

Optimization of Synthetic Oxygenated Fuels for Diesel Engines

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Abstract

During the past year, a systematic experimental study of the sooting tendency of various oxygenated molecules was carried out using oxygenates from the main functional families: ethers, esters, aldehydes, alcohols and ketones. The results from the experimental study were correlated using a novel application of structural group additivity. From the screening data and analysis, several oxygenated fuels with significant potential for particulate emissions reduction from Diesel engines – an ether and a ketone – were selected for detailed study in shock tube and flow reactor experiments. The experimental studies provide data on ignition delay, soot yields and soot induction times, and detailed species evolution profiles for the fuel and major intermediate and product species. Studies using dimethyl ether and dimethyl ether/n-heptane blends have been completed. The results from the experimental studies have been compared with predictions from a detailed reaction mechanism and areas where mechanism improvement are required were identified.

To assess the effectiveness of oxygenated fuels in reducing pollutant emissions in Diesel engines and to optimize the Diesel engine process for the particular fuel characteristics, we are performing a limited set of engine experiments as well as three-dimensional numerical simulations of Diesel engine combustion. The simulations permit a more extensive investigation of effects of engine design and operating conditions on performance and emissions. For the simulations, we are developing a state-of-the-art computational tool which is capable of performing Large Eddy Simulation (LES) of turbulent combustion in Diesel engines. Over the past year, significant progress has been made in the development and implementation of a structured grid solver and a method to model piston motion. The code has been validated by comparison of code predictions with available experimental data on unsteady flows, including a reacting jet in cross flow and a square piston compression machine.

Introduction

The objectives of this project are 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 promising 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 and the significant potential of these fuels offer for reduction in particulate and NO_x emissions. 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 significant 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 [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. We expect to provide the underlying science needed to define this pathway.

Results

Approach

To meet program objectives, an experimental study of the combustion and emissions characteristics of oxygenated hydrocarbon fuel molecules is being carried out. An initial study focused on determining in a systematic way the impact of oxygen content and functionality on sooting tendencies of a variety of oxygenates to guide the selection of compounds to be studied in detail. 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 from a variety of feedstocks.

Smoke Point Test Oxygenate Screening Study

A set of screening experiments to determine the sooting tendency of fuel-oxygenate mixtures was carried out using the ASTM Smoke Point Test. A total of 29 different oxygenates, comprising ethers, esters, aldehydes, alcohols and ketones, were added at 5, 10, 15 and 20 wt% oxygen to either a Diesel surrogate fuel, n-heptane/toluene, or a low sulfur Diesel fuel. The compounds tested and the results by functional groups are displayed in Fig. 1. Higher values of the smoke point correspond to a lower tendency to form soot.

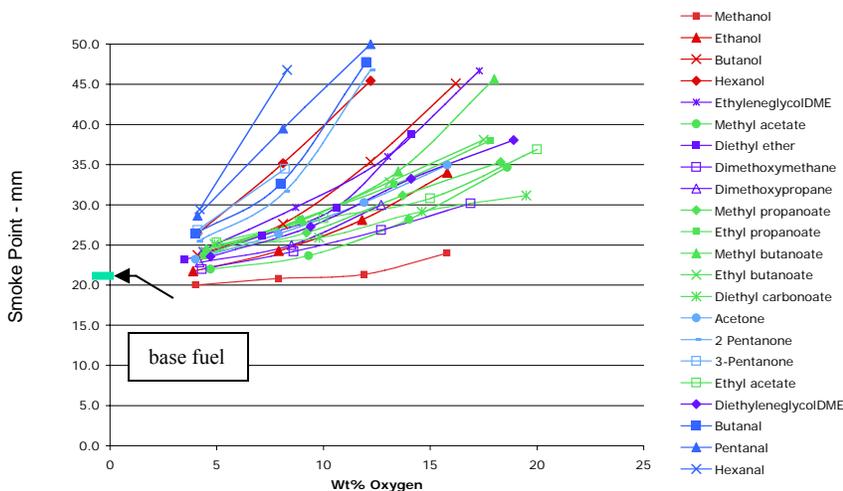


Figure 1: Effect of different oxygenates on the smoke point of a base fuel at various addition levels (Kirby and Boehman, 2006).

To interpret the experimental data, structural group analysis [2] is used to quantify the effect of each oxygenated moiety independently from the hydrocarbon part of the molecule in a systematic fashion. There are two major outcomes of such an analysis: first, it will give a strategy to estimate the sooting tendency of a molecule for which no experimental data are available. Second, it will provide theoretical insights on how to

combine hydrocarbon structures and oxygen moieties in a molecule to get the largest reduction in sooting tendency

The smoke point measurements are first converted to a more convenient, apparatus-independent quantity, the threshold sooting index, or TSI. TSI is defined as a linear function of the molecular weight (MW in g/mol) of a molecule divided by its smoke point (SP in mm):

$$\text{TSI} = a \left(\frac{\text{MW}}{\text{SP}} \right) + b$$

where the constants a and b are fit over a large number of experimental data from various sources. A desirable property of TSI over smoke point is the simple, yet efficient mixing rule proposed by Gill et al. [3] to obtain the TSI of a mixture:

$$\text{TSI}_{\text{mix}} = \sum_k X_k \text{TSI}_k$$

where X_k and TSI_k are, respectively, the mole fraction and TSI of component k in the mixture.

Figure 2 shows the experimental TSIs versus the simulated TSI using a linear mixing rule. The correlation coefficient is nearly 99%, the maximum error is 14.6% while the average error is only 4.15%. Good correlations are obtained regardless of the type of base fuel. The lowest TSI values are obtained with the heptane/toluene base fuel; the highest values are obtained with Diesel fuel.

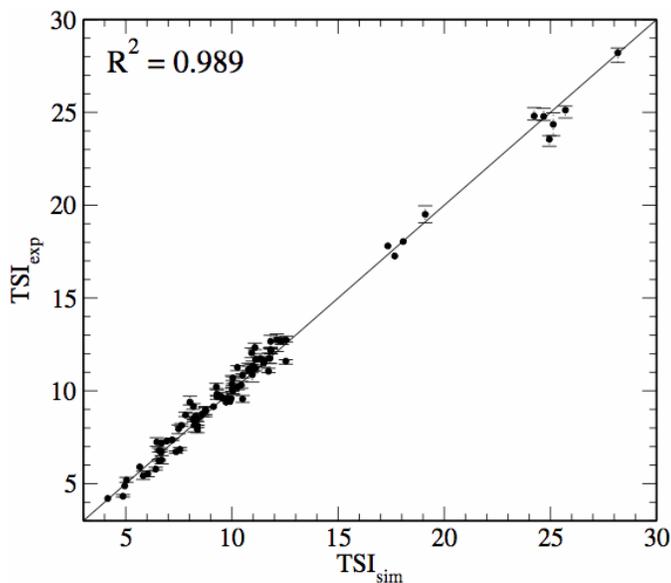


Figure 2: Correlation between experimental and simulated TSIs

The structural analysis of the TSI measurements allows a precise estimate of the efficiency of the different oxygenated functional groups. It also permits simulation of the effect of molecules different from the list of molecules screened experimentally that can be constructed from groups for which a contribution was determined.

Figure 3 compares the efficiency of the functional groups and the contributions to the TSI for the oxygenated additives studied experimentally for a constant mass fraction of oxygen, $Y_O = 4\%$. In this figure, the total reduction is the sum of three TSI contributions: the contribution due to the smaller mole fraction of base fuel in the mixture; the contribution that comes from the hydrocarbon groups contained in the additive molecules (the so-called dilution effect); and, the contribution that comes from the oxygenated groups.

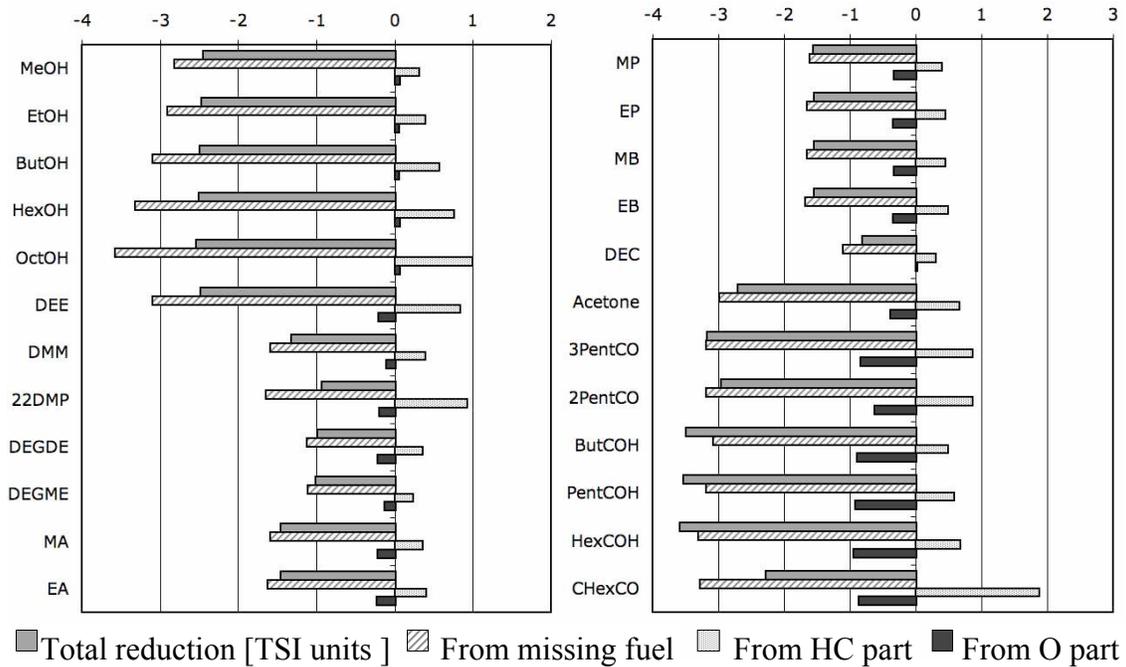


Figure 3: Comparison of TSI improvement per contribution.

An effective additive would be one that has a large negative total reduction of TSI, with a small contribution from the missing fuel part (meaning a small volume of additive), and with the major contribution coming from the oxygen. Hence, we conclude that the carbonyl group is the most effective group, either in ketones or in aldehydes. The model also predicts that for both linear alcohols and aldehydes, the shorter the chain, the better, as the total improvement is similar while the volume of additive needed to reach a constant oxygen mass fraction is smaller for shorter molecules.

Shock Tube and Flow Reactor Studies

Based on the results of the fuel screening study and on the availability of detailed kinetics models, it was decided to study dimethyl ether (DME) as the first oxygenate. DME also is of interest as a Diesel fuel due to its high cetane number and low particulate emissions [4]. Two experimental facilities are being used to investigate the reaction kinetics of ignition, combustion and soot formation in the DME and n-heptane systems - two shock tube facilities (high and low pressure) and a high-pressure flow reactor that have the capability of accessing experimental conditions (temperature and pressure) relevant to diesel engine combustion.

Shock Tube Ignition Experiments

Ignition delay time measurements provide critical targets for evaluating oxidation mechanisms. In the case of DME, two previous ignition delay time studies have been performed, but the body of data is still incomplete. The first study was performed at pressures of 13 and 40 bar using a high-pressure shock tube [5]. All experiments used stoichiometric DME-air mixtures. That study was particularly interesting because it provided excellent measurements of ignition delay time in the negative temperature coefficient (NTC) region. The second ignition delay time study was performed in a shock tube at 3.5 bar [6]. The mixtures consisted of 1% DME in Ar and O₂ at $\phi = 0.5, 1,$ and 2. When combined, the two previous studies provide a complementary set of target data for modelers. However, the previous studies do not provide sufficient information to correlate ignition delay time with pressure and equivalence ratio.

The current shock tube experiments extend past work in two significant ways: they provide the first ignition time data for DME/n-heptane mixtures, and they provide OH time-histories. Mixtures of 1% DME in Ar/O₂ have been studied at $P = 1.8$ and 3.3 atm, and $\phi = 0.5, 1,$ and 2 in order to explore the dependence of ignition delay time on equivalence ratio. For stoichiometric mixtures, ignition delay times have also been measured at pressures from 1.6 – 6.6 atm. A typical pressure and OH* emission traces are shown in Fig. 4.

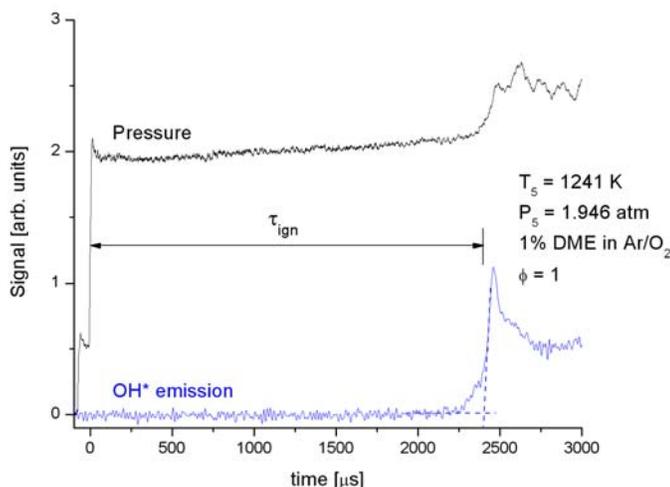


Figure 4: Typical emission and pressure profiles in a DME ignition experiment.

The kinetic mechanism used for comparison of calculated and measured ignition delay times is from LLNL [7, 8, 9]. This model agrees well with 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. Figure 5 shows the results for $\phi = 1$ for pressures from 1.6 – 6.6 atm, along with a comparison to the correlation derived in the current study.

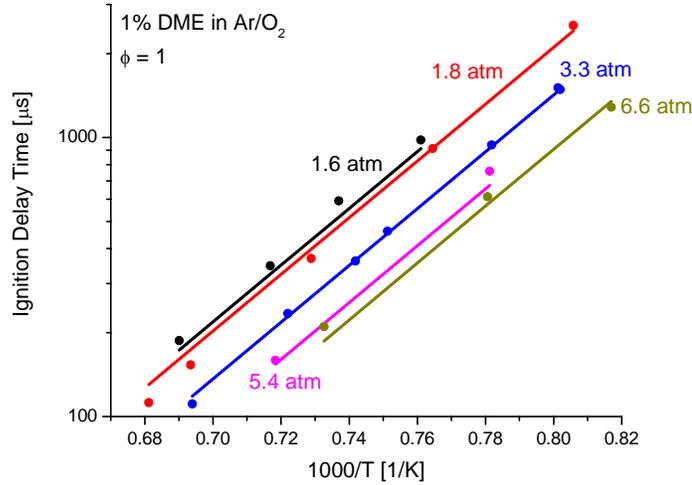


Figure 5: Comparison of measured ignition delay times (symbols) to a correlation derived from the current study (lines).

Ignition delay times were also measured in stoichiometric DME/n-heptane mixtures, for a total fuel mole fraction of 1% with three different DME/n-heptane ratios. A DME/n-heptane kinetics mechanism was developed by combining reactions and species from the LLNL DME mechanism and the LLNL reduced n-heptane mechanism [10]. A comparison between measured and calculated ignition delay times is shown in Fig. 6.

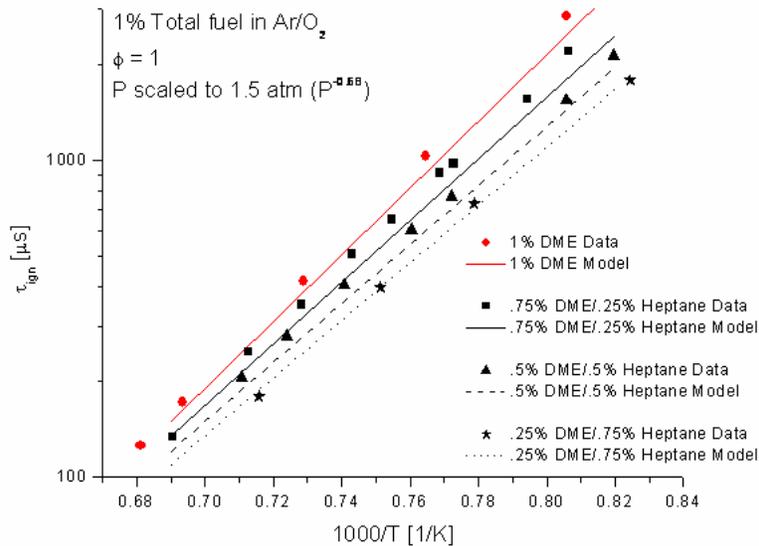


Figure 6: Measured and calculated ignition delay times (symbols) and model results (lines).

The ignition delay time measurements for the DME mixtures agree quite well with the LLNL model. The measured activation energy is just slightly lower than the model prediction. The largest discrepancy between the model and the current study is the pressure scaling. The current study suggests a pressure scaling of $P^{-0.66}$, while the model shows a scaling of about $P^{-0.39}$. The overall magnitude of the ignition delay times measured in this work also agrees well with the one previous high-temperature study [2].

However, the activation energy measured here is considerably higher. Agreement between the DME/n-heptane mixture ignition delay times and the model based on the LLNL mechanisms is also very good.

OH time-histories have been measured using laser absorption in rich DME/O₂/Ar mixtures, $\phi \sim 3$, $P \sim 1.3$ atm, and temperatures from 1400 – 1750 K. Some initial measurements were performed in mixtures containing 1.5% DME, but the concentration was lowered to 0.15% for most experiments in order to minimize the effects of energy release and isolate a smaller group of sensitive reactions. Example measured and calculated OH profiles are shown in Fig. 7.

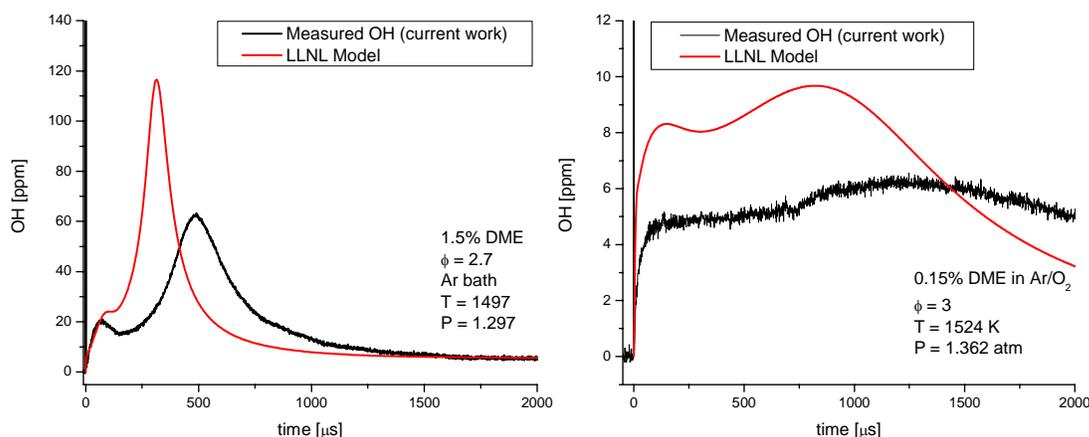


Figure 7: Measured OH profiles in rich DME oxidation and comparison to LLNL model predictions for two different DME concentrations.

Measured OH time-histories show that the LLNL model uniformly overpredicts OH concentration in rich DME oxidation experiments. The model does, however, predict the general shape of the OH profiles, in particular the fact that two OH peaks are present in many conditions. Detailed sensitivity analysis of the OH profiles shows that at early times, the experiment is sensitive to a very limited number of reactions (Fig. 8).

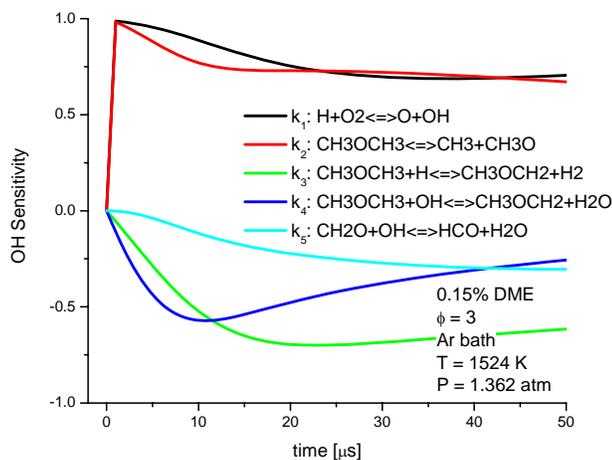
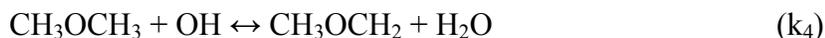


Figure 8: OH sensitivity in rich DME oxidation at early times.

Further analysis also shows that rates of the following reactions can be measured using our techniques very accurately:



and work is in progress to determine these rates.

Shock Tube Soot Formation Experiments

Quantitative measurements of soot formation are needed to validate and refine a combined chemical and physical soot generation mechanism. Shock tube measurements allow direct validation of chemical/physical soot formation models.

Soot formation rate and yield measurements were performed in *n*-heptane and DME mixtures for fuel-rich equivalence ratios. The high-pressure Stanford shock tube provides an excellent test bed for these experiments and produces test conditions at high pressure (20 atm) and high temperature (1500 to 1900 K).

Figure 9 shows example data recorded from a typical soot formation experiment conducted in our high-pressure shock tube. Long test times were achieved using tailored driver gas mixtures which allowed us to extend the test time to 7 milliseconds. The increase in pressure during the test time can be attributed to non-ideal effects in the shock tube, such as the growth of the sidewall boundary layer and shock attenuation. This short-lived, small pressure change (less than 1 ms and 10% pressure rise) does not significantly affect the rate of soot production.

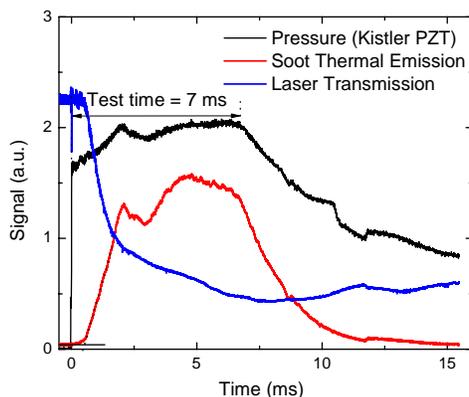


Figure 9: Pressure, soot emission and laser extinction data for *n*-heptane/O₂ ($\Phi = 5$) in 99% argon. $T_5 = 1748\text{K}$, $P_5 = 22.23$ bar.

Soot formation experiments were conducted using neat *n*-heptane and *n*-heptane/DME blends as fuels. The *n*-heptane/oxygen mixture was 0.31% *n*-heptane and 0.69% oxygen diluted in 99% argon by mole. In the *n*-heptane/DME/oxygen mixtures, DME makes up 12.5% of the carbon atoms keeping the equivalence ratio and carbon atom fraction in the mixture the same. The *n*-heptane/DME mixture was 0.27% *n*-heptane, 0.14% DME, 0.68% oxygen by mole (*n*-heptane:DME:oxygen = 2:1:5) and

the balance argon. The comparison experiments were conducted at pressures of 20 bar while varying the temperature. Soot yield data are plotted at discrete times in Fig. 10.

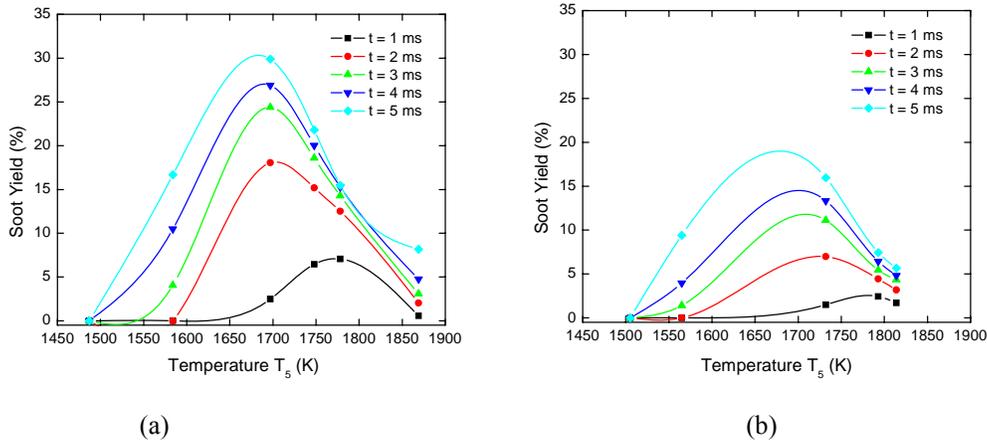


Figure 10: A comparison of soot yield in (a) *n*-heptane/oxygen mixture; and (b) *n*-heptane/DME/oxygen mixture with 12.5% of carbon from DME at different times. The experiments were conducted at $P = 20$ bar, $\Phi = 5$ and constant carbon atom fraction in the mixture.

Noticeable decreases in soot yield at all times are found with the addition of DME to the reactant mixture. At 5 ms, the peak soot yield is suppressed by 30% even though the oxygen mass in DME is only 7% of the total mass of *n*-heptane/DME fuel.

The peak temperature for soot formation for both mixtures at early time (1 ms) is around 1800K; this is consistent with previous shock tube studies of soot formation from *n*-heptane [11]. The peak temperature shifts toward lower temperatures when the test time is extended. This observation can be explained by the fact that at slightly lower temperatures, the soot formation level is higher although the process is slower. The late time peak temperatures are in good agreement with laminar diffusion flame experiments where soot is formed between 1585 and 1700 K [12]. The ability to measure soot formation at longer test times (5 ms) allows both the chemical sub-mechanism of soot formation (at early time) and the physical sub-mechanism of soot particle formation (at later times) to be investigated. Both processes are important in the generation of soot in vehicle engines.

Arrhenius-type expressions are widely used in reporting soot induction time:

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

Although the effect of addition of DME to *n*-heptane on soot yield is quite pronounced, its impact on soot formation induction time is almost negligible as can be seen in Fig. 11 and thus a uniform expression for soot induction time could be used in both mixtures with or without DME. As measured in this study, $n = 0.5$, $E = 182 \pm 10$ kJ/mol, and $A = 3.2 \times 10^5$. This can be compared with values of $n = 0.46$, $E = 149$ kJ/mol and $A = 1.9 \times 10^4$ reported by Kellerer, et al. [10]. It should be noted that soot induction

times measured by Kellerer, et al. are at higher temperatures, up to 2000K, and lower uncertainties in this measurement can be obtained at lower temperatures as was done in this study.

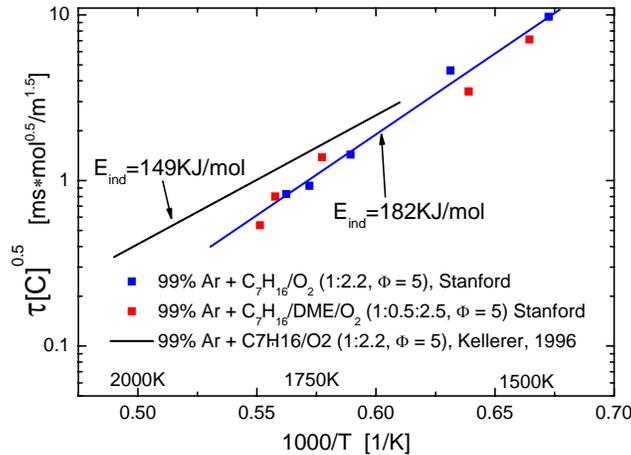


Figure 11: Soot induction time measured in shock tube for fuel rich oxidation in *n*-heptane/oxygen and *n*-heptane/DME/oxygen diluted in 99% argon, $P = 20$ bar, $\Phi = 5$.

Flow Reactor DME Oxidation Experiments

Experiments on DME oxidation also were conducted in a flow reactor. These experiments complement the shock tube experiments, described above, in that they provide concentration profiles of stable reactant, product and intermediate species. Example experimental data and profiles calculated using the LLNL mechanism [7, 8, 9] are shown in Fig. 12 for a $\phi = 2$ DME- O_2 - H_2O - N_2 mixture at an initial temperature of 1200K and a pressure of 1 atmosphere. There is relatively good agreement between the measured and calculated profiles, with the exception of CO, where the model consistently underpredicts the CO concentration. The reasons for this discrepancy are currently under investigation.

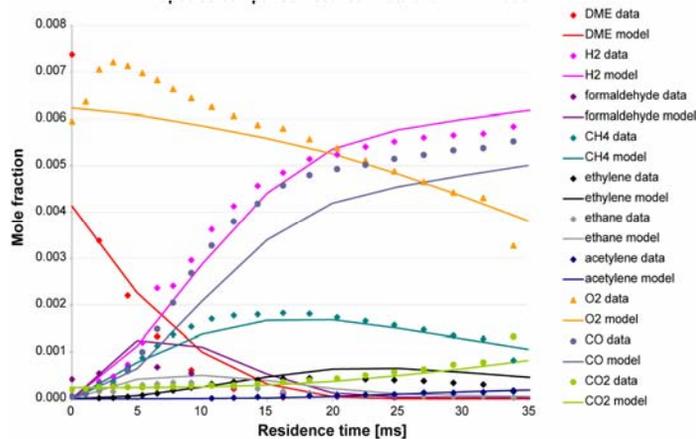


Figure 12: Stable species profiles from the flow reactor for a $\Phi = 2$ DME- O_2 - N_2 - H_2O mixture. The inlet temperature = 1200K; $P = 1$ atm. Solid lines are from the LLNL reaction mechanism.

The main focus of this effort is to assess the effectiveness of oxygenated fuels in reducing pollutant emissions in Diesel engines, and potentially to optimize the Diesel engine process for the fuel characteristics. For this, many simulations of individual cycles will have to be performed, and the models used will have to be sufficiently accurate to provide reliable predictions. To meet these requirements, we are developing a highly efficient and accurate code for internal combustion engines. The code is based on the large-eddy simulation turbulence modeling technique, which has been demonstrated in the past to be more accurate, especially for combustion processes, than the traditional Reynolds-averaged methods.

The approach that we are taking is to develop a new simulation code for internal combustion engines based on an already existing structured LES code. This approach has many advantages. Structured meshes, in contrast to unstructured meshes, always have very good mesh quality. Also, the structured meshes allow use of very accurate staggered discretization schemes. But most importantly, because of the simplicity to the internal memory layout, structured solvers are up to an order of magnitude faster than unstructured solvers. However, unstructured meshes typically cannot support complex geometry. Here, we are using the immersed boundary method to represent the geometry in the structured mesh environment. Complex shapes and even moving valves can be represented by this technique. The piston motion will be represented by moving meshes, since the mesh deformation due to piston motion can be described trivially, and this deformation will not lead to a degradation of the mesh quality by simply adding or removing cell layers.

Several verification and validation cases have been run for the structured LES solver. We have also implemented several of the new techniques that are required for internal combustion engines. For proper resolution of complex geometries in a structured grid solver, the Immersed Boundary (IB) method has been implemented. One of the biggest challenges in simulations of IC engines is the presence of complex geometries like valves and piston bowl, and since a structured grid does not conform to the shape of the boundaries, some modifications must be made to the numerical algorithm. Using the IB method the actual wall is not present in the computational domain, only its effect on fluid motion is considered [13]. The grid nodes adjacent to the boundaries are identified (IB surface), and the numerical algorithm is modified across this IB surface to account for the effect of walls. Everywhere else in the domain, the original algorithm is applied. The IB method will be applied to model the motion of valves and also to represent the complex geometry of the piston bowl.

To model the motion of the piston, we employ a technique known as Arbitrary Lagrangian Eulerian (ALE). In the Eulerian approach, which is usually used in fluid dynamics codes, the grid nodes are stationary. In the Lagrangian approach, often used in solid mechanics codes, the grid nodes move with the material associated with the respective grid nodes. In the ALE method, advantages of both approaches are coupled. In ALE, the grid nodes near the moving boundaries move with the same velocity as the boundaries, whereas in regions where large strain rate is observed, the grid nodes remain stationary as in the Eulerian approach.

In LES, the effect of unresolved scales is modeled using a subgrid-scale model. The dynamic Smagorinsky model and the Lagrangian dynamic model, which have shown good potential for inhomogeneous flows, have been implemented in the code. Highly accurate combustion models for both premixed and non-premixed turbulent combustion are being used in this code. Models for spray breakup and evaporation have also been implemented in this solver. Also available in this code are the state of the art soot models based on the method of moments, which have been shown to perform very accurately, and are computationally inexpensive when compared with Monte-Carlo simulations.

To validate the code a number of test cases have been run. A cross-flow jet combustion system was used to demonstrate the capability of this structured code to handle complex geometries. Using the same structured solver discussed above, the simulation of turbulent combustion in a cross-flow jet combustion system was performed using a steady flamelet model. Figure 13 shows contour plots of velocity, temperature and scalar mixture fraction.

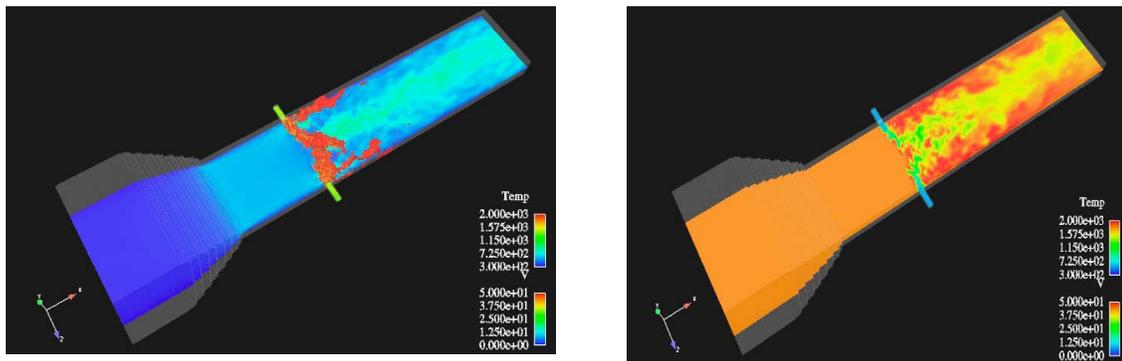


Figure 13: Contour plots of velocity, scalar mixture fraction and temperature for a cross-flow reacting jet.

As a second test case, a square piston compression machine experiment [14] was simulated. This experiment was designed to study the compression and disruption of a tumble vortex to understand flow structures in Spark Ignition (SI) engines. The experiment was conducted with a four-stroke cycle comprising intake, compression, expansion and exhaust.

LES simulations were performed over five cycles to compute mean and fluctuating quantities. The simulations were performed using the Lagrangian dynamic subgrid-scale model. The Reynolds number based on the maximum velocity during the simulation and the dimensions of the piston was of the order of 16,000, which is high enough for the flow to be turbulent. Figure 14 is a representative simulation, showing contour plots of instantaneous velocity at a given instant in time during the intake stroke. The computed velocity field shows good qualitative agreement with the experimental measurements.

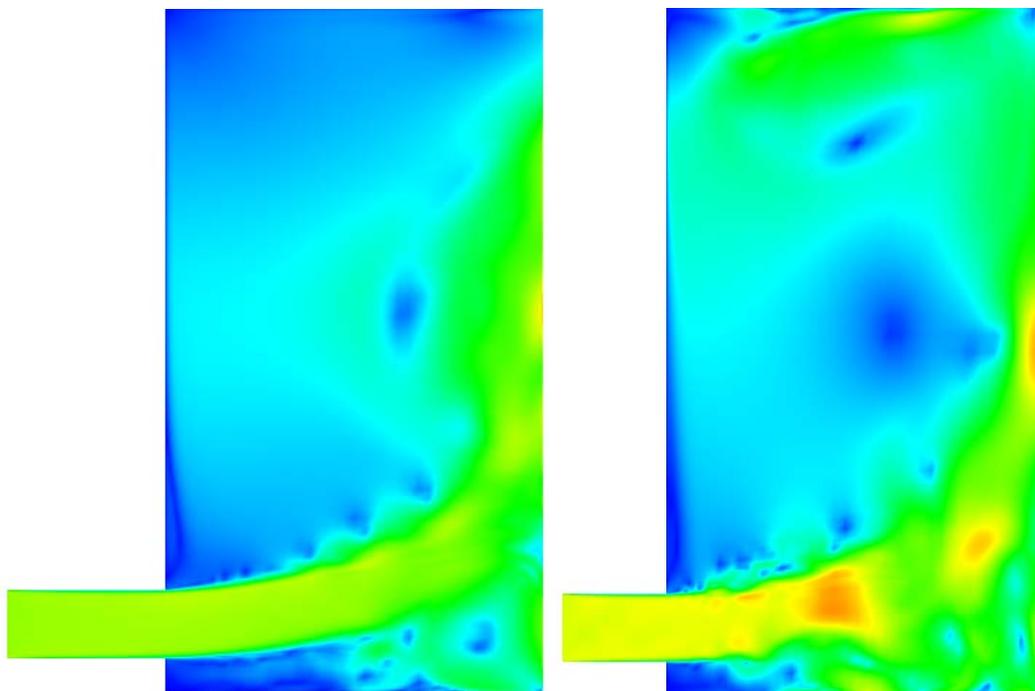


Figure 14: Instantaneous velocity fields during the intake stroke.

Progress

Our experimental studies of effectiveness of various oxygenates in reducing sooting tendency of Diesel fuels, combined with correlation of the data using structural analysis, has revealed the types of oxygen moieties that are most effective in reducing particulate emissions and has shown that the effectiveness of the moiety is independent of the molecule in which the groups appear. From all oxygenated groups, the carbonyl group consistently was found to be the most efficient. Ester and ether groups were also effective in reducing soot formation, but less than the carbonyl group.

Our fundamental studies of DME oxidation in a shock tube and a flow reactor have provided valuable data for development and validation of a detailed reaction mechanism and have quantified the potential of DME as a diesel fuel additive or substitute in reducing diesel engine soot emission.

Significant progress has been made in developing a simulation capability for Diesel engine combustion and for soot formation in these engines.

Future Plans

We will perform shock tube and flow reactor experiments to determine the effects of oxygenates with different molecular structure on ignition characteristics and soot formation under Diesel engine combustion conditions. Concurrently, we will develop detailed reaction mechanisms that describe ignition and soot formation. The current work provides the basis for this database for DME and n-heptane. In the future, we plan to extend these measurements to other oxygenates – acetone and butanal (a simple

aldehyde) – that were found to be the most effective structures in reducing particulate emissions. The development of mechanisms for these oxygenates will provide calibration targets for the development and refinement of larger oxygenate species mechanisms.

To link the results of the experimental and modeling studies with emissions from actual Diesel engines using practical diesel fuels doped with oxygenates, we will perform engine tests under tightly controlled conditions to establish the influence of oxygenate structure and dilution of the base diesel fuel on particulate emissions.

The CFD modeling effort, in support of the experiments described above, will continue. Immediate objectives included coupling an unsteady flamelet chemistry solver with the LES code to provide a more accurate description of the in-cylinder chemistry and to perform realistic engine simulations with spray and combustion.

Methods to synthesize effective oxygenate structures from a variety of feedstocks will be initiated.

Publications

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3. Malhotra, R., Boehman, A.L., Kirby, S.R., Pitsch, H. and Pepiot, P., Sooting Tendency of Oxygenates, to be presented at the ACS Natl. Meeting, Boston, MA, August 2007.

Patent Disclosure

Carbonyl compounds for soot mitigation in diesel engines (under evaluation for patent filing) R. Malhotra, SRI.

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