Global Climate & Energy Project
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Optimization of Synthetic Oxygenated Fuels

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Objective
This project aims to develop novel oxygenated fuels and to establish the chemical kinetic models required to design next-generation combustion engines that run on those fuels.

Background
Mitigation of greenhouse gas emissions from transportation sources will require implementation of a variety of strategies, including improvements in the efficiency of overall vehicle/fuel systems, such as hybrid and new high-efficiency diesel engines, and use of synthetic fuels to replace or supplement petroleum-based fuels. A particularly attractive class of synthetic fuels is oxygenated liquid fuels. These oxygenated fuels are especially attractive for use in advanced diesel engines and diesel-hybrids because of the inherently high thermal efficiencies of these engines compared to spark ignition engines. In addition, these fuels offer significant potential for reduction in particulate and NOx emissions from diesel engines. The current strict regulations on these emissions have proved to be an impediment to introduction of diesel engines into the automotive and light truck sector in the United States. Hence, optimization of oxygenated fuels to be used either as a neat fuel or as an additive offers the prospects of reductions in GHG emissions owing to efficiency gains from advanced diesel engine concepts. Furthermore, if the desired fuels can be synthesized using bio-derived feedstocks, including traditional bio-diesel crops, crop waste and harvested crops, then a further benefit of low net carbon release could be achieved.

In recent studies of the effect of the structure of model oxygenated fuel molecules on particulate formation under diesel engine combustion conditions, it was found that particulate emissions were significantly reduced and that the emissions reductions depended not only on the amount of oxygen in the fuel mix, but also on the oxygenate structure, Figure 1.

Figure 1: Dependence of sooting tendencies on the fraction of oxygen by mass and oxygen functionality in the fuel under diesel engine combustion conditions [1].

It has been postulated that the propargyl radical (C3H3) and propylene (C3H6) are primary precursors of soot formation. These species are formed from long chain- and branched-hydrocarbon fuel molecules under certain combustion conditions, particularly the fuel-rich
premixed reaction zone in a diesel engine (see Figure 2). If the fuel structure can be modified to exclude these soot precursors (as could be done by appropriate oxygen functionality), or the reaction pathways can be engineered such that these radicals are not allowed to form (again, using oxygen to bind the carbon atoms before they can make the 3-member chains), then soot formation in diesel engines can be suppressed.

**Approach**

An experimental study of the combustion and emissions characteristics of oxygenated hydrocarbon fuel molecules will be carried out. Initial studies will focus on determining, in a systematic way, the impact of oxygen content and functionality on combustion and emissions characteristics. These studies initially will employ molecules that have been identified in engine testing and simulations to have potential for reduced soot and NOx emissions (Figure 1). The studies will be carried out in two existing experimental facilities that have the capability of accessing experimental conditions (temperature and pressure) relevant to diesel engine combustion: a high-pressure shock tube (HPST) and a high-pressure flow reactor (HPFR). These two facilities are complementary in that they can access overlapping regimes of temperature and pressure, but provide different experimental data. Data will include the evolution of radical and stable species as well as soot volume fraction and particle size.

Concurrent with the experimental studies, detailed chemical models will be assembled. Using these models, sensitivity and reaction path analyses will be carried out to establish the role of fuel structure in ignition and NOx and soot formation. The experimental data will yield information on the combustion and emissions characteristics of synthetic oxygenated fuels for a range of temperatures and pressures relevant to diesel engine combustion that will be used along with previous knowledge to construct detailed chemical kinetic models for the various fuels.

To extrapolate the fundamental data from the experimental studies to engines, it is important to consider the complex combustion environment of a diesel engine, which is governed by liquid fuel injection and evaporation, swirling flow, complex geometry and the presence of walls. Furthermore, it is necessary to consider a wide range of operating conditions in any optimization process. Hence, the detailed chemical models will be applied in three-dimensional numerical simulations of diesel engine combustion using state-of-the-art methods that allow for the consideration of detailed chemistry. The combination of experiments and modeling will allow us to study and understand how the oxygenated fuels reduce soot emissions in diesel engines, both at a general and at a very detailed level that will guide the design of optimized fuel structures.

The results of experimentation and modeling will be translated into strategies for formulating new fuels. Molecules will be designed whose pyrolysis and combustion will produce those radical species identified to be most effective in reducing soot precursors. Production methods for these compounds will be explored with an emphasis on synthesizing them at a large scale from a variety of feedstocks. Finally, two of the best candidate oxygenated molecules will be identified, synthesized in limited quantities and tested in the experimental apparatus.

**References**

1. Adapted from Westbrook and Pitz; Energy Efficiency and Emissions in Transportation, Washington DC, October, 2002