Optimization of Synthetic Oxygenated Fuels for Diesel Engines

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Introduction

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 these fuels. To achieve these objectives, a combined experimental, modeling and computational study is being carried out. In addition, strategies for production of such oxygenated fuels on a large-scale basis from a variety of feedstocks are being explored.

Background

Mitigation of greenhouse gas (GHG) 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 NO_x 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, but also on the oxygenate structure, Fig. 1. To date, studies of the effect of oxygenated fuel structure on performance and emissions have been largely empirical in nature so that a defined pathway for optimizing fuel structure for lowest emissions and best performance is not currently available.

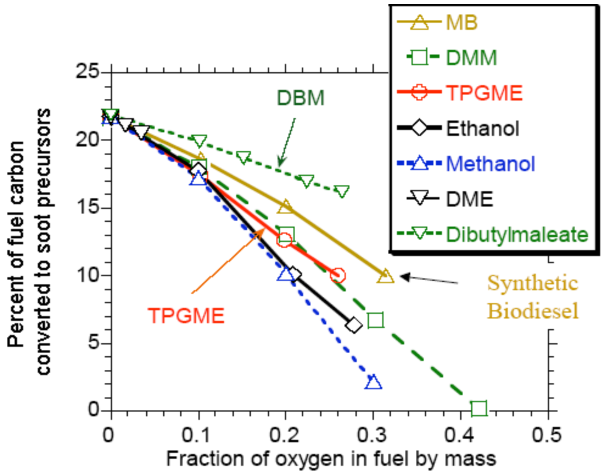

Figure 1: Dependence of sooting tendencies on the fraction of oxygen by mass and oxygen functionality in the fuel under diesel engine combustion conditions [1].

Results and Progress

Approach

To meet program objectives, an experimental study of the combustion and emissions characteristics of oxygenated hydrocarbon fuel molecules is being carried out. Initial studies will focus on determining in a systematic way the impact of oxygen content and functionality on combustion and emissions characteristics. The studies are being conducted in two experimental facilities that have the capability of accessing 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.

Concurrent with the experimental studies, detailed chemical models will be assembled to establish the role of fuel structure in ignition and NO_x and soot formation for a range of temperatures and pressures relevant to diesel engine combustion.

To extrapolate the fundamental data from the experimental and modeling studies to engines, it is necessary 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 from the above studies 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 simulation will allow us to study and understand how 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, modeling and simulation will be translated into strategies for formulating new fuels. Production methods for these compounds will be explored with an emphasis on synthesizing them at a large scale from a variety of feedstocks.

Experimental Studies

The initial experimental studies investigate soot formation and the reaction kinetics of ignition in mixtures of DME - one of the compounds shown in Figure 1 – and n-heptane – a surrogate Diesel fuel. We have performed two types of experiments in shock tubes: laser extinction measurements of soot yields and formation rates during n-heptane pyrolysis, and ignition delay times in low-pressure DME/oxygen/argon mixtures. The initial results of these experiments are summarized below.

We have measured soot volume fraction and induction time for n-heptane using a single-wavelength laser extinction method. The optical beam passes through the shock tube 2 cm from the end wall where soot volume fraction is measured. Pressure is simultaneously recorded at the same location by a pressure transducer. Example results are shown in Fig. 2. The upper curve represents the pressure trace in the shock tube and the lower curve is the laser extinction through the shock tube due to the presence of soot. Time zero is determined by the arrival of the reflected shock wave. The time interval between time zero and the point where the tangent of the laser extinction curve crosses the x-axis is defined as the soot induction time.

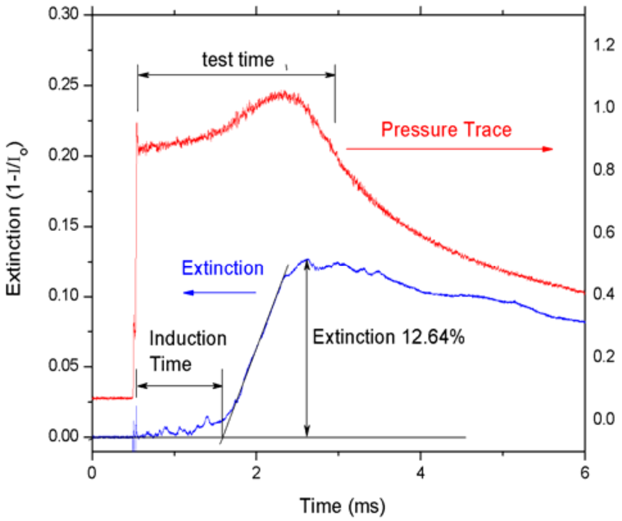

Figure 2: Example extinction and pressure time-histories. Initial shock conditions: 1837 K, 19.0 bar, 1000 ppm n-heptane/argon.

Several n-heptane pyrolysis experiments were performed at a nominal pressure of 20 bar. The present soot yield measurements are compared with the results of Kellerer et al. [2]. The trend of soot yields with temperature and the magnitude of soot yield are similar to Kellerer et al, which were conducted at higher pressures and in the presence of oxygen.

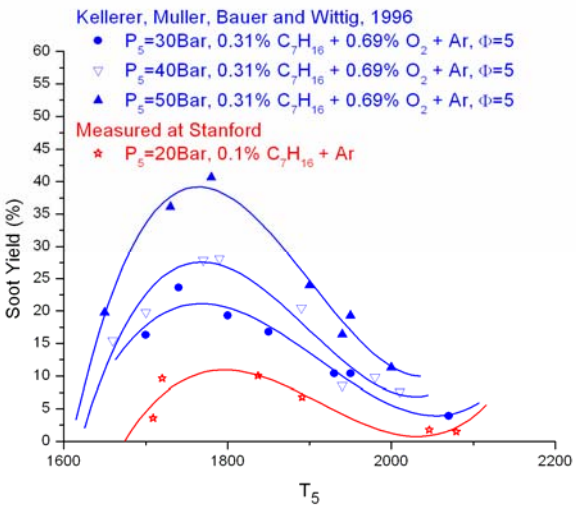

Figure 3: Soot yield of n-heptane pyrolysis at 20 bar.
Current data, red symbols; Kellerer et al. [2], blue symbols.

Soot induction times, τ (ms), are often expressed using an Arrhenius-type expression of the form:

$$\frac{1}{\tau} = A \cdot [C]^n \cdot \exp(-\frac{E}{RT})$$

where $[C]$ is the carbon atom concentration (mol/m^3). The Stanford induction time data, plotted in Fig. 4, are in agreement with the measurements of Kellerer, et al. A fit to the Stanford data yields, n = 0.5 and E = 152 kJ/mol, which are in agreement with the Kellerer, et al. values of n = 0.46 and E = 149 kJ/mol.

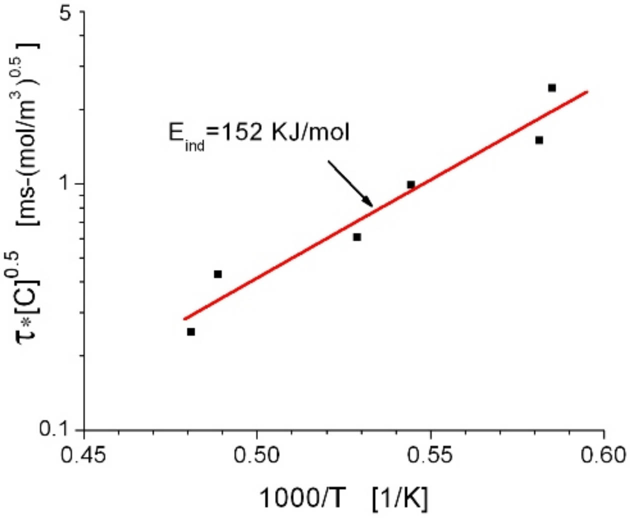

Figure 4: Soot induction times in 20 bar n-heptane pyrolysis experiments.

Ignition delay time measurements are needed to evaluate the overall behavior of fuel oxidation mechanisms. In the case of DME, two previous ignition delay time studies have been performed, but the body of data is incomplete. The first study was performed at pressures of 13 and 40 bar using a high-pressure shock tube [3]. All of the experiments used stoichiometric DME-air mixtures. These data are particularly interesting because they provide measurements of ignition delay time in the negative temperature coefficient (NTC) region. The second study was performed in a shock tube at 3.5 bar [4] using mixtures comprising 1% DME in Ar/O_2 with fuel-air equivalence ratios, $\phi = 0.5$, 1, and 2. When combined, the two previous studies provide a complementary set of data for modelers. However, the existing data do not provide enough information to correlate ignition delay time with pressure, equivalence ratio, and dilution.

We have performed DME ignition experiments using a second shock tube facility designed to operate at low and intermediate pressures. Two different diagnostics were used in these experiments. Light emission from electronically excited CH* and OH* was recorded as a function of time following shock-heating. In addition, pressure-time histories were measured. Mixtures of 1% DME in Ar/O_2 and $\phi = 1$ and 2 have been examined so far. A typical pressure and OH* emission trace is shown in Fig. 5. The time of ignition is defined here as the time where a line tangent to the point of maximum slope in the emission trace intersects the zero emission line (shown by the blue dashed lines). Figure 5 also demonstrates how well the ignition delay times derived from different diagnostics typically agree.

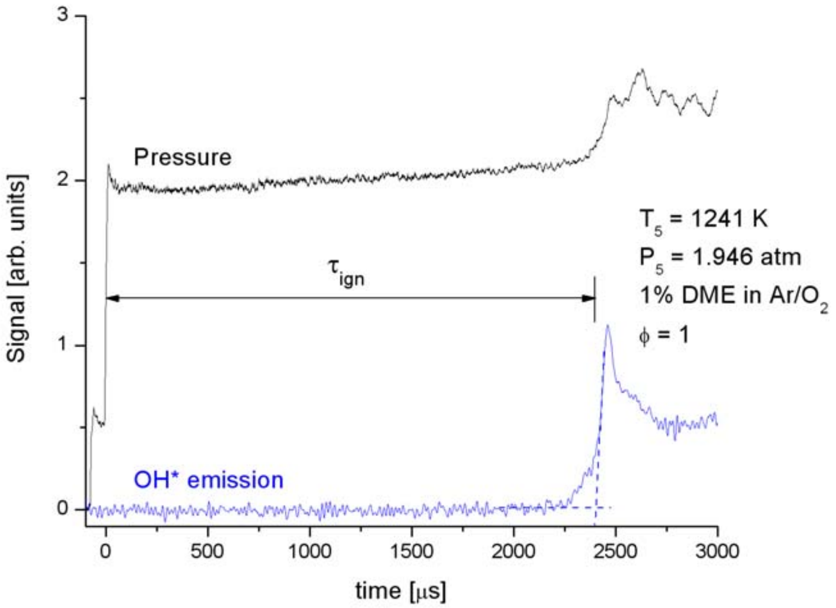

Figure 5: Example emission and pressure profiles during an ignition experiment. Reflected shock conditions: 1241 K, 1.946 atm, 1% DME in O_2/argon, $\phi = 1$.

The ignition data shown in Fig. 5 can be compared with predictions from a detailed reaction mechanism. The mechanism used for these comparisons was developed by Curran, et al. [5, 6]. This model agrees well with the previous shock tube ignition delay time measurements as well as most of the species profiles from jet-stirred reactor and variable pressure flow reactor experiments. Our recent experimental results along with a comparison to the model are shown in Fig. 6. Good agreement is found for the magnitude of ignition delay time, although the experimental activation energy for $\phi = 2$ case appears to disagree slightly with the model. The data at 3.5 bar from [4] show a similar trend.

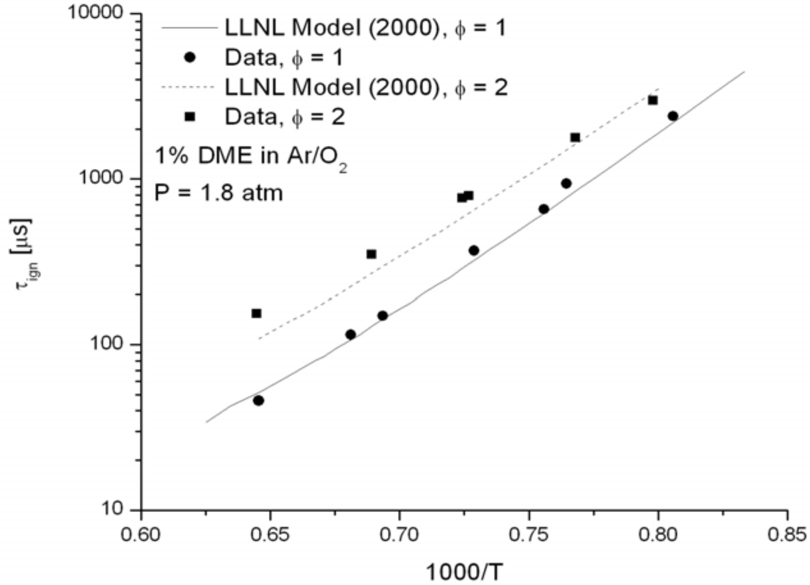

Figure 6: Ignition delay times for mixtures of 1% DME in Ar/O_2 and $\phi = 1$ and 2 and comparison with the Curran, et al. model [6].

Since there are a large number of oxygenated compounds with differing oxygen functionality and since the database on the effectiveness of different oxygenated species in suppressing soot is limited, we are teaming with Professor A. Boehman of Penn State to perform screening tests to help us select the model compounds to be investigated in detail in our future work. These tests employ the ASTM smoke-point method to provide the sooting tendency of fifty different oxygenated compounds. The structural types include alcohols, ethers, esters, ketones and aldehydes. Within each structural type, chain length will be varied to study the effect of volatility and/or molecular weight.

Modeling Studies

In parallel with the shock tube experimental investigations, we have begun a modeling effort to develop reaction mechanisms to describe soot formation in the shock tube experiments and in practical devices. This development extends from the gas-phase ignition of diesel surrogates and oxygenates through the production of soot precursors to the formation and aggregation of soot particles.

We are currently using a mechanism developed by Curran, et al. [6] to model the gas-phase ignition of DME and n-heptane. As described in the previous section, a preliminary comparison of this mechanism with our initial shock tube ignition delay time measurements finds that there is fair agreement between model and experiment over a limited temperature, pressure and fuel concentration range. Efforts are underway to merge this DME/heptane mechanism with a soot precursor mechanism such as that proposed by Frenklach, et al. [7]. This chemical model will be combined with a physicochemical mechanism to describe the growth of soot particles to permit the comparison of our soot yield measurements with modeling results.

Simulation Studies

As noted above, in order to extrapolate the fundamental data from our experimental and modeling studies to engines, we are applying three-dimensional numerical simulations of diesel engine combustion using state-of-the-art methods that allow for the consideration of detailed chemistry, turbulence and the complexity of the engine geometry to test the effectiveness of oxygenated fuels in reducing pollutant emissions in actual engine environments.

There are several challenges in simulating in-cylinder flows for reciprocating engines and specifically for diesel engines. Inherently, the flow is three-dimensional and is highly unsteady due to differing time scales for combustion, piston motion, and turbulence. Due to the presence of a wide range of length scales, it becomes necessary to harness the potential of a flow solver that can accurately resolve the important features of the flow. In large eddy simulations (LES), the turbulent length scales are spatially filtered so that only the large turbulent scales remain and can be resolved on an affordable computational mesh. This approach typically leads to quite accurate predictions, since the large turbulent scales, which are computed directly in LES, contain most of the turbulent kinetic energy and govern the flow dynamics.

Engine geometries are extremely difficult to simulate, because of the presence of sharp edges and corners in the combustion chamber and the moving boundaries which lead to issues regarding the computational mesh. Most meshing technologies today require a large time investment to correctly resolve the geometry with adequate detail. Meshing algorithms that automatically generate meshes from CAD designs are the logical path to take. Traditional body conforming unstructured meshes can be generated automatically, but are prohibitively expensive. A fast code that obtains geometry from CAD outputs and that simulates the flow over the body on structured Cartesian grid is needed to capitalize on the speed and efficiency of structured meshes. The need for accurate handling of the multiphase injection and mixing of the fuel with the oxidizer, coupled with an accurate combustion and turbulence model is paramount. Our plan is to create a state-of-the-art engine simulation code that will perform LES and combine an Immersed Boundary (IB) method with an Arbitrary Lagrangian Eulerian (ALE) algorithm. The above technology will be implemented in two different flow solver environments: 1) a fast structured flow solver to increase simulation turn-around time and 2) an unstructured code to better represent the geometry [8].

Engine simulations typically are performed using body-conforming tetrahedral meshes that deform based on the motion of the piston and valves. This requires the tracking of the nodal position of the mesh attached to the boundary faces, which often causes a loss in accuracy due to a highly distorted grid and high turn-around time due to re-meshing. The IB method is a novel technology that can be used to solve flow problems in and around geometries with irregular or sharp boundaries using a simple structured grid. This approach retains some of the advantages of an unstructured mesh, such as high order of accuracy, while reducing the computational cost and turn-around time of a simulation and maintaining the low cost of solving the Navier-Stokes (NS) equations in a structured environment.

Although the IB method was introduced in the 70's, many advances have been made to improve the method, especially to simulate flows in industrial applications. In the current implementation, we reconstruct the velocity information in the vicinity of the IB surface. Any solid geometry can be represented on a structured mesh that allows a mapping of the geometric surface on the given mesh. The velocity and pressure nodes closest to this IB surface are identified and modified to the values that satisfy the no-slip and no-penetration boundary conditions that apply on the exact position of the geometric surface. Since the velocity nodes will not exactly coincide with the IB surface, the velocities for the velocity nodes and the pressure coefficients for the pressure solver in the environment of the IB are determined by interpolation schemes [9]. The points in the rest of the domain are solved using the NS solver. A combustion model for this approach also is required. We are implementing the method in a structured-mesh code using a fractional step method. An important aspect of this implementation is to ensure that mass is conserved on a local and global scale. The most effective way to ensure this would be to use a finite volume treatment on all the cells cut by the IB surface. This method was found to be prohibitively expensive and thus an improved velocity reconstruction method will be used to satisfy the global mass flux across the IB surface [10].

The NS equations can be solved on a domain with moving boundaries by either using the IB method, described in the previous section, or by using the Arbitrary Lagrangian Eulerian (ALE) approach. Typically any algorithm for solving the NS equations on a domain with moving boundaries should be capable of handling large deformations and also should be able to accurately track the moving boundaries. Traditionally, flow solvers are based on an Eulerian description. In these solvers, the computational mesh remains stationary and the fluid moves with respect to the grid. The distortions of the fluid, such as vortices, can be handled easily. However the major shortcoming of this Eulerian description is the loss of precise boundary information if the boundary is moving. Some structural mechanics algorithms are based on a Lagrangian description, where each individual node of the computational mesh is given a velocity equal to velocity of the particle at that point, thus allowing for precise tracking of the boundary. However, large-scale distortions cannot be handled by this approach. ALE combines the advantages of both approaches by specifying velocities to the computational nodes, and thus allows for the nodes to arbitrarily remain stationary or move with the material [11, 12]. As the mesh motion can be chosen arbitrarily, this approach offers an extra advantage of applying the boundary condition at the nodes adjacent to the moving boundary, which can be given the same velocity as the boundary. In the regions where huge deformation of the continuum is found, the mesh motion can be controlled. ALE differs from the Eulerian formulation by the addition of terms involving the position and velocities of the moving grid.

At the present time, IB with an improved velocity reconstruction method to conserve mass has been implemented on a structured flow solver. The current test cases compute the von Karman vortex street behind a circular cylinder and a Taylor vortex superimposed on the IB surface. Figure 7 shows preliminary results of a 2-D simulation pushing fluid through a narrow channel using the IB method.

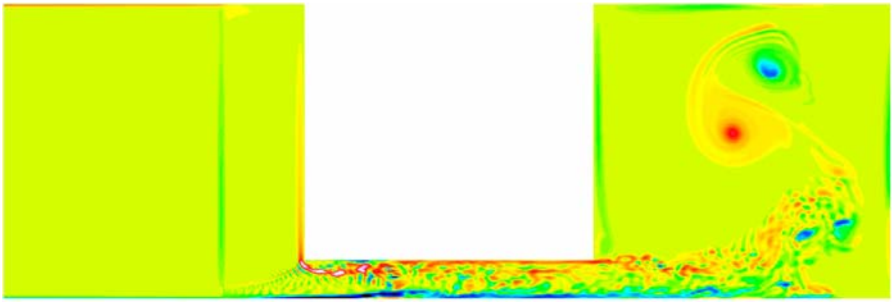

Figure 7: 2-D piston wall motion simulated using IB method. Re = 3000.

ALE with re-meshing capability has been implemented in the structured flow solver and is being tested. Figure 8 shows the flow solution for the wall motion for a flow at an intermediate time step performed using the ALE algorithm.

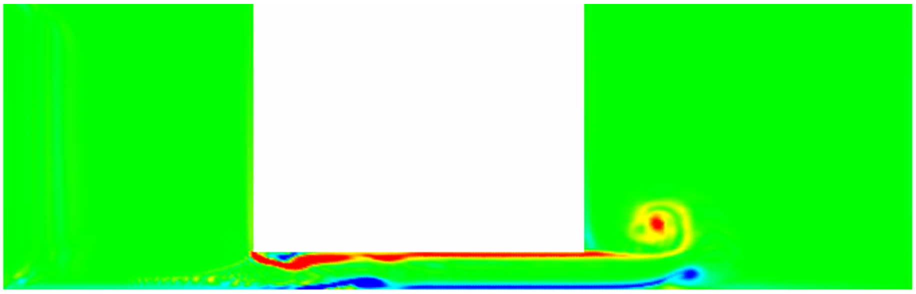

Figure 8: 2-D piston wall motion generated using ALE. Re = 3000.

Future Plans

Additional soot yield experiments over a wider range of temperature, pressure and fuel loading in the n-heptane and n-heptane/DME system will be conducted in the HPST to form a comprehensive sooting database. These data will also be compared with the experimental results of Kellerer, et al. and with the modeling results of Pitsch, et al.

We also plan to extend the range of the shock tube ignition delay time measurements of DME to higher pressures (3.5 atm) and increased fuel concentration, as well as expanding the measurements to $\phi = 0.5$. In addition, since DME is of primary interest as a fuel additive, it is important to examine how well ignition times can be predicted when the DME model is combined with existing hydrocarbon fuel oxidation models. Therefore, we will also measure the ignition delay times of various mixtures of DME and n-heptane. In addition to ignition delay times, we will identify key radical species (such as OH or CH_3) and obtain species time-histories to further test the model. This information is of particular interest in very rich cases ($\phi > 2$) where there is no distinct ignition event, making ignition delay time targets unavailable. Additional oxygenated compounds, selected from the list of compounds investigated in the smoke-point screening study will be studied. Finally, shock tube measurements will be performed at conditions overlapping with high-pressure flow reactor experiments in order to directly compare the results from the two different experimental facilities. These experimental studies will be interpreted using detailed chemical models that will be assembled and modified as required.

In the computational effort, we plan to represent the structural geometry of the engine using CAD outputs, such as STL file formats, and have the IB readily detect the surface features. We plan to combine the promise of IB technology and ALE algorithm to effectively simulate the piston and valve motions using LES. ALE can be used to simulate the 1-D piston motion, and IB will be used to define the valve motion and the piston bowl in a diesel engine. In order to allow for large density gradients and the propagation of pressure waves, the above two techniques need to be implemented into a compressible flow solver. The solver then will be coupled with state-of-the-art combustion models.

Strategies for synthesizing oxygenated fuels from various feedstocks will be investigated.

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