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Chemical Kinetic Models for HCCI and Diesel Combustion

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Objectives

- Develop detailed chemical kinetic models for fuel components used in surrogate fuels for diesel and HCCI engines
- Develop surrogate fuel models to represent real fuels and model low temperature combustion strategies in HCCI and diesel engines that lead to low emissions and high efficiency
- Characterize the role of fuel composition on low temperature combustion modes of advanced combustion engines

Accomplishments

- Validated a low and high temperature mechanism for normal alkanes from C8 to C16, including n-hexadecane, a primary reference fuel for diesel engines.
- Further validated a detailed chemical kinetic mechanism for a large biodiesel surrogate.
- Developed a reduced mechanism for a large biodiesel surrogate for use in CFD codes.

Future Directions

- Develop and validate a detailed chemical kinetic mechanism for heptamethylnonane, a primary reference fuel for diesel engines.

Introduction

Hydrocarbon fuels for advanced combustion engines consist of complex mixtures of hundreds or even thousands of different components. These components can be grouped into a number of chemically distinct classes, consisting of n-paraffins, branched paraffins, cyclic paraffins, olefins, oxygenates, and aromatics. Biodiesel contains its own unique chemical class called methyl esters. The fractional amounts of these chemical classes are quite different in gasoline, diesel fuel, oil-sand derived fuels and bio-derived fuels, which contributes to the very different combustion characteristics of each of these types of combustion systems.

Approach

To support large-scale computer simulations of each kind of engine, it is necessary to provide reliable chemical kinetic models for each of these chemical classes in fuels. However, few specific hydrocarbon components of some of these fuel classes have been modeled. For example, models for benzene and toluene have been developed, although models for few if any larger aromatic compounds such as naphthalene or styrene currently exist. Similarly, detailed models for small iso-paraffins such as iso-octane have been developed, but detailed models do not yet exist for the much larger versions such as heptamethylnonane, characteristic of diesel fuels. Biodiesel is composed of large methyl esters, but few detailed chemical kinetic models of these components have been developed. Current approaches to this problem are to construct a detailed model, containing one or more representatives of each class of components to serve as a surrogate mixture. In order for such a surrogate mixture model to be useful, each component must have a well-tested detailed kinetic model that can be included. This high-level approach can create realistic substitutes for gasoline or diesel fuel that reproduce experimental behavior of the practical real fuels. Detailed kinetic models for surrogate fuels can then be simplified as needed for inclusion in multidimensional CFD models or used in full detail for purely kinetic modeling.

Results

There is a need to extend chemical kinetic models to address large alkanes because they are recommended as surrogate components for diesel fuel and one particular recommended for component is n-hexadecane [1]. Recently, the LLNL chemical kinetics team developed a chemical kinetic model for all n-alkanes from n-octane to n-hexadecane [2]. This model allows the simulation of both low and high temperature chemistry of these n-alkanes. The inclusion of low temperature chemistry 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. This year, the LLNL kinetics team validated their new model for C8 to C16 n-alkanes and published it in one of the most recognized combustion journals, Combustion and Flame [2]. Figures 1 and 2 show some examples of the mechanism validation by comparison of computed results with experimentally measured results. Figure 1 compares predictions from the LLNL detailed chemical kinetic model and measurements [3] of intermediate species in a stirred reactor when n-hexadecane is the fuel. The agreement between the predicted and measured intermediate species concentrations is good. Figure 2 shows a comparison of predictions of the model with experiments when n-decane is the fuel component. The n- experiments were performed at engine-like conditions of 80 bar and at temperatures from 800 to 1100 K, including the negative temperature coefficient region [4]. Predictions of n-decane ignition compared well with experimental measurements (Fig. 2). The comparison covers the full low to high temperature chemistry regime which is important for low temperature combustion strategies in diesel combustion. Finally 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 to an internal combustion engine (Fig. 3). 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 has the advantage of allowing the use of a much smaller chemical kinetic model requiring 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 for diesel fuel. For example, broad range of n-alkanes is needed to model the distillation characteristics of the diesel fuel and properly simulate the diesel spray volatility in the engine.

In FY2008, we further validated our detailed chemical kinetic model for a biodiesel surrogate. We use methyl decanoate, a large methyl ester, to represent biodiesel. Since there is not a lot of experimental data available on methyl decanoate, we compare the computed ignition behavior of methyl decanoate with experiments on n-decane [5], a similarly sized n-alkane (Fig. 4). 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 Combustion and Flame paper that we composed and published on methyl decanoate during the last year [6].

It is important to reduce large chemical kinetic models so that they can be used effectively in multidimensional reacting flow simulations. 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 method for mechanism reduction called the directed relational graph (DRG) method [7]. 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. The flame configuration has relevance to diesel engines because the fuel and air are initially separate in this 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 [8]. Figure 5 shows good agreement between experimentally measured and computed ignition temperatures in the counter flow flame. This work will be published in the Proceedings of the Combustion Institute [9].

Conclusions

- A chemical kinetic model for C8-C16 n-alkanes was validated for low and high temperature chemistry regimes. This model is available to represent n-alkanes in diesel fuel [10]
- The detailed chemical kinetic mechanism for methyl decanoate was further validated. The chemical kinetic model is available [10]
- A reduced chemical kinetic mechanism for biodiesel surrogate was developed and validated for use in a reacting flow code

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FY 2008 Publications/Presentations

1. C. K. Westbrook, W. J. Pitz, O. Herbinet, H. J. Curran and E. J. Silke, "A Detailed Chemical Kinetic Reaction Mechanism for n-Alkane Hydrocarbons from n-Octane to n-Hexadecane," Combust. Flame (2008), In press.
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Special Recognitions & Awards/Patents Issued

1. Charles K. Westbrook: 2008 Bernard Lewis Gold Medal award by the Combustion Institute.
2. Charles K. Westbrook: 2008 - 2012 President of the Combustion Institute.
2. 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}]
C8: A fuel molecule with 8 carbon atoms
C16: A fuel molecule with 16 carbon atoms
CFD: Computational fluid dynamics
CO: Carbon dioxide
CH4: methane
C2H4: ethene
C2H6: ethane
1C6H12: 1-hexene
DRF: Directed relational graph method for mechanism reduction
HCCI: Homogeneous-charge, compression-ignition engine
LLNL: Lawrence Livermore National Laboratory
T_2: Temperature of air at autoignition [K]

Figure Captions

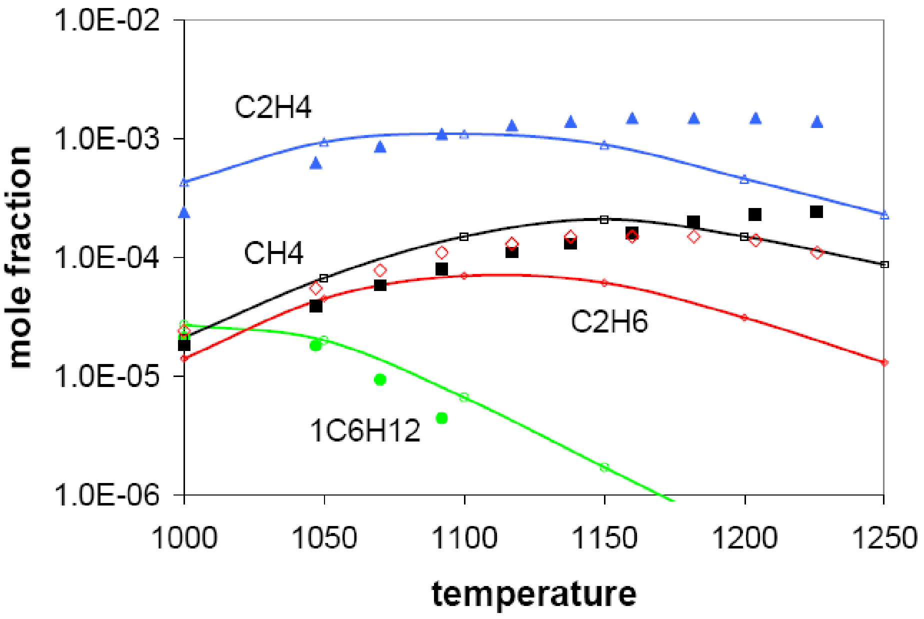

Figure 1. Comparison between computed and experimental [3] results for intermediate species in n-hexadecane oxidation in a jet stirred reactor. Conditions are equivalence ratio = 1.5, 1 atm pressure, and 0.07 s residence time.

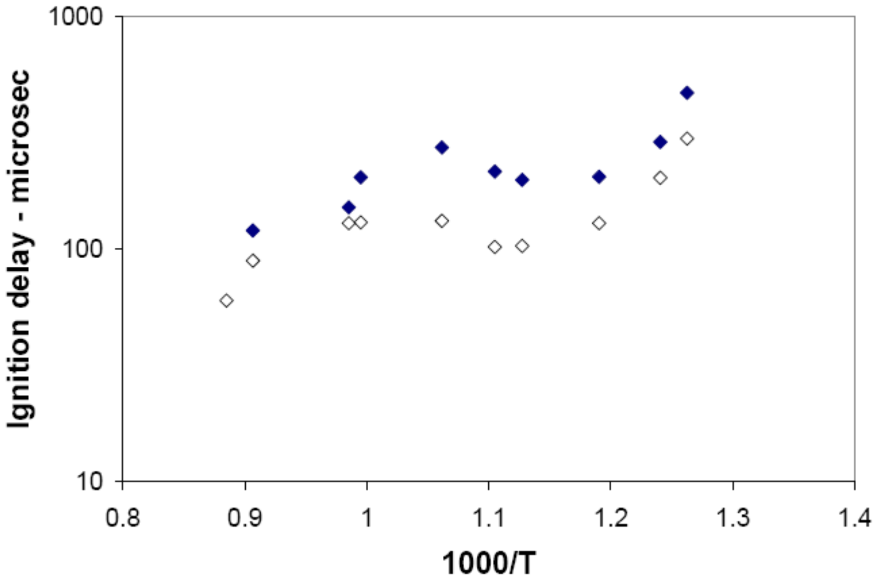

Fig. 2. Computed and experimental ignition delay times for stoichiometric, n-decane/air at 80 atm pressure versus inverse temperature [K^{-1}]. Experiments (◊) from Zhukov et al.[4], present model (♦).

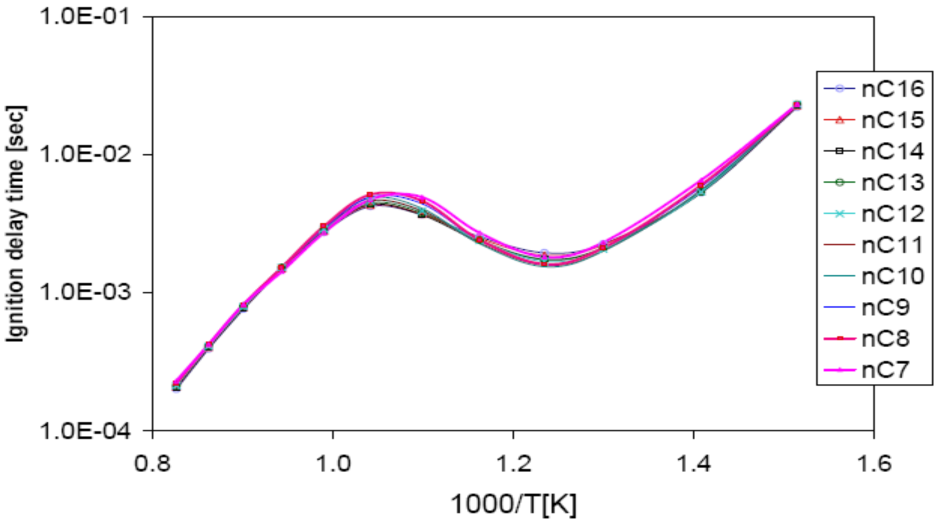

Figure 3. Computed ignition delay times for stoichiometric mixtures of n-alkanes in air at 13.5 bar [2].

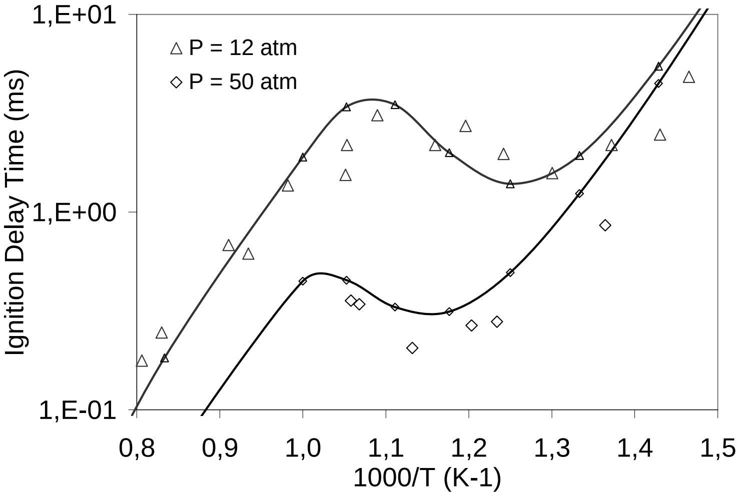

Figure 4. Comparison of fuel reactivity under shock tube conditions in stoichiometric fuel/air mixtures. Lines – methyl decanoate model predictions. Open symbols – n-decane experimental data [5].

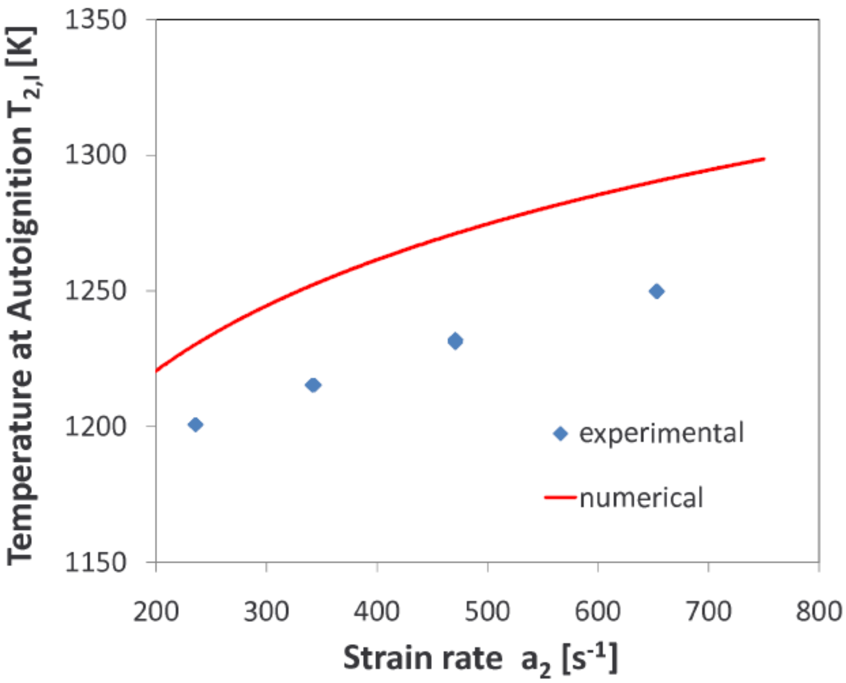

Figure 5. The measured and predicted temperature for autoignition in a counterflow flame [11]. The air flow is heated up slowly until ignition occurs. The strain rate increases with the velocity of the air flow.