Combustion Energy Frontier Research Center (CEFRC)
EFRC Director: Chung K. Law
Lead Institution: Princeton University

Mission Statement*: To develop a validated, predictive, multi-scale combustion modeling capability which can be used to optimize the design and operation of evolving fuels in advanced engines for transportation applications*.

Technical Summary: As the world transitions away from petroleum-derived transportation fuels, the diversity of alternative fuels, particularly biomass-derived fuels, together with simultaneous changes in energy conversion device design/control strategies, pose immense technical challenges. Combustion of the new fuels is governed by coupled chemical and transport processes at multiple length and time scales ranging from electron excitation to molecular rearrangements to nanoscale particulate formation to turbulent fuel/air mixing. As such, satisfactory utilization of these alternative fuels to achieve improved efficiency and reduced emissions require coordinated efforts by researchers in the diverse disciplines of quantum chemistry, chemical kinetics, reactive flow simulations and experimentation, high-performance computation, and advanced diagnostics – expertise provided by the 15 principal investigators of the CEFRC.

The CEFRC has selected bio-butanol as the immediate fuel of investigation because, compared to ethanol which is the dominant bio-fuel presently marketed, bio-butanol has higher energy content, mixes well with gasoline, is not corrosive, and is under active development by energy and chemical industries for commercialization. A major advance since inauguration of the Center has been the development of the first-generation reaction mechanism describing the oxidation and pyrolysis of butanol at elevated pressures relevant for engine combustion, and validation of this new model in many different experiments. Notable advances are the following:

<u>Theory of Reactions</u>

- Development and validation of a high-accuracy *ab initio* quantum mechanics method suitable for studying bond-breaking in large molecules.
- New method developed for accurately modeling effects of multiple conformations on kinetics.
- Development of empirically-corrected DFT methods that achieve high accuracy at very low CPU cost.
- Identification of the decomposition routes of the radicals from the H-abstractions of small alcohols.
- Studies of collisional energy transfer crucial in determining pressure-dependent rate coefficients.

<u>Development of Reaction Mechanisms</u>

- Detailed probing of the combustion chemistry of biofuels by using the major classes of experimental instrumentation: shock tubes, variable-pressure turbulent flow reactors, rapid compression machines, low-pressure burner stabilized flames, and counterflow premixed and diffusion flames coupled with advanced laser diagnostics and synchrotron photoionization mass spectrometry, allowing access to a wide range of pressures, temperatures and stoichiometries for probing combustion reaction chemistry.
- Construction of a detailed chemical kinetics model for combustion of all four butanol isomers, tested against the literature data as well as data measured by other members of the CEFRC team.
- Kinetic models of propanol isomers and methyl butanoate are updated.
- Kinetic model for the H_2/O_2 system has been updated to predict burning rates at high pressures.
- Chemistry and kinetics of sooting processes in *n*-butanol and *i*-butanol have been examined.

- Mathematical and numerical procedure for kinetic parameter uncertainty quantification, propagation and minimization has been developed for combustion modeling over a large range of length and time scales.

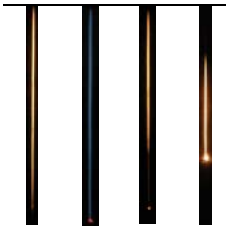
Chemistry/Transport Coupling

- Experimental data of laminar flame speeds, extinction/ignition limits, and soot/NOx emissions measured for hydrogen, C1-C7 hydrocarbons, C1-C4 alcohols, C1-C10 methyl-esters, and some important ethers, aldehydes, and ketones up to 25 atm. Kinetics models and transport properties of these fuels have been validated and improved.
- An efficient multi-timescale model reduction method has been developed and applied to direct modeling of homogeneous charge compression ignition (HCCI) combustion.
- A new combined method using large eddy simulation (LES), probability density function (PDF), and *in situ* adaptive tabulation (ISAT) to include the turbulence-chemistry interactions and to enable the efficient implementation of detailed mechanisms in turbulent flame simulations was developed.
- Direct numerical simulation (DNS) of the effect of thermal and concentration stratification in turbulent HCCI combustion for n-heptane and dimethyl ether was performed and analyzed.

Blending Strategy of Biodiesel, Diesel, and Ethanol

- A strategy of blending ethanol and biodiesel in diesel has been developed to synergistically moderate the soot emission propensity of diesel and the non-volatility of biodiesel. The concept capitalizes on the low-sooting property of biodiesel and the volatility of ethanol, resulting in the soot reduction through chemical interaction and improved atomization through the substantial volatility differential between ethanol and biodiesel. Such blending strategies hold promise for the design of future clean-burning and robust bio-fuels synthesized from a wide stream of bio-feedstocks.

Flame streaks of streams of burning droplets of various compositions



(a) (b) (c) (d)

a) Diesel, showing yellow, sooty flame
b) Biodiesel, showing blue, non-sooty flame
c) 50-50% Diesel-biodiesel, showing reduced soot
d) 50-50% Diesel-ethanol, showing droplet explosion and hence facilitated gasification

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