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Milestone Report

Non-Petroleum-Based Fuels

Report on the relationship between molecular structure and compression ignition fuels, both conventional and HCCI

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Executive Summary

The U.S. Department of Energy (DOE) is committed to increasing our nation's energy security by decreasing our dependence on imported petroleum. The Fuels Technologies Subprogram within DOE's Office of Freedom Car and Vehicle Technology (OFCVT) supports research that allows the United States to develop advanced fuels that enable efficient engines with low emissions. This document reports the completion of NREL FY 2004 Annual Operating Plan milestone 10.2: "Report on the relationship between molecular structure and compression ignition fuels, both conventional and HCCI." This work is an incremental step toward the OFCVT Multi-Year Program Plan APBF/NPBF Milestone No. 3: "Establish fuel and lubricant constituents that are required for advanced combustion regime engines."

We must understand the effects of fuel chemistry on ignition to develop fuels that enable more efficient engine designs, using both today's technology and future advanced combustion concepts. NREL has conducted two parallel activities aimed at understanding how molecular structure affects ignition properties. First, we developed an empirical tool to predict the cetane number (CN) of pure compounds with only the molecular structure as input. Then, we experimentally investigated the ignition properties of pure chemicals with varying functional groups.

In the first activity, we conducted a comprehensive search of CN data in the published literature to understand how molecular structure affects compression ignition. This resulted in CN data for 275 pure compounds, including 147 hydrocarbons and 128 oxygenates. These compounds were then input into a Quantitative Structure Activity Relationship (QSAR) software package. Then we calculated a set of approximately 100 molecular descriptors from the molecular structure of each compound. These descriptors were based on the geometry, connectivity, functional groups, electrotopological state, etc. of the molecule. A genetic algorithm was used to determine which of the many possible descriptors was most relevant to model the CN. One comprehensive QSAR model could be derived for the entire database, but it was more effective to develop models from subsets of the database for specific classes of compounds. These included big classes such as hydrocarbons and oxygenates, and smaller subclasses such as cyclic compounds, saturated hydrocarbons, and esters. The QSAR models demonstrate the utility of a predictive model for CN using only the molecular structure as input.

In the second activity, we experimentally investigated the impact of molecular structure on ignition properties with the Ignition Quality Tester. We measured the CN and how the ignition delay varies as a function of temperature. The results show that all hydrocarbon fuels tend to show approximately the same temperature dependence (when plotted on an Arrhenius plot). However, certain oxygenates (such as acetals) show a reduced temperature dependence. For example, dipropylene glycol monomethyl ether has a cetane number of 42 under normal test conditions (550°C), but ignites faster than *n*-hexadecane (CN=100) at 400°C. This reduced temperature dependence is related to the activation energy of hydrogen abstraction reactions from the fuel molecule. Blending these oxygenates with diesel fuel shows an approximately linear effect of reducing the ignition temperature dependence that could have a significant impact on cold-start behavior in conventional compression ignition engines. The impact on homogeneous charge compression ignition is not straightforward, but hypotheses are discussed.

We have increased our understanding of the effects of molecular structure on the ignition properties of fuels, as interpreted in the context of free-radical combustion chemistry. This understanding will be applied in future testing of hypotheses about "cetane enhancement" on cold-start behavior and homogenous charge compression ignition through modeling.

Introduction

A primary goal of the U.S. Department of Energy is to reduce the nation's dependence on imported petroleum. In the transportation sector, this is being pursued both by increasing the efficiency of fuel use and by replacing petroleum with non-petroleum based fuels and blending components. Both tasks require an understanding of how fuel properties affect efficiency and emissions so fuels can be screened (or tailored) based on their predicted performance in a particular type of engine.

A central issue in screening fuels for use in current compression ignition engines or advanced combustion engines is ignition quality. In current compression ignition engines, ignition quality is typically quantified in terms of cetane number (CN), which is a measure of the delay between injection and start of combustion. Currently, there is no definitive scale to rank the appropriateness of a particular fuel for use in advanced combustion engines, which employ strategies such as homogeneous charge compression ignition (HCCI) or smokeless rich combustion to obtain high fuel economy with dramatically reduced pollutant emissions.

The aim of this document is to report the completion of NREL FY 2004 Annual Operating Plan milestone 10.2, which states that NREL is to "Report on the relationship between molecular structure and compression ignition fuels, both conventional and HCCI." This document details two areas of active research at NREL on relating molecular structure to ignition properties of fuels. In the first project, a Quantitative Structure Activity Relationship (QSAR) was developed from CN data in the literature. In the second project, ignition properties of many fuels and pure components were measured in the Ignition Quality Tester (IQT™) to determine how the molecular structure affects the temperature dependence of ignition delay. This work is an incremental step toward the OFCVT Multi-Year Program Plan APBF/NPBF Milestone No. 3: "Establish fuel and lubricant constituents that are required for advanced combustion regime engines."

Development of a QSAR to Predict Cetane Number

Cetane Number Database

A database of CN values for pure compounds was assembled as a first step to understanding the relationship between molecular structure and ignition properties. We searched for all literature data on the CN of pure compounds and collected data for 275 compounds. The numbers of compounds for each class are shown in Table 1. Where compounds had multiple functional groups and could be placed in two subclasses, they were assigned to the group most representative for this table. In those cases, the compounds were included in both subclasses for model regression. A compendium of these data and information on the sources are reported separately as an NREL publication (in preparation).

Table 1: Number of Compounds in Various Classes Compiled in CN Database

n-alkanes	17	Saturates = 67	Hydrocarbons = 147
iso-alkanes	29		
cyclolakanes	21	Cyclic = 77	
aromatics	42		
polyaromatics	13		
olefins	25		
alcohols	17		Oxygenates = 128
ethers	18		
ketones	1		
esters	84		
triglycerides	8		

There are many possible sources of error in the data; some are readily apparent where there are duplicate data. Errors that may have a significant impact on measured CN may arise from impurities in the chemical sample (such as peroxides); other errors are associated with the testing method. Additionally, results for some compounds have significant uncertainty because different apparatus were used and often only blending CN values are reported. For compounds where multiple data values were available, we scrutinized and chose the data that seemed most reliable. In any case, this compilation represents the best available CN data, and to the authors' knowledge, this is the most comprehensive database assembled to date. This database is used as the "training set" as we regress models to predict the CN of other pure compounds.

QSAR Modeling Approach

To develop an empirical model for CN, the molecular structure and CN of each compound are input into the QSARIS software package (MDL Corp.). The software then calculates more than 100 molecular descriptors that may be used to model the activity parameter (in our case, CN). These descriptors may be as simple as a count of the number of each functional group (group contributions method) or as complicated as connectivity indices calculated from graph theory. Other descriptors are related to the shape, charge distribution, flexibility, electronic state, etc.

Once the descriptors are calculated, a selection process must be employed to determine which are most relevant in modeling the CN. QSARIS uses a genetic algorithm to determine the descriptors necessary for the model. The basic operation of a genetic algorithm consists of random mutation, genetic recombination, and evaluation according to a fitness criterion. Practically speaking, a genetic algorithm is a sophisticated method for optimizing a model to fit experimental data. Genetic algorithms have the benefit of not getting "stuck" in local minima and generally approach the global optimum based on the objective function (fitness criterion). For all the models regressed in this study, we allowed the genetic algorithm to run for 3000 generations. In all cases, the model reached a stable result no later than 2500 generations; we saw no improvement beyond that point.

QSAR Results

Many regressed models have been derived for different subsets of the complete database. In this section, we use the set of all hydrocarbons as an example to show representative results. A summary for a few other models is presented to demonstrate the range of results.

When a QSAR model is regressed, there is balance between the number of descriptors the user allows and the quality of fit. For the hydrocarbon QSAR model, 147 molecules were included in the dataset. A regressed model with 14 descriptors has a standard error in predicted CN of 8.6 units (Multiple R^2=0.91). For the same dataset, a model with 23 descriptors predicts CN with a standard error of 7.1 units (Multiple R^2=0.94). A parity plot of the calculated value of CN using the 23-descriptor model versus the value reported in the dataset is shown in Figure 1. Clearly there are several outliers, but most compounds are predicted reasonably well. Some of the scatter and outliers may be due to errors in the CN values reported in the literature.

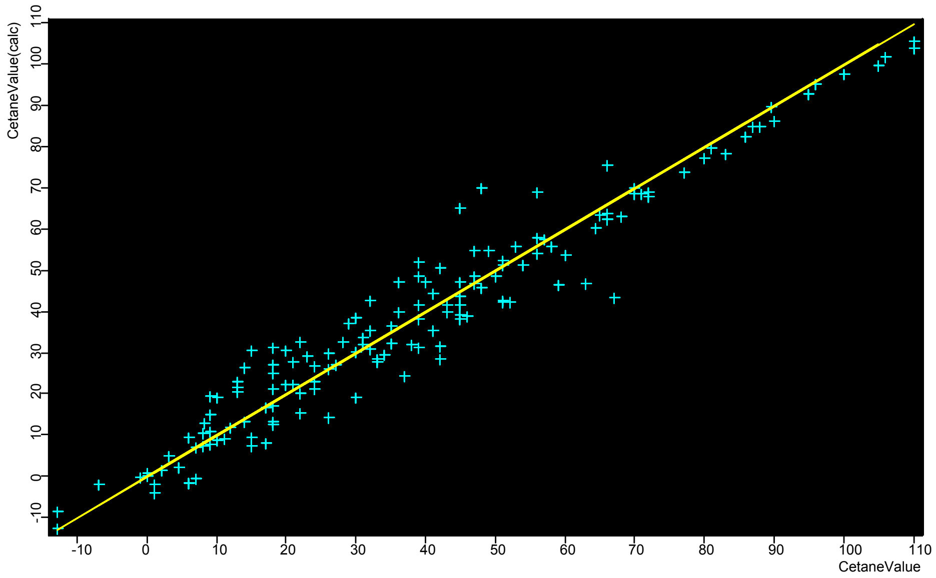


Figure 1: Parity plot for hydrocarbon QSAR with 23 descriptors

Table 2 shows several other results for QSAR models from the database. Datasets with narrow scope (such as olefins) are predicted well with a small number of descriptors. On the other hand, datasets such as “All oxygenates” that include many functional groups require significantly more descriptors for a good model fit. In addition to the sets shown in Table 2, models were regressed for every subset of compounds and for datasets where outlier compounds were removed. A more complete set of results will be published in a journal article that is currently in preparation.

Table 2: QSAR Model Fits for Selected Subsets of the Database

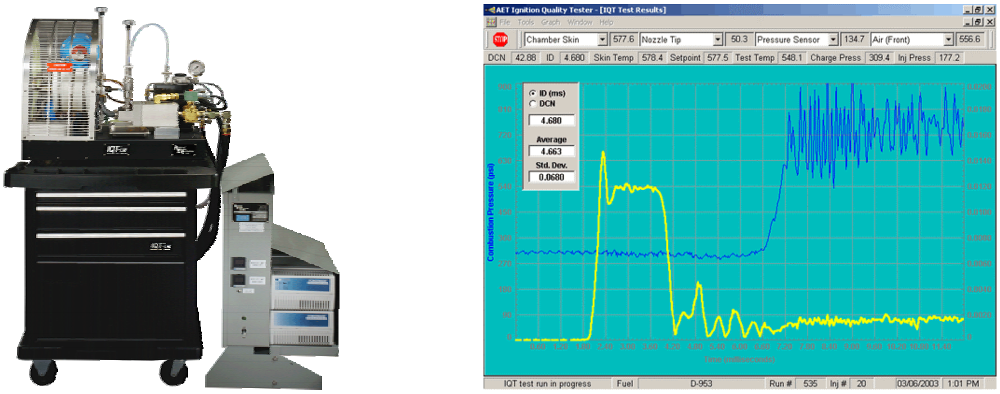
Compound Class	Number in Class	No. of Descriptors	Multiple R^2	Standard Error (CN units)
All compounds	275	23	0.91	9.1
Olefins	25	6	0.99	2.9
All Cyclic	79	17	0.92	5.9
All oxygenates	128	17	0.93	7.4
Esters	84	7	0.88	8.4

The utility of these QSAR models has been demonstrated in several collaborative research projects. Last year, NREL collaborated with Proctor & Gamble to determine which compounds could be derived from glycerin that would have reasonable ignition quality. We used the QSAR to identify several promising compounds and subsequently tested them in the Ignition Quality Tester (IQT™). The ability to identify promising compounds with a model rather than by synthesizing every possible derivative saved time and cost in this project. In a current project with collaborators at the University of Oklahoma (OU), QSAR models are being used to determine the ignition quality of compounds derived from a low value refinery stream containing decalin, tetralin, and naphthalene. The goal is to identify target products (or even favorable functional groups to target) so the researchers at OU can develop catalysts that will upgrade this low quality (waste) stream into a high quality fuel. Results from this project will be published in the next fiscal year.

Investigation of Ignition Quality Effects of Pure Compounds

Ignition Quality Tester

The ignition delay of a fuel or pure compound can easily be measured with the IQT constant volume combustion bomb. The IQT is equipped with a pintle-type fuel injector and a high-speed pressure transducer. The ignition delay is measured as the elapsed time from injection to the time when the chamber pressure reaches $P_{initial}$ + 50 psi. The user may set the charge temperature and pressure arbitrarily, but to be in accordance with ASTM D6890-03a, the standard settings for the charge air are 310 psig and 550ºC. A correlation has been developed to convert the measured ignition delay under these conditions into a derived cetane number (DCN), which corresponds well with the CN measured by ASTM D613 (cetane engine). The system is fully automated; an experiment consists of 15 pre-injections (to equilibrate system temperatures) followed by 32 injections. The reported DCNs are the averages of these 32 injections. For a more comprehensive description of this test methodology, see Allard et al. [i]. In our previous milestone report, we reported the DCN for 18 pure compounds that represent many chemical classes [ii]. A picture of the IQT and sample output from the apparatus are shown in Figure 2. In the sample output picture, the yellow line corresponds to the injector needle position and the blue line represents the combustion chamber pressure.


AET Ignition Quality Tester - [IQT Test Results]

Chamber Skin 577.6 Nozzle Tip 50.3 Pressure Sensor 134.7 Air (Front) 556.6

DCN 42.88 ID 4.680 Skin Temp 578.4 Setpoint 577.5 Test Temp 548.1 Charge Press 309.4 Inj Press 177.2

ID (ms): 4.680
Average: 4.663
Std. Dev.: 0.0680

IQT test run in progress | Fuel | D-953 | Run # 535 | Inj # 20 | 03/06/2003 1:01 PM

Figure 2: Picture of IQT and sample output of ignition delay measurement

Although the IQT is typically used to measure the DCN of fuels, it can also be used to measure how ignition delay varies with temperature, pressure, and charge composition (oxygen concentration). In this project, the ignition delay was measured for charge air (21% O_2) at 310 psig and temperatures of 360°–580°C. Fourteen fuels were investigated, including 5 "real" fuel mixtures and 9 pure compounds. The "real" fuel mixtures included CARB specification diesel, CARB diesel blended with 20% biodiesel, ultra low sulfur diesel (BP-15) additized with 2000 ppm 2-ethyl hexyl nitrate (EHN is a cetane improver), Fischer-Tropsch (F-T) diesel, and F-T jet fuel (JP5). The pure compounds included heptane, cetane, heptanol, hexyl methyl ether (HME), 2-heptanone, methyl caproate, di- and tri-propylene glycol monomethyl ether (DPGME & TPGME), and triethylene glycol monomethyl ether (TEGME).

Experimental Ignition Delay Results

The data can be conveniently plotted as a log of the rate versus the inverse of temperature (Arrhenius plot) to determine how a reaction rate varies with temperature. Arrhenius plots are typically used for determining activation energies from rates of elementary reactions, where the activation energy (slope of plot) is a metric for how strongly the rate varies with temperature. Although the spray ignition in the IQT is clearly not a single elementary reaction (spray, evaporation, mixing, ignition chemistry), there is some justification for plotting ignition delay results on an Arrhenius plot. This plotting makes sense if we think of ignition in reaction kinetic terms such as the time it takes for the reaction to produce a certain concentration of some reactive intermediate (such as OH•) or as the time it takes for a certain fraction of the fuel to be consumed. In this manner, the slope of the plot is analogous to an activation energy for ignition.

Figure 3 shows an Arrhenius-type plot of the ignition delay measurements for all fuels investigated [1]. These curves are nonlinear because the rate is not an elementary reaction and the physical delay (spray, evaporation, mixing) is lumped with the chemical delay.

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[1] To be precise, an Arrhenius plot should be the logarithm of a rate. In this case, a characteristic rate would be the inverse of the ignition delay. The resulting plot would be equivalent to multiplying all values by -1, in which case the negative of the slope would equal the pseudo-activation energy.

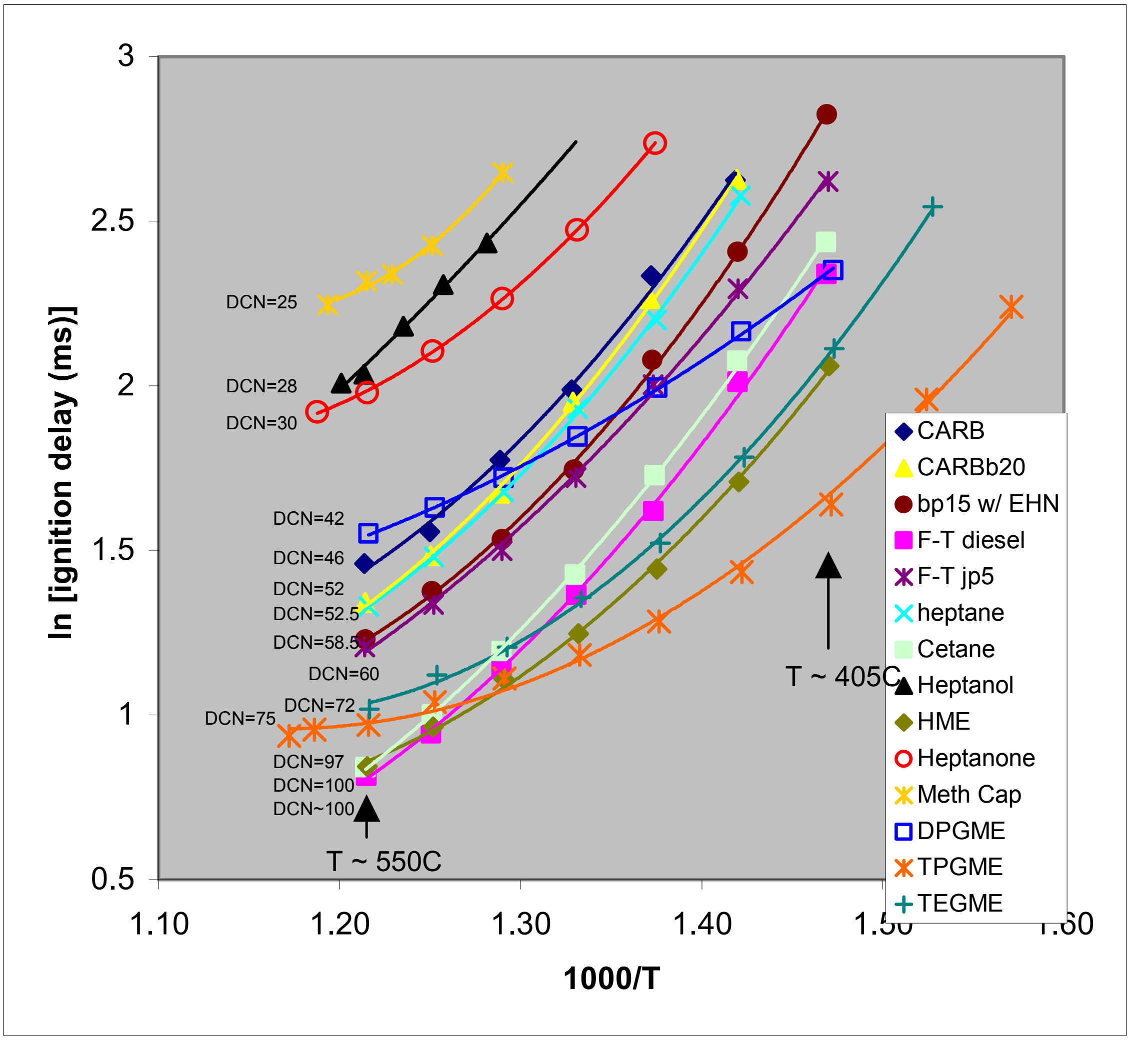

Figure 3: Ignition delay data on an Arrhenius-type plot for all fuels and pure compounds

Figure 3 shows how the ignition delay of various classes of molecules has different dependence on temperature (i.e., different slopes on the Arrhenius plot). All the hydrocarbon fuels show approximately the same temperature behavior. That is, the curves for all hydrocarbons look similar in shape and slope, but are shifted vertically by the DCN, which corresponds to the ignition delay at 550°C. Since the slopes are almost the same, the molecules have approximately the same activation energy for ignition. In contrast, many of the oxygenates show a much weaker dependence on temperature (reduced relative slope) compared with the hydrocarbon fuels. Most notably different are the acetals[2] (DPGME, TPGME, and TEGME), but HME, 2-heptanone, and methyl caproate also show a reduced slope relative to the hydrocarbon fuels. Heptanol is the only oxygenate that does not show reduced temperature dependence.

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[2] Acetals are molecules with at least two ether functional groups.

Discussion of Fuel Temperature Dependence

The reason for the reduced temperature dependence is related to the primary reaction pathway for ignition. During preignition, the initial reaction step is a hydrogen abstraction from the fuel molecule (typically by an OH• radical)[3]. This is followed by an oxygen addition that creates a peroxy radical and then an internal rearrangement (which amounts to another H-abstraction). The remaining steps in the reaction sequence are a second oxygen addition and then several fast reactions that result in chain branching. The reactions are shown symbolically in Eqns. 1-5, where RH represents a generic fuel molecule and Q is the same as R with one H atom removed.

$$RH + OH\bullet \rightarrow R\bullet + H_2O \tag{1}$$

$$R\bullet + O_2 \rightarrow RO_2 \tag{2}$$

$$RO_2 \rightarrow \bullet QOOH \tag{3}$$

$$\bullet QOOH + O_2 \rightarrow \bullet OOQOOH \tag{4}$$

$$\bullet OOQOOH \rightarrow\rightarrow\rightarrow 2OH\bullet + \text{other small products} \tag{5}$$

Since the reactions in Eqns. 1 and 3 both involve H-abstractions and are rate-limiting steps, it is logical to conclude that the overall activation energy for this series of reactions will be influenced by the energy barrier for these two steps. Furthermore, the energy barrier for these H-abstractions will be proportional to the strength of the relevant C-H bonds in the fuel molecule and the abstraction will occur fastest where the C-H bonds are weakest.

In a fuel molecule with an electron-withdrawing functional group such as ether or carboxyl, the adjacent C-H bonds are significantly weakened from their normal values. This effect is in addition to the typical C-H bond strengths, where a primary CH_3 has much stronger C-H bonds than a secondary CH_2 that is in turn much stronger than a tertiary CH group. Molecules with the weakest C-H bonds show a reduced activation energy, which explains the reduced temperature dependence. The weakest type of C-H bonds found in these selected compounds are tertiary C-H bonds adjacent to either an ether linkage or a carboxyl group, such as those found in DPGME and TPGME (see Figure 4). The next weakest C-H bonds are secondary C-H bonds adjacent to an ether linkage. In Figure 4, the tertiary C-H bonds adjacent to an ether linkage are shown with the small red circles. Likewise, the secondary C-H bonds adjacent to an ether linkage, alcohol, or carboxyl group are shown with small blue circles.

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[3] The first inititation reaction is an H-abstraction by O_2 since no OH• are present. However, after the first initiation reaction, H-abstraction is dominated by OH•.

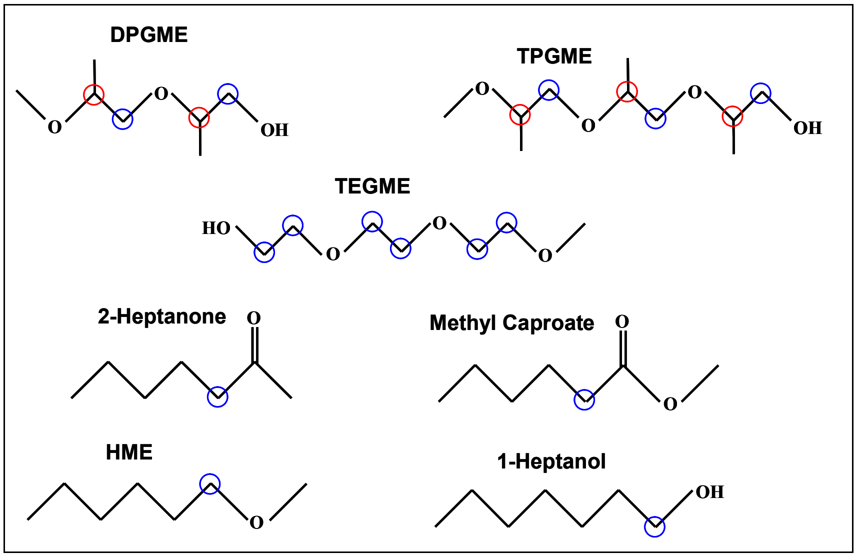

Figure 4: Structures of oxygenates tested in IQT™ with weakened C-H bonds circled

Furthermore, there is a second H-abstraction (Eqn. 3) that occurs in the ignition chemistry after the peroxy radical is formed. The activation energy for this step will again be proportional to the strength of the C-H bond and depend on the location on the molecule relative to the peroxy radical group. Since 6-membered transition state rings have the lowest ring strain, the most likely location for the internal H-abstraction is on a carbon atom that is 2 atoms away from where the initial abstraction occurred. A 7-membered transition state ring is only a slightly higher energy barrier.

Clearly, the activation energy for DPGME and TPGME would be the lowest of the compounds tested because both have a tertiary C-H bond adjacent to an ether linkage where the initial abstraction would occur (see Figure 4). Subsequently, the internal rearrangement could occur either to a secondary C-H adjacent to an ether with a 6-membered transition state ring or to a tertiary C-H adjacent to an ether with a 7-membered transition state ring. TEGME has the next lowest activation energy because of its secondary C-H bonds adjacent to ethers for both the initial abstraction and the internal rearrangement. The molecules with the carboxyl group (2-heptanone and methyl caproate) have the next lowest activation energy; followed by hexyl methyl ether. Although the alcohol functional group does decrease the adjacent C-H bond strength, no reduced temperature dependence was seen relative to the hydrocarbon fuels.

Impact on Compression Ignition Fuels

The reduced temperature dependence of these acetals could have a significant impact on cold-start behavior in a conventional diesel engine. For example, DPGME has a DCN of 42 under standard test conditions (550°C). However, at 400°C DPGME ignites faster than cetane (DCN = 100) because of the lower activation energy. The result is that a vehicle fueled with DPGME would have an effective CN of >100 during cold-start. As the engine warms up, the fuel would behave more like a typical diesel fuel. One possible result of this "effective cetane boost" at low temperatures is better cold-start performance and reduced emissions. Another possible result is that OEMs could design light-duty diesel engines with a lower compression ratio, which could improve engine thermal efficiency (i.e., reduce fuel consumption)[4].

Replacing hydrocarbon fuels with 100% oxygenates is economically impractical, but blending oxygenates with hydrocarbons at a level of 20% is quite feasible. Often ignition properties of blends do not scale linearly with composition, so it was necessary to measure this low-temperature "cetane boost" at a 20% blend level. An Arrhenius-type plot of diesel fuel, DPGME, and a 20% blend of DPGME in diesel fuel is shown in Figure 5. Linear fits were applied to the data so the average slopes could be compared.

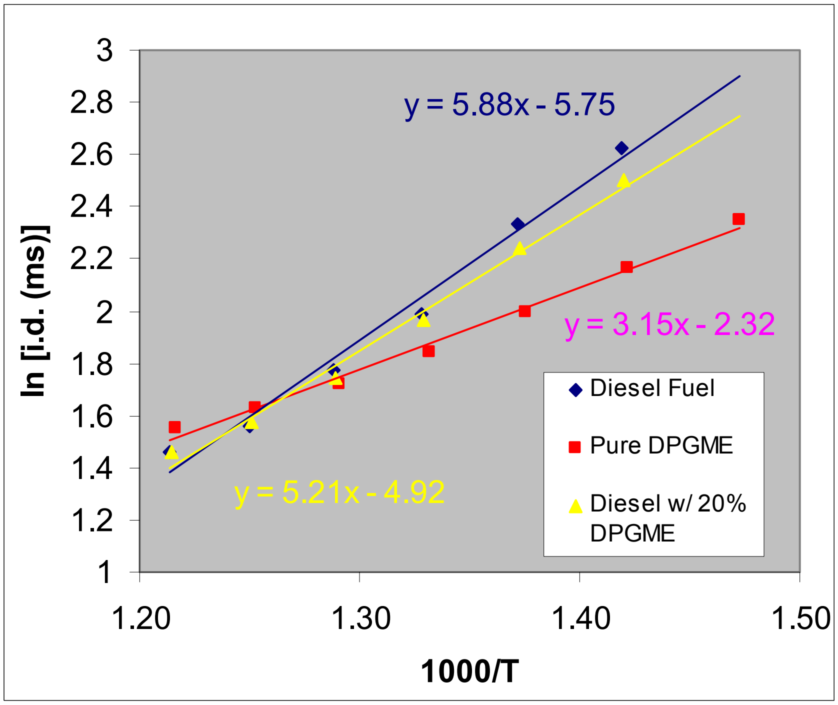

Figure 5: Effect of DPGME blending on activation energy for ignition

Figure 4 shows that the slope of the blend is reduced from that of the diesel fuel. Comparing the slope values from the linear fit shows that the effect is directly proportional to blending level. There is a 20% decrease relative to the difference in slope between the pure diesel and DPGME lines. From the curves of ignition delay for hydrocarbon fuels, we can estimate the effective CN of the 20% DPGME blend versus temperature. The result is a "cetane boost" of 6 CN units at 450°C and 10 CN units at 400°C. Plans are underway to conduct engine or vehicle testing of these blends under cold-start conditions.

The effect of a fuel's ignition delay having reduced dependence on temperature in an HCCI engine is less clear. This is because ignition in an HCCI engine depends on the temperature and pressure of the charge throughout the whole compression stroke. So ignition chemistry that is relatively faster at lower temperatures will cause an HCCI fuel

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[4] Light-duty diesel engines are often designed with a higher compression ratio (often greater than 20) to achieve a high enough charge temperature for cold-start. If the OEM could reduce the compression ratio to ~16, frictional losses could be reduced resulting in higher thermal efficiency.

to ignite faster than a hydrocarbon fuel with the same CN. Typically, this would not be desired since diesel-like HCCI often ignites too quickly anyway. However, one significant challenge in HCCI control strategies is that the ignition is highly variable with temperature, pressure, composition, and the history of all these. One benefit of a fuel with reduced temperature dependence is that ignition timing would not vary so dramatically as the engine warms up or as the temperature increases at higher load. This could make control of combustion phasing easier. HCCI engines would benefit from a fuel with a low CN but also a reduced dependence on temperature.

One fuel that might be promising for these requirements is ethanol. Although the alcohol in our test did not show reduced temperature dependence, C-H bond strengths adjacent to the OH group are weakened so the activation energy for ignition should be reduced. Additionally, ethanol has a very low CN, which minimizes the problem of ignition too early in the compression stroke. Both ethanol and methanol have been tested in HCCI engine operation and have demonstrated a much wider achievable operating range than traditional hydrocarbon fuels [iii]. One reason for this may be that ethanol has a reduced temperature dependence for ignition.

Recommendations and Future Work

As a result of these two projects, the following future work is recommended:

- Expand collaborative projects with industry and academia to use the CN QSAR and improve its accuracy.
- Test the effect of oxygenated fuels on cold-starting behavior of compression ignition direct injection engines.
- Use CFD modeling tools to determine the effect of fuels' reduced ignition temperature dependence in an HCCI engine.
- Examine the relationship between molecular structure and other combustion chemistry properties such as elevated pressure autoignition temperature.

Additionally, results of this work will be made widely available by publishing the following reports and peer reviewed journal articles:

- Cetane Database (In process, NREL document, 9/2004)
- QSAR Modeling (Submit to peer reviewed journal by 10/2004)
- Collaborative work with OU that applies QSAR model (Peer reviewed journal TBD)
- Effect of Molecular Structure on a Fuel's Temperature Dependence of Ignition Delay (Peer reviewed journal TBD)

Conclusions

Research at NREL has increased our understanding of the relationship between molecular structure and compression ignition fuel properties. This understanding was demonstrated by the development of a QSAR modeling tool that allows the user to predict CN with only the molecular structure as input. The utility of this predictive tool was shown in projects with collaborators in industry and academia. In the second section of this report, the effect of temperature on ignition delay (as measured in the IQT) for 14 fuels and pure compounds was presented in terms of an activation energy for ignition. The mechanism by which molecular structure affects the temperature dependence of ignition delay was described in the discussion of the IQT measurements. This second project identified several oxygenates that may have cold-start ignition benefits, which will be investigated further in a future research project. Furthermore, the fundamental understanding of why these compounds would be beneficial may guide future research into other compounds that may exhibit similar behavior.

References

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[i] Allard, L.N., G.D. Webster, T.W. Ryan III, A.C. Matheaus, G. Baker, A. Beregszaszy, H. Read, K. Mortimer, G. Jones, "Diesel Fuel Ignition Quality as Determined in the Ignition Quality Tester (IQT™) – Part IV." Society of Automotive Engineers, 2001, Technical Paper No. 2001-01-3527.

[ii] Taylor, J., R. McCormick, and W. Clark, "Develop In-House Laboratory Capability for Fuel Screening Relevant to CIDI and Advanced Combustion Concepts" NREL FY04 Milestone Report, NREL/MP-540-34904.

[iii] Oakley, A., H. Zhao, N. Ladommatos, and T. Ma, "Dilution Effects on the Controlled Auto-Ignition (CAI) Combustion of Hydrocarbon and Alcohol Fuels" Society of Automotive Engineers, 2001, Technical Paper No. 2001-01-3606.