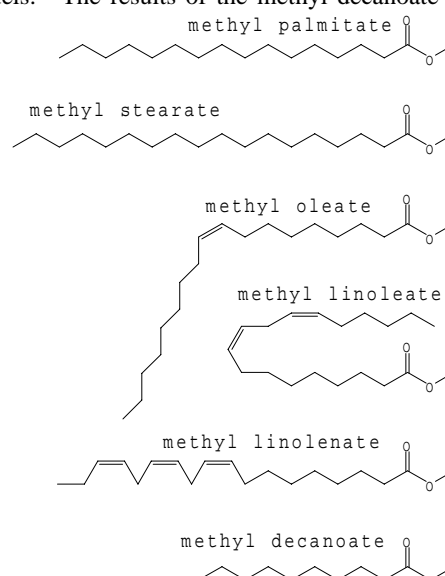
Fig. 8 Molecular structure of the components found in soybean and rapeseed oils methyl esters and of methyl decanoate [20].

compared to rapeseed oxidation experiments in a jet stirred reactor (Fig. 9). The experiments were performed at 10 atm so that they are relevant to pressures found in internal combustion engines. It can be seen from the comparison of computed and measured results that the methyl decanoate model is a quite good surrogate for rapeseed-derived methyl esters.

Methyl esters form carbon dioxide at low temperatures directly from the methyl ester structure. [20, 36, 37]. When methyl esters are used as biodiesel, this direct formation of $CO_2$ wastes some of the oxygen in the fuel that can otherwise help to prevent carbon in the fuel from leading to soot formation in the engine [36, 38]. As seen in Fig. 9, the methyl decanoate model well simulated the formation of $CO_2$ [20] at low temperature.
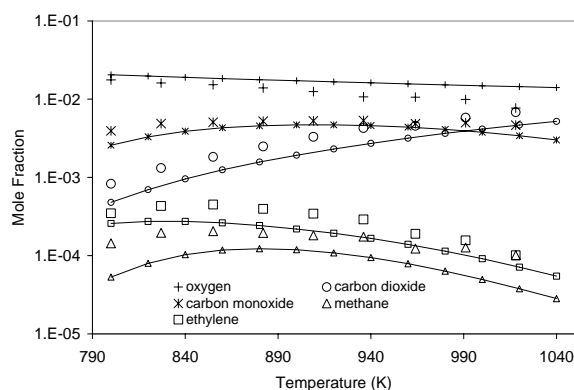


Fig. 9 Comparison of model predictions (methyl decanoate) with experimental measurements (rapeseed-based methyl esters) [39] in a jet stirred reactor at 10 atm (equivalence ratio of 0.5, fuel/$O_2$/$N_2$ mixtures, residence time of 1.0 sec).

## Summary

The LLNL chemical kinetics group has developed significant capabilities to model the detailed chemical kinetics of components relevant to practical fuels like gasoline, diesel, jet, biodiesel and oil-sand derived fuels. These component models can be combined into fuel surrogate models to treat the combustion of practical fuels. These new capabilities enhance the ability to model the chemical kinetics of fuels in practical devices.

## Acknowledgments

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