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Development of Kinetic Mechanisms for Next-Generation Fuels and CFD Simulation of Advanced Combustion Engines

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V.5 Development of Kinetic Mechanisms for Next-Generation Fuels and CFD Simulation of Advanced Combustion Engines

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Overall Objectives

- Develop predictive chemical kinetic models for surrogate components and surrogate mixtures to represent next-generation fuels
- Use these models in computational fluid dynamics (CFD) simulations to optimize alternative fuel formulations and advanced engine combustion for maximum engine efficiency and very low pollutant emissions, thereby allowing the utmost petroleum displacement

Fiscal Year (FY) 2015 Objectives

- Design and build a prototype microliter fuel tester, and perform initial modeling effort
- Develop an accelerated, rapid compression machine model
- Use detailed chemical kinetic modeling to interpret direct injection spark-ignition (DISI) experiments on intermediate blends of gasoline–ethanol
- Develop mechanism for biofuel cyclopentanone

FY 2015 Accomplishments

- Octane Number correlations for gasoline surrogate fuels, including ethanol
- Computed flame speed correlations to help interpret dilute DISI engine experiments using gasoline–ethanol mixtures
- Preliminary simulations of leaner lifted-flame engine combustion of methyl decanoate
- Preliminary fired simulations of lean/dilute DISI engine experiments at Sandia National Laboratories

Future Directions

- Develop chemical kinetic models for biofuel components and biofuel mixtures that enhance fuel octane ■

Introduction

Predictive chemical kinetic models are needed to represent next-generation fuel components and their mixtures with conventional gasoline and diesel fuels. These kinetic models will allow the prediction of the effect of alternative fuel blends in CFD simulations of advanced spark-ignition and compression-ignition engines. Enabled by kinetic models, CFD simulations can be used to optimize fuel formulations for advanced combustion engines so that maximum engine efficiency, fossil fuel displacement goals, and low pollutant emissions goals can be achieved.

Approach

Chemical kinetic models for each next-generation fuel component of interest for blending with gasoline and diesel are developed. Next, models for next-generation fuel components and for conventional fuel components are combined to make models for surrogates (or mixtures) used to represent next-generation ground transportation fuels. The mechanisms are used in a multidimensional code using multi-zone method with parallel CFD solvers for simulating advanced combustion engines. These chemistry-enabled CFD engine codes can be used to simulate combustion processes in advanced spark-ignition and compression-ignition engines to assess fuel property effects and to optimize fuel and engine design for the best performance and engine efficiency, and for minimum pollutants.

Results

Cyclopentanone is a bio-derived fuel component with a high autoignition resistance [1] that is potentially

attractive for blending with gasoline. The overall performance of cyclopentanone in a homogeneous combustion compression ignition engine engine is similar to that of ethanol [1]. In collaboration with the National University of Ireland, Galway, rates of abstraction of H atoms from cyclopentanone by OH and HO_2 radicals have been calculated using fundamental chemistry methods. These rate constants are important in controlling the rate of autoignition of cyclopentanone under engine conditions. Also, decomposition rates of cyclopentanone radicals have been computed. These rates are difficult to estimate because of the cyclic nature of cyclopentanone and the presence of a ketone group in the ring. These new rate constants are valuable towards the development of a predictive chemical kinetic model for cyclopentanone.

The ability of mimicking the chemical behavior of real fuel through simpler surrogate mixture models is a fundamental prerequisite for the simulation of engine combustion. In the past years LLNL has developed a methodology based on simple ignition delay calculations to match surrogate mixtures to real gasolines. The numerical procedure developed by LLNL is based on correlations between calculated ignition delay times and measured octane numbers (expressed as Anti-Knock Index [AKI] and sensitivity: Research Octane Number - Motor Octane Number [RON - MON]) of a large database of gasoline components and their mixtures. Previous versions of these correlations were based exclusively on fuels that did not contain oxygenates. More recently, the octane number database of fuel component mixtures used to extrapolate the correlation has been revised to include mixtures containing increasing fractions of ethanol and excluding fuels containing aromatic concentrations in excess of the existing legal limits. The result is a new set of correlations that can be applied to fuels relevant to commercial gasoline with an arbitrary amount of ethanol mixed in (Figure 1).

LLNL gasoline–ethanol models have been used to make simulations to guide DISI operation. One way to increase efficiency of ethanol–gasoline fueled engines is to operate under more dilute conditions. However, under dilute operation, the flame speeds are reduced and misfire may result. To assess this effect, the flame speeds of ethanol–gasoline fuel mixtures under dilute conditions in the engine have been simulated and the functional dependence of the burning velocity on in-cylinder temperature and pressure has been evaluated at different stoichiometries relevant to engine operations. The flame speed expressions for different fuels (e.g., RD387 gasoline, E30 [blend of 30% ethanol, 70% gasoline], and E85 [blend of 85% ethanol, 15% gasoline]) have been shared with Magnus Sjöberg at Sandia National

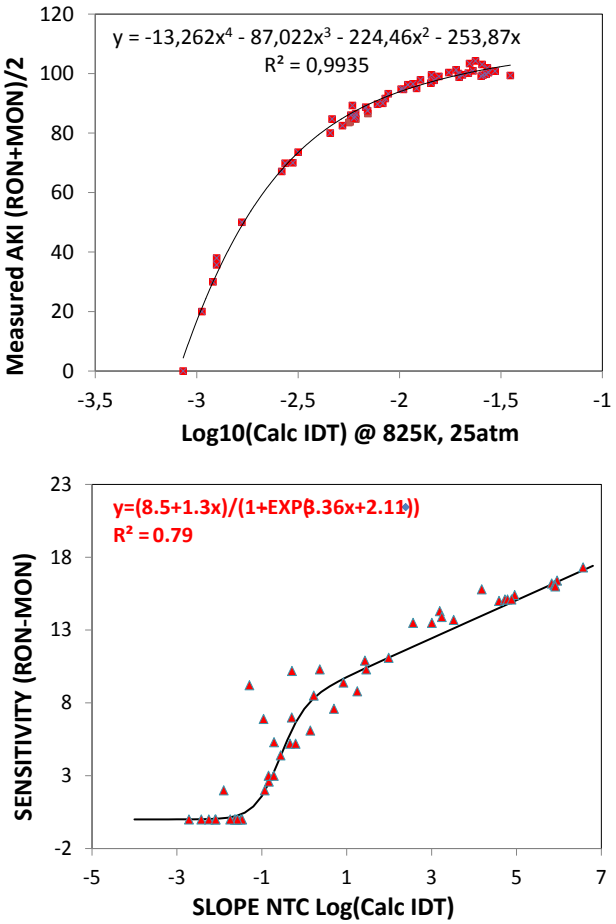

Figure 1. Correlation between computed ignition delay (at 850 K and 25 atm) of a gasoline–ethanol surrogate and measured AKI of gasoline components and their mixtures (upper plot). Correlation between computed slope in the negative temperature coefficient (NTC) region of a gasoline–ethanol surrogate and measured sensitivity of gasoline components and their mixtures (lower plot).

Laboratories to assist the interpretation of his experiments and to provide insight into the behavior of his DISI engine operating with gasoline–ethanol mixtures (Figure 2).

LLNL and Louisiana State University are developing the microliter Fuel Ignition Tester (μ–FIT, pronounced micro-fit). μ–FIT offers the potential to provide high-throughput, low volume fuel testing to provide rapid evaluation of promising new fuel blends, bio-derived components, and additives. During this performance period, Prof. Schoegl (Louisiana State University), built the first prototype of μ–FIT (see Figure 3) to measure the autoignition and extinction behavior of flames with repetitive extinction and ignition (FREI) in a millimeter-scale quartz tube. The prototype is based on an earlier design of Maruta et al. [2–3]. Prof. Schoegl demonstrated the ability to measure quantitatively the flame dynamics using an inexpensive

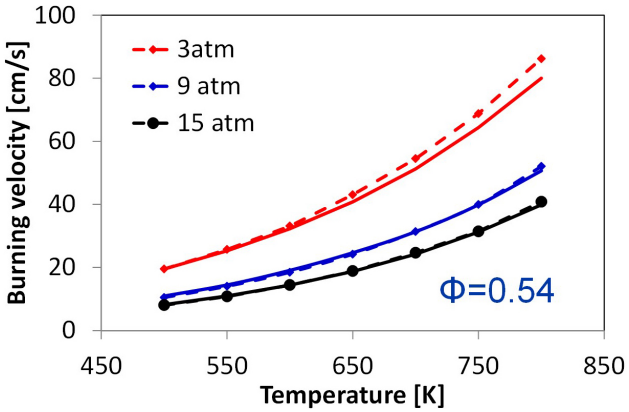

Figure 2. Burning velocity of E85 (dashed lines) and RD587 (solid lines) as a function of unburned gas temperature and pressure. For E85, burning velocity = $2.49P^{-0.515}e^{(0.00522*T)}$. For RD387, burning velocity = $2.63P^{-0.479}e^{(0.005011*T)}$.

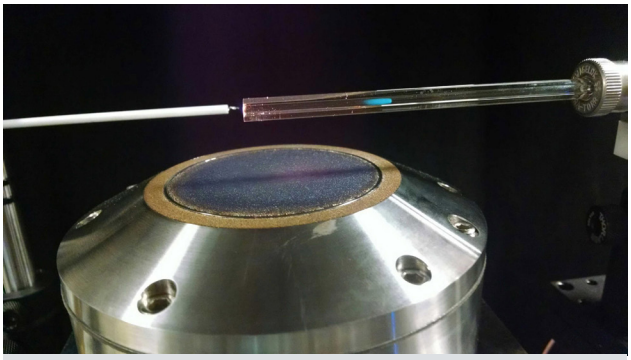

Figure 3. μ–FIT prototype developed at Louisiana State University by Prof. Schoegl. A McKenna burner (H_2/air) is used to externally heat the quartz tube. A premixed fuel-air mixture flows from right to left inside the tube. The premixed flow velocity is slower than the flame speed so that the flame spontaneously ignites in the downstream (hotter) region and then propagates upstream (colder) until it is extinguished due to heat loss to the wall. The image exposure is sufficiently long that the thin propane flame is smeared out between the ignition and extinction points.

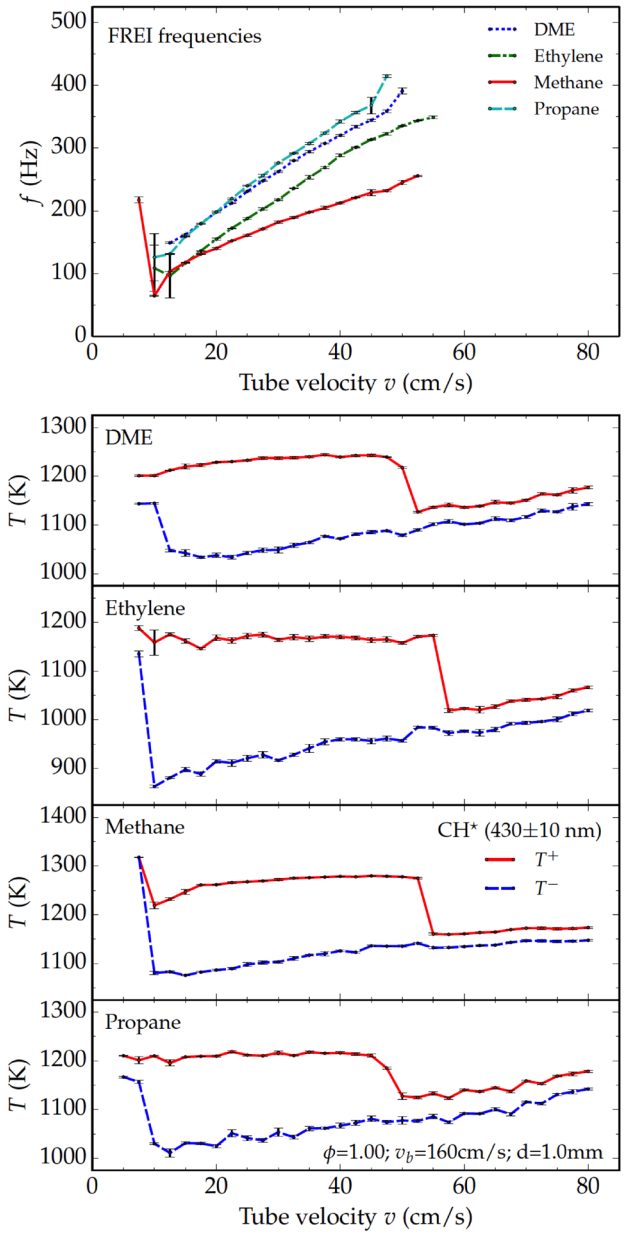

Figure 4. Comparison of the μ–FIT measurements for four gaseous fuels: (top) frequency of the flame repetitive ignition and extinction (FREI) events as a function of the pre-mixed flow velocity; and (bottom) the ignition T+ and extinction T- points as a function of flow velocity that show the transition from the high and low speed stable flames.

microphone, which the authors believe is the first published example. Thorough measurements were made to isolate and evaluate the impact of the external heat source and tube geometry on the flame dynamics. Finally, the kinetic behavior of the fuel–air mixture was related to the flame dynamics for four gaseous fuels (methane, ethane, ethylene, and dimethylether [DME]) as shown in Figure 4.

CFD simulations of alternative fuel research engine experiments were performed which leverage this project's kinetics efforts to improve understanding of the interaction of chemical kinetics with other engine physics including gas-exchange and fuel sprays. Despite advances in computationally efficient integration of large chemical mechanisms developed in this and related projects, it is still necessary to use reduced mechanisms for practical simulation time in detailed fluid dynamics calculations. Simulations of a diesel engine fueled by methyl-decanoate

were performed to study leaner lifted flame combustion which holds the promise of efficient and soot-free diesel combustion. The engine experiments were performed by C. Mueller of Sandia National Laboratories as part of the Fuel & Lubricant Technologies subprogram. Methyl-decanoate is a promising biodiesel methyl-ester because of its stability and volatility. The simulations showed good agreement with experimental heat release rates and timing. The intake and exhaust plenums where included which enable accurate simulation of the breathing process. Figure 5 shows iso-surfaces of fuel concentration and temperature during the injection, showing the lifted flame behavior at these conditions. These results were obtained with a 115 species chemical mechanism that was reduced from the 3,299 species mechanism developed in this project.

Simulations were also performed to analyze partial fuel stratification in a DISI engine fueled with E85. Partial fuel stratification enables control of the combustion timing at lean and dilute conditions, which enables cleaner and more efficient operation. The DISI experiments were performed by M. Sjöberg of Sandia National Laboratories as part of the Fuel & Lubricant Technologies subprogram. The simulations are able to capture the compression, intake swirling, and spark ignition and flame propagation in this configuration. The chemical kinetics model used a 312 species mechanism reduced from a 1,389 species mechanism developed in this project for ethanol–gasoline blends. Figure 6 shows the combustion chamber with iso-surfaces of fuel and temperature during the primary combustion event. These simulations employed the fast kinetic solver algorithms developed at LLNL for a 2x reduction in simulation time. Future work in these simulations will incorporate the full intake and exhaust geometry once the components have been measured by the experimenters.

Conclusions

- New correlation has been developed for matching surrogate gasolines containing ethanol with real gasoline containing ethanol
- Flames speed expressions as a function of temperature and pressure have been developed for RD587 reference gasoline, E30, and E85
- μ–FIT built and autoignition and extinction behaviors of four gaseous fuels have been measured
- CFD engine simulations performed using fast kinetic solver algorithms developed at LLNL:
  - Leaner, lifted-flame combustion in a diesel engine fueled with methyl decanoate
  - Lean, stratified DISI combustion fueled with E85

Acknowledgements

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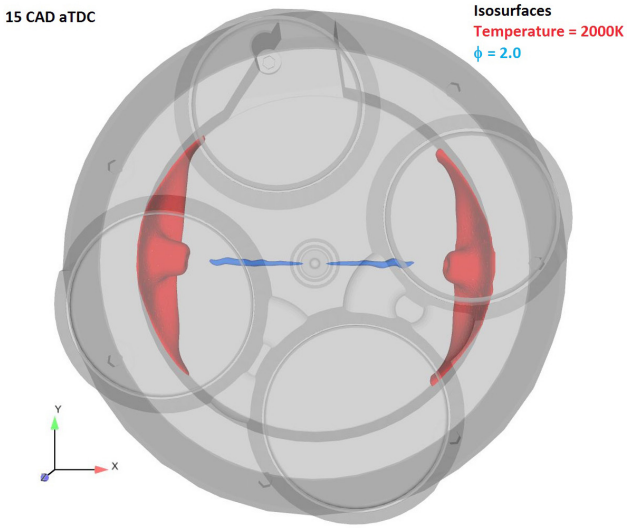

CAD – crank angle degree

Figure 5. Isosurfaces of the equivalence ratio equal to 2.0 (blue) and temperature equal to 2,000 K (red) during leaner lifted flame combustion of methyl-decanoate at 15 degrees after top dead center (aTDC).

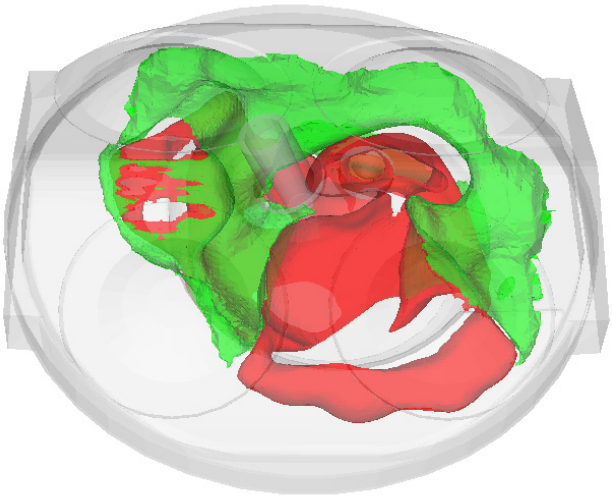

Figure 6. Iso-surfaces of fuel mass fraction equal to 0.05 (green) and temperature equal to 1,500 K (red) during stratified, DISI combustion of E85 at 4° aTDC.

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2. K. Maruta, J.K. Parc, K.C. Oh, T. Fujimori, S.S. Minaev, R.V. Fursenko, Combust. Explos. Shock Waves 40 (5) (2004) 516–523.

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FY 2015 Publications/Presentations

1. Burke, U., Pitz, W.J. and Curran, H.J., "Experimental and Kinetic Modeling Study of the Shock Tube Ignition of a Large Oxygenated Fuel: Tri-Propylene Glycol Mono-Methyl Ether," Combustion and Flame Propylene Glycol Mono-Methyl Ether," Combustion and Flame 162 (2015).

2. C.K. Westbrook, W.J. Pitz, M. Mehl, "A Chemical Kinetic Study of Octane Sensitivity", 9th U. S. National Combustion Meeting, Cincinnati, OH, May 17–20, 2015, paper # 2F12.

3. R.A. Whitesides and M.J. McNenly, "Practical Combustion Kinetics with CUDA," GPU Technology Conference, San Jose, CA, March 17–20, 2015.

4. E. Elmtoft, A.S. Cheng, N.J. Killingsworth, and R.A. Whitesides, "Injected Droplet Size Effects on Diesel Spray Results with RANS and LES Turbulence Models," SAE 2015 World Congress & Exhibition Paper 2015-01-0925.

5. G. Petitpas, M.J. McNenly, and R.A. Whitesides, "Accounting for experimental and model uncertainties in HCCI Simulation," AEC Working Meeting, Livermore, CA, February 9–12, 2015.

6. Nakamura, H., Curran, H., Córdoba, A.D.P., Pitz, W.J., Dagaut, P., Togbé, C., Sarathy, S.M., Mehl, M., Agudelo, J. and Bustamante, F., "An Experimental and Modeling Study of Diethyl Carbonate Oxidation," Combustion and Flame 162 (4) (2015) 1395–1405.

Special Recognitions & Awards/ Patents Issued

1. R&D 100 Award for Zero-order Reaction Kinetics software (Matt McNenly and Russell Whitesides).