LLNL-TR-663108

Chemical Kinetic Models for Advanced Engine Combustion

W. J. Pitz, M. Mehl, C. K. Westbrook

October 22, 2014

Disclaimer

This work performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

II.10 Chemical Kinetic Models for Advanced Engine Combustion

William J. Pitz (Primary Contact), Marco Mehl, Charles K. Westbrook
Lawrence Livermore National Laboratory (LLNL)
P. O. Box 808, L-288
Livermore, CA 94551

DOE Technology Development Manager
Leo Breton

Overall Objectives

- Develop detailed chemical kinetic models for fuel components used in surrogate fuels for compression ignition (CI), homogeneous charge compression ignition (HCCI) and reactivity-controlled compression-ignition (RCCI) engines.
- Combine component models into surrogate fuel models to represent real transportation fuels. Use them to model low-temperature combustion strategies in HCCI, RCCI, and CI engines that lead to low emissions and high efficiency.

Fiscal Year (FY) 2014 Objectives

- Develop detailed chemical kinetic models for larger alkyl aromatics relevant to diesel fuels
- Develop more accurate surrogate kinetics models for gasoline surrogate fuels
- Develop chemical kinetic model for a large alkyl-cyclohexane as a diesel surrogate component
- Develop chemical kinetic model for a naphtho-aromatic as a diesel surrogate component
- Develop a preliminary model for a large polycyclic aromatic hydrocarbon as a soot precursor

FY 2014 Accomplishments

- Developed a chemical kinetic model for tri-methylbenzene, a surrogate component surrogate diesel fuel
- Developed a chemical kinetic model for n-butyl-cyclohexane, a surrogate component for diesel fuel
- Developed a chemical kinetic model for tetralin, a surrogate component for diesel fuel
- Performed detailed chemical kinetic modeling of surrogates of gasoline fuels

Future Directions

- Continue to develop detailed chemical kinetic models for additional cycloalkanes for gasoline and diesel fuel
- Develop gasoline surrogate fuels for additional Fuels for Advanced Combustion Engines (FACE) fuels
- Develop improved models for incipient soot

✧ ✧ ✧ ✧ ✧

INTRODUCTION

Predictive engine simulation models are needed to make rapid progress towards DOE's goals of increasing combustion engine efficiency and reducing pollutant emissions. In order to assess the effect of fuel composition on engine performance and emissions, these engine simulations need to couple fluid dynamic and fuel chemistry submodels. Reliable chemical kinetic submodels representative of conventional and next-generation transportation fuels need to be developed to fulfill these requirements.

APPROACH

Gasoline and diesel fuels consist of complex mixtures of hundreds of different components. These components can be grouped into chemical classes including n-alkanes, iso-alkanes, cycloalkanes, alkenes, oxygenates, and aromatics. Since it is not practicable to develop chemical kinetic models for hundreds of components, specific components need to be identified to represent each of these chemical classes. Then detailed chemical kinetic models can be developed for these selected components. These component models are subsequently merged together to produce a "surrogate" fuel model for gasoline, diesel, and next-generation transportation fuels. This approach creates realistic surrogates for gasoline or diesel fuels that can reproduce experimental behavior of the practical real fuels that they represent. Detailed kinetic models for surrogate fuels can then be simplified as needed for inclusion in multidimensional computational fluid dynamic models of engine combustion.

RESULTS

Mueller et al. [1] have proposed a nine-component surrogate to represent the ignition behavior of representative diesel fuels in terms of distillation characteristics, density, and chemical composition. In previous years at LLNL, chemical kinetic models for five of these components were developed. In FY 2014, new chemical kinetic models were developed to represent three of the remaining four components. These models were for 1,2,4-tri-methylbenzene to represent alkyl-aromatics, tetralin to represent naphtha-aromatics, and n-butyl-cyclohexane to represent alkyl-cyclohexanes in diesel fuel. These new chemical kinetic models were validated by comparison of results from the model to measurements of ignition delay times in shock tubes and rapid compression machines (RCMs). The agreement between the model and experiment was generally good (e.g. Figures 1-3). Only one model for the remaining component needs to be developed to complete the nine-component surrogate model for diesel fuel.

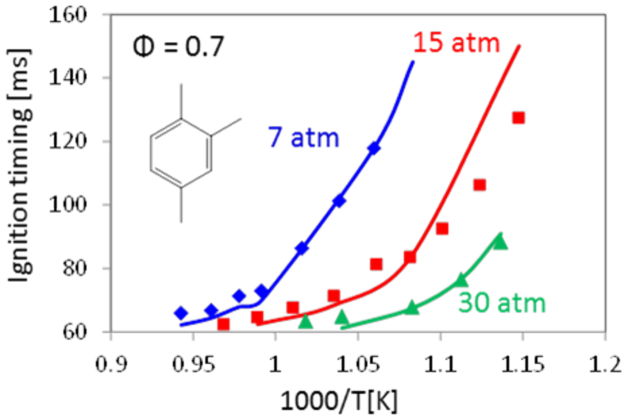

FIGURE 1. A comparison of ignition behavior computed from the chemical kinetic model (curves) and measured in the experiments (symbols) for 1,2,4-trimethylbenzene in the RCM. Times are referred to the start of the compression. The experimental measurements are from Prof. Sung's group at the University of Connecticut.

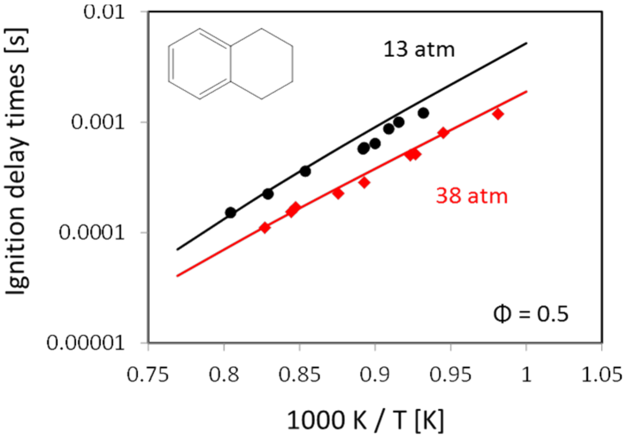

FIGURE 2. Comparison of ignition delay times for tetralin in a shock tube at an equivalence ratio of 0.5. Lines are from the LLNL model and symbols from the experiments [7].

FACE fuels for gasoline have been developed to provide researchers with controlled compositions that can be used to assess the fuel effects on advanced engine combustion [2]. In FY 2014 at LLNL, a 10-component gasoline surrogate palette was developed to represent the properties of FACE gasoline fuels. Subsequently, a gasoline surrogate model based on components in this palette was used to simulate the ignition behavior of FACE A and C. Ignition delay times from the model were compared to those measured in shock tubes and RCMs for FACE A and C at pressure and temperature conditions found in engines. Good agreement was found between the predictions and experimental measurements (Figure 4) [3].

To simulate combustion in direct-injection spark-ignition engines, chemical kinetic models need to accurately predict flame speeds. In FY 2014, flame speeds for a series of alkyl-benzenes were simulated including LLNL chemical kinetic models for toluene, ethyl-benzene, n-propyl-benzene and n-butyl-benzene. Comparisons of these model calculations were made to measurements performed at the National Center for Scientific Research, France [4]. The experimentally observed behavior was reproduced both qualitatively and quantitatively (Figure 5). After the effect of adiabatic flame temperature was accounted for, it was found that the observed behavior of the alkyl-benzenes could be explained by their relative propensity to form benzyl radicals: A higher formation rate of benzyl radicals corresponds to a relatively lower flame speed.

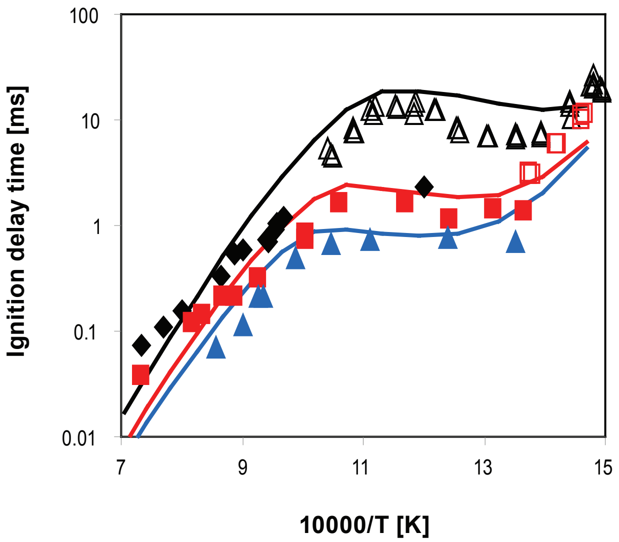

FIGURE 3. A comparison of ignition behavior from the chemical kinetic model (curves) and the experiments (symbols) for a stoichiometric mixture of n-butyl cyclohexane in air. The closed symbols are results from the shock tube and the open symbols are from the RCM. Experiments were performed by Prof. Curran's group at the National University of Ireland, Galway.

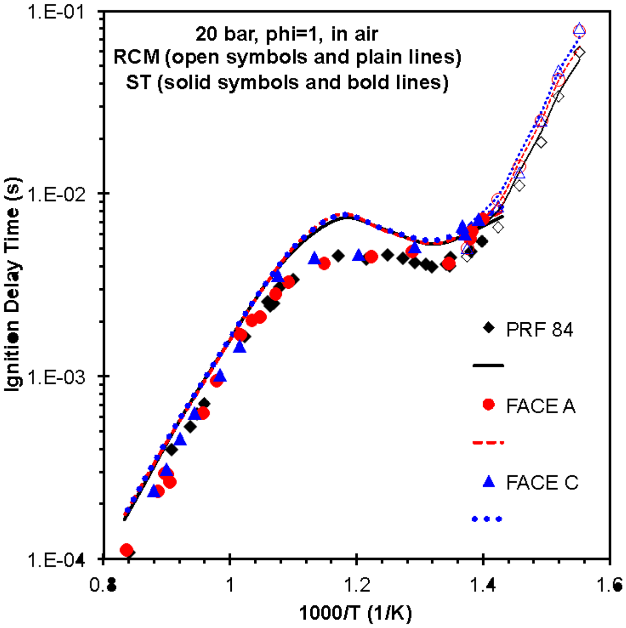

FIGURE 4. Comparison of the gasoline surrogate model (curves) with shock tube (filled symbols) and RCM (open symbols) ignition experiments for FACE gasoline fuels A and C. Comparisons are also made to PRF84, a primary reference fuel mixture of 84% isooctane and 16% n-heptane with similar ignition characteristics. Experimental data from the shock tube were taken by Prof. Oehlschlaeger's group at Rensselaer Polytechnic Institute and from the RCM by Dr. Sarathy's group at the King Abdullah University of Science and Technology [3].

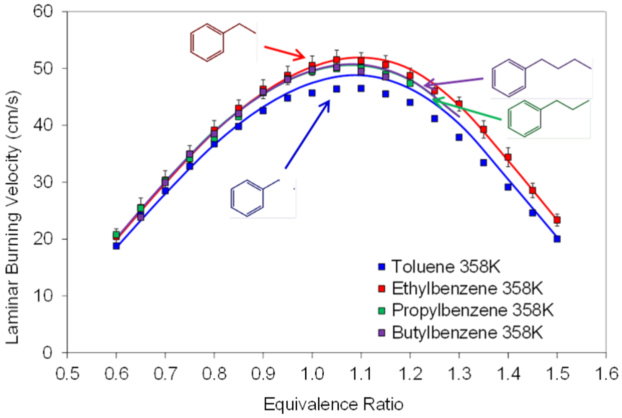

FIGURE 5. Comparison of laminar flame velocities (symbols: experiments, lines: calculations) as a function of equivalence ratio for alkyl-benzenes from toluene up to n-butyl-benzene at 358 K [4]. The lines for n-propyl-benzene and n-butyl-benzene overlap.

In collaboration with Argonne National Laboratory and University of Connecticut, a two-component diesel surrogate model was developed for use in a multidimensional engine simulation code. First, a two-component detailed chemical kinetic model of n-dodecane and m-xylene was assembled at LLNL and validated by comparison to shock tube and flow reactor data for the neat components and their mixture. These components were chosen because they can represent the alkane and aromatic fractions in diesel and the resulting mechanism is computationally manageable in the engine simulation code. The detailed chemical kinetic model was reduced at the University of Connecticut and used at Argonne National Laboratory to simulate diesel reacting sprays in a constant volume vessel [5]. The reduced mechanism was able to simulate the experimentally measured ignition delays [6] in a spray chamber (Figure 6).

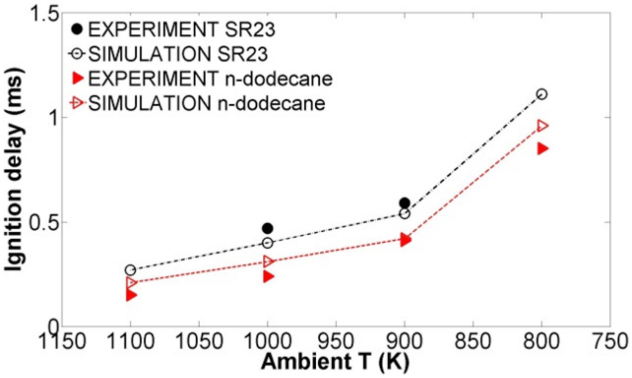

FIGURE 6. Simulated [5] and experimentally-measured [6] ignition delays for n-dodecane and an n-dodecane/m-xylene mixture in a spray chamber of Dr. Pickett at Sandia National Laboratories.

CONCLUSIONS

- New mechanisms have been developed for three of the four remaining components in a nine-component surrogate for diesel fuel.
- A reduced, two-component mechanism for diesel has been developed in collaboration with Argonne National Laboratory and the University of Connecticut.
- A surrogate palette to represent FACE gasoline fuels has been developed and used to develop a chemical kinetic model for FACE A and C.
- A mechanism for alkyl-benzenes was validated for prediction of flame speeds important for direct-injection spark ignition engines.
- This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract DE-AC52-07NA27344.

REFERENCES

1. C.J. Mueller, W.J. Cannella, T.J. Bruno, B. Bunting, H.D. Dettman, J.A. Franz, M.L. Huber, M. Natarajan, W.J. Pitz, M.A. Ratcliff and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *Energy & Fuels* 26 (6) (2012) 3284–3303.

2. "FACE gasoline fuels," http://www.crcao.org/Publications/advancedVehiclesFuelsLubricants/FACE/index.html, 2013.

3. S.M. Sarathy, G. Kukkadapu, M. Mehl, W. Wang, T. Javed, S. Park, M.A. Oehlschlaeger, A. Farooq, W.J. Pitz and C.-J. Sung, "Ignition of alkane-rich FACE gasoline fuels and their surrogate mixtures," *Proc. Combust. Inst.* (2015).

4. M. Mehl, O. Herbinet, P. Dirrenberger, R. Bounaceur, P.-A. Glaude, F. Battin-Leclerc and W.J. Pitz, "Experimental and Modeling Study of Burning Velocities for Alkyl Aromatic Components Relevant to Diesel Fuels," *Proc. Combust. Inst.* (2015).

5. Y. Pei, W. Liu, M. Mehl, S. Som, T. Lu and W.J. Pitz, "A Multi-Component Blend as a Diesel Fuel Surrogate for Compression Ignition Engine Applications," ICEF2014-5625, (2014).

6. "Engine Combustion Network," http://www.sandia.gov/ecn/, 2014.

7. H. Wang, W.J. Gerken, W. Wang and M.A. Oehlschlaeger, "Experimental Study of the High-Temperature Autoignition of Tetralin," *Energy & Fuels* 27 (9) (2013) 5483–5487.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. Mehl, M., Herbinet, O., Dirrenberger, P., Bounaceur, R., Glaude, P.-A., Battin-Leclerc, F. and Pitz, W.J., "Experimental and Modeling Study of Burning Velocities for Alkyl Aromatic Components Relevant to Diesel Fuels," Proceedings of the Combustion Institute (2015).

2. Sarathy et al., Reference 3 above.

3. Goldsborough, S.S., Johnson, M.V., Banyon, C., Pitz, W.J. and McNenly, M.J., "Experimental and Modeling Study of Fuel Interactions with an Alkyl Nitrate Cetane Enhancer, 2-Ethyl-Hexyl Nitrate," Proceedings of the Combustion Institute (2015).

4. Pei et al., Reference 5 above.

5. Allen, J. C., Pitz, W. J. and Fisher, B. T., "Experimental and Computational Study of n-Heptane Autoignition in a Direct-Injection Constant-Volume Combustion Chamber," Journal of Engineering for Gas Turbines and Power 136(9) (2014).

6. Weber, B.W., W.J. Pitz, M. Mehl, E.J. Silke, A.C. Davis and C.-J. Sung (2014). "Experiments and Modeling of the Autoignition of Methylcyclohexane at High Pressure." Combustion and Flame 161 (8) (2014) 1972-1983.

7. C.K. Westbrook and W.J. Pitz, "Fundamental Chemical Kinetics," in Encyclopedia of Automotive Engineering (David Crolla; David E. Foster; Toshio Kobayashi; Nicholas Vaughan, Eds.), Wiley Online Library (2014).

8. Vuilleumier, D., Kozarac, D., Mehl, M., Saxena, S., Pitz, W.J., Dibble, R., Chen, J. and Sarathy, M., "Intermediate Temperature Heat Release in an HCCI Engine Fueled by Ethanol / N-Heptane Mixtures: An Experimental and Modeling Study," Combustion and Flame 161 (3) (2014).

9. Sarathy, S.M., Javed, T., Karsenty, F., Heufer, A., Wang, W., Park, S., Elwardany, A., Farooq, A., Westbrook, C.K., Pitz, W.J., Oehlschlaeger, M.A., Dayma, G., Curran, H.J. and Dagaut, P., "A Comprehensive Combustion Chemistry Study of 2,5-Dimethylhexane," Combustion and Flame 161 (6) (2014) 1444–1459.

10. Darcy, D., Nakamura, H., Tobin, C.J., Mehl, M., Metcalfe, W.K., Pitz, W.J., Westbrook, C.K. and Curran, H.J., (2013). "An Experimental and Modeling Study of a Surrogate Mixtures of n-Propyl- and n-Butylbenzene in n-Heptane to Simulate n-Decylbenzene Ignition," Combustion and Flame 161 (6) (2014) 1460-1473.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Charles Westbrook and William Pitz recognized on the Thomson Reuters' list of The World's Most Influential Scientific Minds.