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Chemical Kinetic Modeling of Advanced Transportation Fuels

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Chemical Kinetic Modeling of Advanced Transportation Fuels

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Objectives

- Develop detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum based fuels. These fuels models include components from vegetable-oil-derived biodiesel, oil-sand derived fuel, alcohol fuels and other advanced bio-based and alternative fuels.
- Develop detailed chemical kinetic reaction models for mixtures of non-petroleum and petroleum-based components to represent real fuels and lead to efficient reduced combustion models needed for engine modeling codes.
- Characterize the role of fuel composition on efficiency and pollutant emissions from practical automotive engines.

Accomplishments

- Developed a detailed chemical kinetic model for a biodiesel surrogate that contains large saturated and unsaturated methyl esters characteristic of vegetable-oil-derived biodiesel.
- Further validation of methyl decanoate, a large surrogate fuel to represent biodiesel.
- Developed a reduced mechanism for a large biodiesel surrogate for use in CFD codes.

Future Directions

- Develop improved chemical kinetic models for fuel surrogate components and fuel blends to represent advanced petroleum-based fuels
- Develop improved chemistry models for biodiesel surrogates

Introduction

Development of detailed chemical kinetic models for advanced petroleum-based and non-petroleum based fuels is a difficult challenge because of the hundreds to thousands of different components in these fuels and because some of these fuels contain components that have not been considered in the past. It is important to develop detailed chemical kinetic models for these fuels since the models can be put into engine simulation codes used for optimizing engine design for maximum efficiency and minimal pollutant emissions. For example, these chemistry-enabled engine codes can be used to optimize combustion chamber shape and fuel injection timing. They also allow insight into how the composition of advanced petroleum-based and non-petroleum based fuels affect engine performance characteristics. Additionally, chemical kinetic models can

be used separately to interpret important in-cylinder experimental data and gain insight into advanced engine combustion processes such as HCCI and lean burn engines.

Approach

Detailed chemical kinetic models are developed to represent the various components in advanced petroleum-based and non-petroleum based fuels. These advanced fuels include biodiesel, oil-sand derived diesel, alcohol fuels, Fischer-Tropsch fuels and new advanced bio-derived fuels. Then these components models are assembled into mixture or "surrogate" models to represent advanced fuels. Model calculations are carried out with these combined reaction mechanisms to compute ignition, soot precursor formation, and NOx and other toxic species production under practical engine conditions. The mechanisms are then reduced for use in multidimensional fluid mechanics codes for simulating engine combustion. This approach has been used extensively for diesel and HCCI engine combustion, providing better understanding of ignition, soot production, and NOx emissions from these engines in fundamental chemical terms.

Results

In FY2008, we made accomplishments in three areas: 1) We further validated our detailed chemical kinetic model for a larger biodiesel surrogate, methyl decanoate. 2) We developed a biodiesel surrogate that is a mixture of both unsaturated and saturated components. 3) We reduced our detailed chemical kinetic model for methyl decanoate for use in computational fluid dynamic codes. In this section, we'll discuss each accomplishment in turn.

We used a large methyl ester called methyl decanoate to represent biodiesel. Previous surrogate models to represent biodiesel used much smaller molecules like methyl butanoate to represent biodiesel. However, methyl butanoate with 5 carbon atoms (C5) is much smaller than the C16 to C19 molecules in soy and rapeseed based biodiesel. In Fig. 1, we compare the computed ignition behavior of methyl decanoate with experiments on n-decane [1] , a similarly sized n-alkane, because there is not a lot of experimental data available on methyl decanoate. As can be seen, the ignition times of methyl decanoate nearly match those of n-decane. We found that the ignition behavior of methyl decanoate matches n-decane for a variety of shock tube experiments and for flame speed. This point is further illustrated in a Combustion and Flame paper that we composed and published on methyl decanoate during the last year [2]. This paper was the second most downloaded paper in Combustion and Flame from July to September 2008 [3].

Biodiesel fuel that is derived from soy-based and rapeseed-based feedstocks contains saturated and unsaturated methyl esters that need to be included in a surrogate fuel model. Component models are needed to represent each of these classes of methyl esters. We use methyl decanoate to represent saturated methyl esters. We also need a component model to represent unsaturated methyl esters. During FY08, we developed a detailed chemical model for a large unsaturated methyl ester called methyl decenoate. Since the ignition behavior of methyl decenoate is affected by the location of the double bond in the carbon chain, we developed chemical kinetic models for two forms of methyl decenoate: one with a double bond on the end of the carbon chain and one with a double bond in the middle. In Fig. 2, we compare the ignition of these two forms of methyl decenoate with methyl decenoate which has no double bond in the carbon chain. Methyl decenoate with the double bond on the end of the carbon chain has the shortest ignition delay time and is the most reactive methyl ester component. The least reactive component is methyl decenoate with a double bond in the middle of the carbon chain. Methyl decanoate (with no double bond) has a reactivity that lies in between the two other molecules. Our work shows that the position of a double bond in the alkyl chain of a fuel component is very important in

determining its reactivity. By adjusting the amount of each of these molecules in a biodiesel surrogate mixture, the targeted reactivity of real biodiesel methyl esters can be achieved.

The inclusion of unsaturated methyl decenoate and saturated methyl decanoate gives a more accurate and improved surrogate for biodiesel. However the long carbon chain on methyl decanoate (C10) is shorter than the typical of biodiesel methyl ester (C16-C19). Since a lot of the reactivity of a methyl ester component is attributed to the reactivity of the carbon chain, n-heptane (C7) was added to the surrogate mixture model as a way to compensate for the short carbon chain in methyl decanoate. The carbon chain length of n-heptane (C7) plus the length of the carbon chain of methyl decanoate (C10) gives a total carbon chain length in surrogate (C17) which is close to that of biodiesel methyl esters (C16-C19). The specific components and amounts in the surrogate mixture used to represent biodiesel are given in Fig. 3. This surrogate mixture was tested by comparing predictions of its corresponding chemical kinetic model with experimental measurements [4] of the oxidation of rapeseed-based methyl in a stirred reactor (Figure 4). The comparison shows that the mole fractions of species predicted from the model and measured in the experiments agree relatively well at different reactor temperatures at 10 atm.

It is important to reduce large chemical kinetic models so that they can be used in multidimensional computational fluid dynamic codes. Detailed chemical kinetic models usually have too many reactions and species, and require too much computational resources to be included in CFD codes. During the last year, we reduced our large chemical kinetic mechanism for a biodiesel surrogate so that it could be used in a reacting flow code. The work allowed us to test a new and promising method for mechanism reduction called the directed relational graph (DRG) method [5]. This method is a graphical technique that analyses the reaction paths in the mechanism and removes paths that do not affect the concentration of important species of interest. The DRG method reduced the detailed mechanism of methyl decanoate from 3036 species and 8555 reactions down to 125 species and 713 reactions. The number of species was reduced by a factor of 5, a dramatic reduction. Since a conservation equation must be solved for each species considered in a reacting flow code, reducing the number of species greatly shortens code execution times. To validate the reduced mechanism, we employed a counterflow flame configuration which consists of fuel and air flowing in opposite directions, towards each other. When ignition occurs, a flame develops near the stagnation plane formed by the two flows. This flame configuration has relevance to diesel engines because the fuel and air are initially separate in the flame just as it is the case in a conventional diesel engine. Also, the counter flow flame includes the effect of fluid dynamic strain, an effect also found in diesel engine flows. To compute this flame, a 1-D reacting flow code that computes fluid flow, transport of heat and species, and chemical reactions is required [6]. Figure 5 shows good agreement between experimentally measured and computed ignition temperatures in the counter flow flame. This work is published in the Proceedings of the Combustion Institute [7].

Conclusions

- The methyl decanoate model used to represent saturated components in biodiesel has been further validated. The chemical kinetic model is available [8].
- New chemical kinetic component models of two large, unsaturated methyl esters have been developed.
- Using both saturated and unsaturated methyl ester components, a biodiesel surrogate mixture model has been developed and compared to experimental measurements of rapeseed- derived methyl esters used in biodiesel.

- A reduced chemical kinetic mechanism for a biodiesel surrogate was developed and validated for use in a reacting flow code.

Acknowledgements

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Special Recognitions & Awards/Patents Issued

1. Charles K. Westbrook: Elected to the 2008-2009 Class of Fellows of the Society of Automotive Engineers (SAE).
2. Charles K. Westbrook: 2008 Bernard Lewis Gold Medal award by the Combustion Institute.
3. Charles K. Westbrook: 2008 - 2012 President of the Combustion Institute.
4. William J. Pitz: Invited Plenary Lecture at the 2008 International Conference on Modeling and Diagnostics for Advance Engine Systems (2008 COMODIA), Sapporo, Japan.

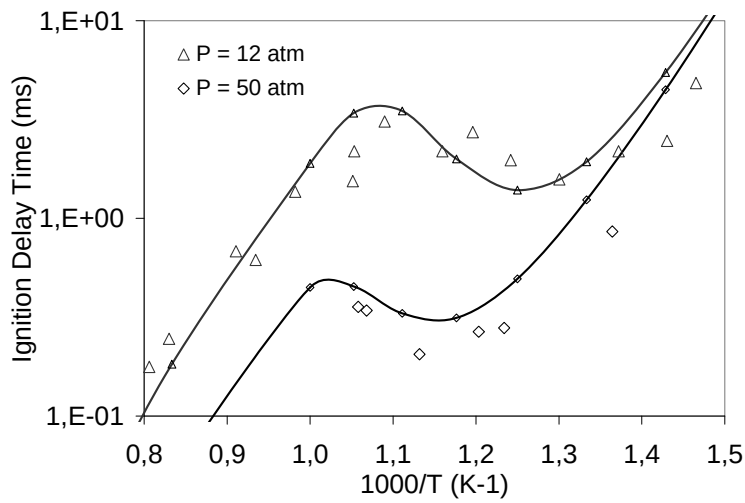
Acronyms

A_2: Strain rate based on air side of stagnation plane [s^{-1}]
C7: A fuel molecule with 8 carbon atoms
C16: A fuel molecule with 16 carbon atoms
CFD: Computational fluid dynamics
DRF: Directed relational graph method for mechanism reduction
FY08: Fiscal year 2008
HCCI: Homogeneous-charge, compression-ignition engine
LLNL: Lawrence Livermore National Laboratory
T_2: Temperature of air at autoignition [K]

Figure Captions

Figure 1: Comparison of fuel reactivity under shock tube conditions in stoichiometric fuel/air mixtures. Lines – methyl decanoate model predictions. Open symbols – n-decane experimental data [1].
Figure 2: Ignition behavior of saturated and unsaturated methyl esters for stoichiometric, fuel-air mixtures at 12 atm. The top and bottom methyl ester components are isomers of decenoate and the middle structure is methyl decanoate.
Figure 3: Components in a surrogate for biodiesel (methyl decanoate, methyl decenoate and n-heptane).
Figure 4: Comparison of an LLNL biodiesel surrogate model with rapeseed-based methyl esters. Concentration of intermediate species formed from the reaction of the rapeseed-based methyl esters are shown as a function of temperature in a jet stirred reactor at 10 atm, equivalence ratio

of 0.5, and a residence time of 1 sec. The experiments (symbols) are from Dagaut et al. [4]. The symbols are from the LLNL detailed chemical kinetic surrogate model for biodiesel. The saturated and unsaturated components in the surrogate model are those shown in Fig. 3.
Figure 5: The measured and predicted temperature for autoignition in a counterflow flame [7]. The temperature of the air flow is increased slowly until ignition occurs. Autoignition temperatures are given at different strain rates which are controlled by the velocity of the air flow.



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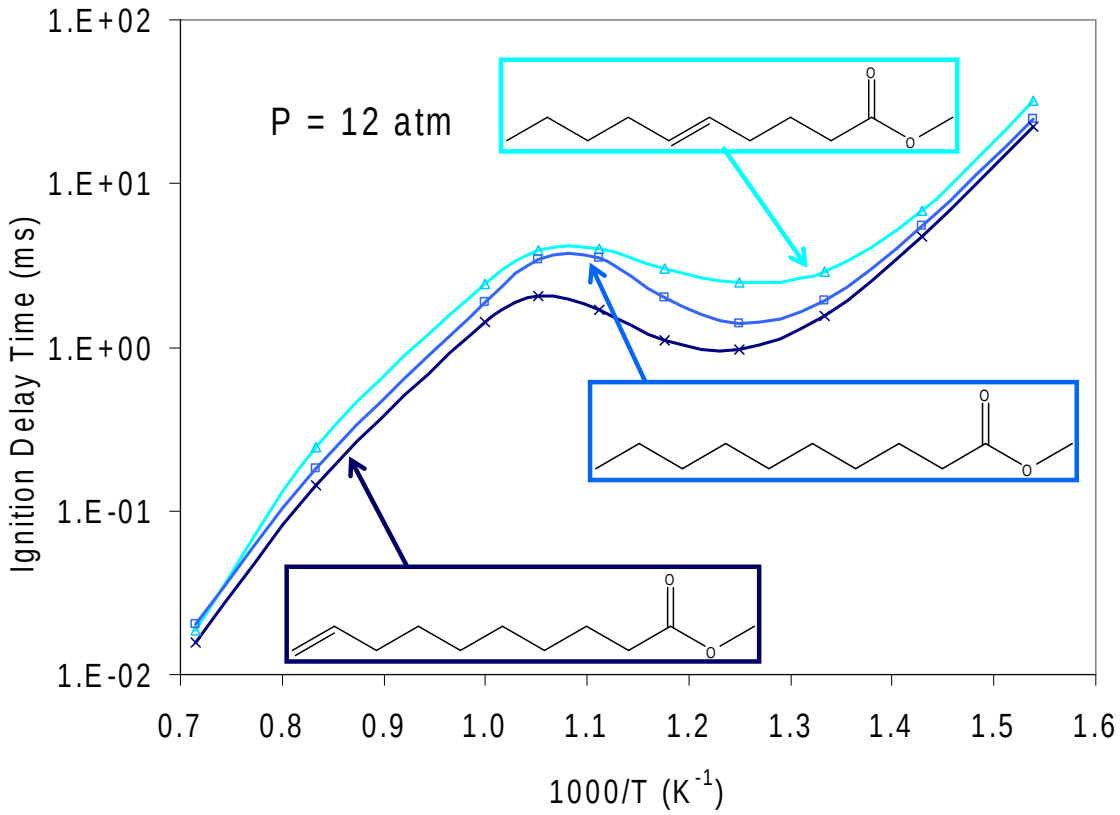

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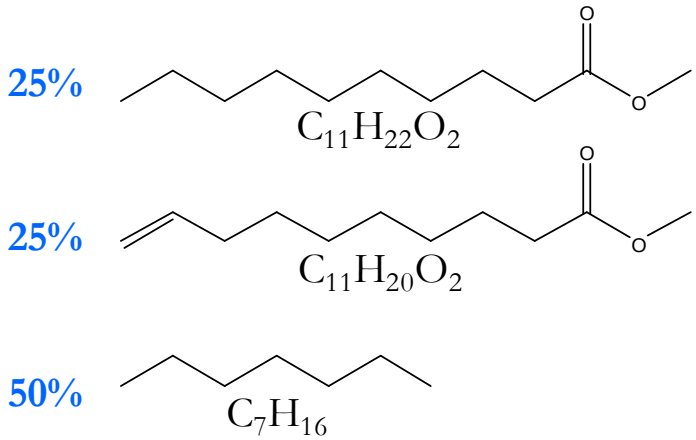
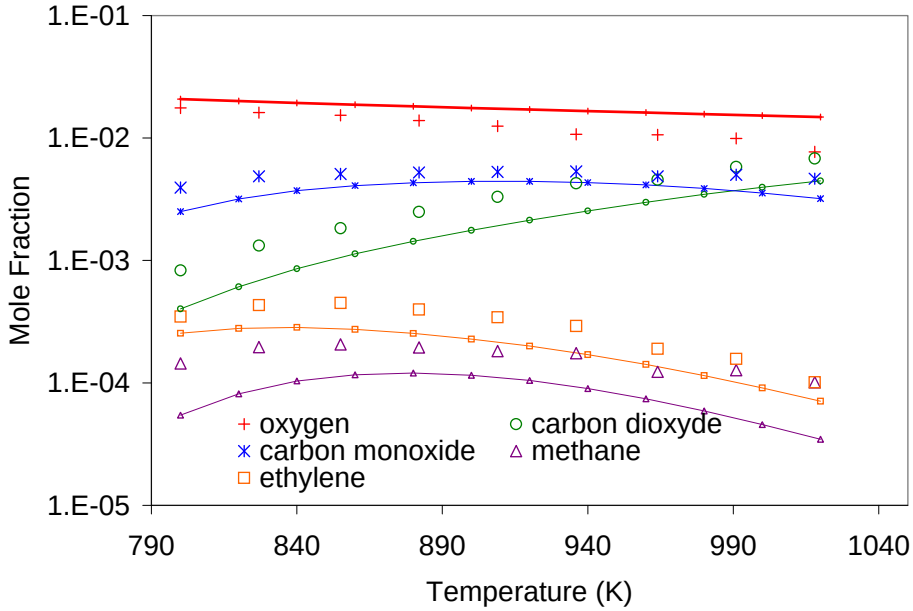


Figure 3: Components in a surrogate for biodiesel (methyl decanoate, methyl decenoate and n-heptane).



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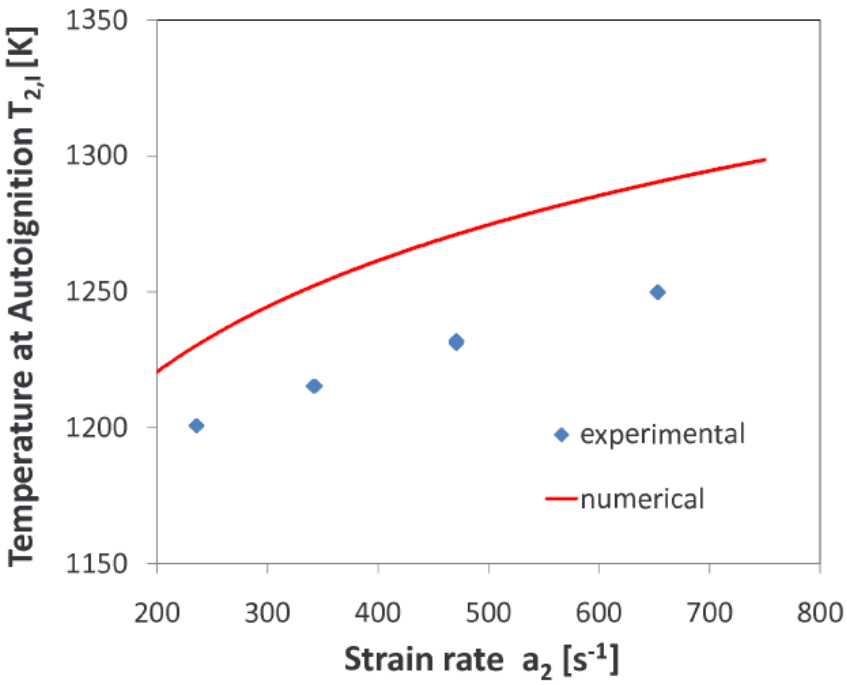

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