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Fuels & Lubricant Technologies

VEHICLE TECHNOLOGIES OFFICE

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annual progress report

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FY 2012 PROGRESS REPORT FOR FUEL & LUBRICANT TECHNOLOGIES

Energy Efficiency and Renewable Energy
Vehicle Technologies Office

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I.1 ADVANCED PETROLEUM-BASED, NON-PETROLEUM-BASED, AND RENEWABLE FUELS FOR A CLEAN AND SECURE HIGHWAY TRANSPORTATION SYSTEM

On behalf of the Department of Energy's Vehicle Technologies Office (VTO), we are pleased to introduce the Fiscal Year (FY) 2012 Progress Report for Fuel & Lubricant Technologies. The potential benefits of advanced fuel and lubricant technologies include:

- Energy security: Advanced fuels enable more efficient engines that reduce fuel use, and non-petroleum-based fuels reduce the demand for petroleum fuel, much of which is imported.
- Environmental sustainability: Cleaner fuels enable efficient and durable emissions control technologies for reduced vehicle emissions. Advanced and non-petroleum-based fuels reduce the emissions of greenhouse gases.
- Economic improvement: A more diverse portfolio of fuels in transportation will improve the economy by reducing price volatility and stimulating new market activity in areas such as renewable fuels.

The Fuel & Lubricant Technologies subprogram supports fuels and lubricants research and development (R&D) to provide vehicle users with cost-competitive options that enable high fuel economy with low emissions, and contribute to petroleum displacement. Transportation fuels are anticipated to be produced from future refinery feedstocks that may increasingly be from non-conventional sources including, but not limited to, heavy crude, oil sands, shale oil, and coal, as well as renewable resources such as biomass, oils derived from plants and algae, and waste animal fats. The impact of changes in refinery feedstocks on finished fuels is an area of relatively new concern to engine manufacturers, regulators and users. Advanced engine technologies are more sensitive to variations in fuel composition than were earlier engines, in addition to facing tightening emissions standards. The Fuel & Lubricant Technologies subprogram activities focus on the properties and quality of the finished fuels derived from these sources, not primarily on their production.

The Fuel & Lubricant Technologies subprogram consists of two activities: Advanced Petroleum-Based Fuels, and Non-Petroleum-Based Fuels and Lubricants. The goals are: (1) to enable post-2010 advanced combustion regime engines and emission control systems to be more efficient while meeting future emission standards; and, (2) to reduce reliance on petroleum-based fuels through direct fuel substitution by non-petroleum-based fuels. These activities are undertaken to determine the impacts of fuel and lubricant properties on the efficiency, performance, and emissions of current engines as well as to enable emerging advanced internal combustion engines, and are coordinated with and supportive of the Environmental Protection Agency's (EPA's) fuels- and emissions-related activities, as mentioned in their strategic plan.

The Energy Independence and Security Act (EISA) of 2007 established aggressive goals for renewable fuel use that might require significant changes to the nation's fueling infrastructure. The EISA mandates the use of as much as 36 billion gallons annually by 2022 of renewable fuels, which will mainly be ethanol. The U.S. vehicle fleet consumed 0.89 billion gallons of biodiesel and 12.9 billion gallons of ethanol in 2011 compared to 0.26 and 12.9 billion gallons in all of 2010, respectively. Nearly all of the ethanol consumed was in the form of E10 (10% ethanol, 90% gasoline) sold as gasoline at fueling stations. The nation's 8.6 million flexible-fuel vehicles (as of 2010) can operate on E85 (85% ethanol, 15% gasoline), but relatively few fueling stations are equipped to dispense E85. Because of E10 and E85's limited ability to absorb increases in U.S. ethanol production to meet the EISA goal of 36 billion gallons of annual renewable fuel consumption by 2022, a solution would be to require vehicles to use intermediate ethanol blends such as E15 (15% ethanol, 85% gasoline) or E20 (20% ethanol, 80% gasoline). On October 13, 2010, EPA granted the first partial waiver for E15 for use in model year 2007 and newer light-duty motor vehicles (i.e., cars, light-duty trucks and medium-duty passenger vehicles). On January 21, 2011, EPA granted the second partial waiver for E15 for use in model year 2001-2006 light-duty motor vehicles. The Fuel & Lubricant Technologies subprogram has examined the impact of intermediate blends on passenger vehicles, outdoor equipment, and generator sets, with research focusing on regulated and unregulated tailpipe emissions, fuel economy, and emission system durability. Materials compatibility, evaporative emissions, and vehicle driveability were also investigated.

The Fuel & Lubricant Technologies subprogram is an integral part of the U.S. DRIVE (formerly the FreedomCAR and Fuel Partnership) government/industry partnership and a key means of pursuing the U.S. DRIVE mission to develop more energy-efficient and environmentally friendly highway transportation technologies that enable America to use less petroleum in transportation. The work in advanced petroleum-based fuels is conducted through joint programs with the energy and automotive industries and utilizes the expertise of DOE national laboratories and universities. Advanced petroleum-based fuels are even more important to the 21st Century Truck Partnership, which proposes to dramatically increase heavy-duty vehicle fuel economy while continuing emissions reduction. For heavy over-the-road trucks, combustion engines operating on liquid fuels are the only viable options for the foreseeable future based on our current transportation fuels distribution infrastructure. The Fuel & Lubricant Technologies subprogram works closely with the Advanced Combustion Engine R&D subprogram of the VTO, which is focused on removing critical technical barriers to commercialization of higher efficiency, advanced internal combustion engines in light-duty, medium-duty, and heavy-duty vehicles. Fuel & Lubricant Technologies subprogram activities are also coordinated with appropriate DOE/industry technical teams; the light-duty automotive, heavy-duty engine, and energy industries; and federal, state, and local government agencies. Some activities are undertaken in coordination with the Biomass Program, the Hydrogen and Fuel Cells Program, and the Office of Fossil Energy (via the Fuels Cross-Cut Team) to ensure maximum synergy and to avoid duplication of effort.

Goals

- By 2013, identify fuel formulations optimized for use in light-duty advanced combustion regime engines that provide high efficiencies and very low emissions, which incorporate use of non-petroleum-based blending components with the potential to achieve at least a 10 percent replacement of petroleum fuels by 2025.
- By 2015, identify fuel formulations using non-petroleum-based blending components that are optimized for use in high efficiency heavy truck engines (those with at least a 50 percent thermal efficiency) while meeting prevailing EPA emissions standards, with the potential to achieve at least a 15 percent replacement of petroleum fuels by 2030.

To accomplish its goals, the Fuel & Lubricant Technologies subprogram collaborates with DOE's national laboratories and universities to advance basic fuel and combustion science and with industry partners—including auto and engine manufacturers, ethanol and biodiesel producers, and parts suppliers—to test and validate new technologies. The subprogram also works closely with other DOE programs (e.g., the Biomass Program) to ensure that fuels resulting from their R&D are compatible with existing infrastructure.

Transportation Fuels and Energy Security

Petroleum-derived fuels account for 97% of all fuel used in the U.S. highway transportation sector. Because of the lack of alternative sources of energy in this sector, a widespread disruption of petroleum supplies due to natural disaster, political maneuvering, market disruptions, or resource depletion has the potential to severely disrupt personal and commercial mobility in the U.S. This was vividly illustrated during the summer months of 2005 when several hurricanes hit the Gulf Coast of the U.S., disrupting at one point 28% of domestic crude oil production and 29% of U.S. refining capacity.

The Energy Information Administration believes that the following supply and demand fundamentals are the main drivers behind recent oil price movements:

1. Strong world economic growth driving growth in oil use,
2. Moderate non-Organization of the Petroleum Exporting Countries (OPEC) supply growth,
3. OPEC members' production decisions,
4. Low OPEC spare production capacity,
5. Organization for Economic Cooperation and Development inventory tightness,
6. Worldwide refining bottlenecks, and
7. Ongoing geopolitical risks and concerns about supply availability.

Barring a significant change in events going forward, it is likely that the U.S. will be faced with significantly higher transportation fuel prices than has been the norm for most of the 1980s and 1990s.

Petroleum currently supplies about 36% of all the energy used in the U.S., with 71% of this petroleum going to the transportation sector. The transportation sector alone consumes more petroleum than is produced in the U.S. Meanwhile, the increase in U.S. crude oil production in the Gulf of Mexico and elsewhere, combined with increasing biofuel and coal-to-liquids production, is expected to reduce the need for imports over the longer term. Vehicles and their refueling infrastructure will need to adapt to these changes in fuel resources.

Research sponsored by the Fuel & Lubricant Technologies subprogram focuses on tailoring petroleum-based fuels to accommodate and enable more efficient use, and on increasing use of renewable and non-petroleum-derived fuels. For example, oil-sand-derived fuels from Canada, Fischer-Tropsch fuels made from natural gas, and biofuels derived from fats and vegetable oils will play increasingly important roles as both replacements and extenders to conventional diesel fuel. Approximately 40% of the crude oil produced in Canada is from oil sands and production of oil sands liquids is projected to grow significantly over the next several years. Since Canada is our largest supplier of crude oil and we import between 80 and 90% of their production, it is likely that oil sands liquids will represent an increasing portion of our transportation fuel.

As previously mentioned, the EISA mandates increasing production of ethanol for use in transportation vehicles. Besides blending ethanol into gasoline, there are currently 8.6 million flexible-fuel vehicles that can use E85 (85% ethanol and 15% gasoline), gasoline, or any blend in between. These E85 vehicles are currently optimized for gasoline operation. The Fuel & Lubricant Technologies subprogram is sponsoring the development of engines for the next generation of flexible-fuel vehicles designed specifically to exploit the desirable fuel properties of E85, such as its high octane, which will increase the fuel economy of vehicles running on E85. Advanced controls and combustion systems should enable these next-generation engines to operate at high efficiency regardless of ethanol concentration, achieving fuel savings beyond that of gasoline displacement alone.

Biodiesel is a popular renewable, non-petroleum fuel to displace diesel fuel. In addition, biodiesel tends to have beneficial effects on the regeneration of diesel particulate traps relative to use of pure diesel fuel. However, recent quality problems with biodiesel resulted in filter-clogging problems in many trucks. As a result of this and similar problems with the quality of U.S. biodiesel, the Fuel & Lubricant Technologies subprogram partnered with the National Biodiesel Board to improve ASTM (an international standards organization) biodiesel fuel specifications and ensure that suppliers adhere to the specifications. Surveys of marketed biodiesel conducted by the Fuel & Lubricant Technologies subprogram in 2005, 2007, 2008, 2010, and 2011 showed a large improvement in compliance with the ASTM standard over this period, including more consistent biodiesel concentration and reduced levels of impurities. The fuel-quality improvement resulted in increased willingness among engine manufacturers to endorse biodiesel use in their engines.

Transportation Fuels and the Environment

The combustion process used to convert the energy in petroleum fuels to propulsion for current highway vehicles creates criteria pollutants in large enough quantities to be detrimental to the environment and dangerous to human health, particularly in densely populated areas. Criteria pollutants include carbon monoxide (CO), oxides of nitrogen (NOx), particulate matter (PM), volatile organic compounds, and sulfur dioxide. The Fuel & Lubricant Technologies subprogram is evaluating advanced petroleum-based fuels and non-petroleum-based fuels for their impact on engine-out emissions and emission control system efficiency and durability. For example, detailed research is being conducted on biodiesel combustion to understand its impact on NOx emissions and its ability to enhance the performance of diesel particulate filters. Optimized engine designs are being explored to use E85 with high efficiency while achieving very low emissions.

Combustion of petroleum fuels also releases greenhouse gases (GHGs, primarily CO_2, plus nitrous oxide and methane) that are believed to contribute to global warming. Advanced petroleum-based fuels can reduce GHGs through more efficient combustion resulting in less fuel used per unit of work performed. Non-petroleum-based fuels can reduce GHGs not only through more efficient combustion, but also through use of renewable resources that consume CO_2 during their growth.

Emissions of harmful pollutants and greenhouse gases from combustion processes depend in large part on the conditions affecting combustion and on fuel properties. Among fuel properties, sulfur content has attracted the most attention due to its damaging effects on emission control devices. The Fuel & Lubricant Technologies subprogram led a government-industry collaboration in demonstrating that the sulfur content of diesel fuel had to be reduced to enable the use of advanced emission control systems. Diesel vehicles need these advanced emission control systems, such as lean-NOx catalysts, to meet stringent emissions standards. Fuel & Lubricant Technologies subprogram-sponsored research led the EPA to require that all highway diesel fuel contain a maximum of 15-ppm sulfur. Before this ruling went into effect in 2006, diesel fuel for on-road use contained an average of 350-ppm sulfur, with a legal maximum of 500 ppm.

Transportation Fuels and the Economy

The potential economic benefits of implementing advanced vehicle and fuels technologies in the U.S. are many. The value of petroleum products imported into the U.S. represents one-third of our entire trade deficit. Technologies that improve fuel economy will reduce the amount consumers spend on fuel, allowing consumers to spend more in ways that enhance their lives, and also reduces the trade deficit. Renewable fuels such as ethanol and biodiesel offer opportunities for expanding economic activity, especially in the agricultural sector; when used to replace or supplement petroleum fuels, they also improve the trade balance.

The Fuel & Lubricant Technologies subprogram is conducting research that will yield substantial benefits to the energy security of our country, to our environment, and to our economy. By cooperating with other DOE programs to leverage synergies, this subprogram greatly improves the prospects for advanced fuels and advanced vehicle technologies.

Subprogram Laboratory Capabilities

The Renewable Fuels and Lubricants (ReFUEL) Lab at the National Renewable Energy Laboratory (NREL) is dedicated to future fuels and advanced medium- and heavy-duty vehicle powertrain research. It features a heavy-duty chassis dynamometer test cell capable of testing the performance and emissions of vehicles from 8,000 to 80,000 lbs, a 600 hp alternating current engine dynamometer test cell capable of certification-quality emissions testing and an altitude simulation system that provides conditioned air (temperature and humidity) at atmospheric conditions (pressure) from sea-level to the mile-high environment of Denver. The lab also includes a second engine test cell that accommodates a single-cylinder research engine that is used to develop advanced combustion strategies in support of DOE's Fuel & Lubricant Technologies subprogram.

The ReFUEL Laboratory also includes high-speed data acquisition systems that enabled the two engine test cells and the vehicle chassis dynamometer test cell to have the highest possible utilization factors to support simultaneous testing activities. A Horiba Mexa emissions analyzer as well as Fourier transform infrared and fast mobility particle sizer instruments are available to support ReFUEL's portfolio of measurement equipment to provide faster and more accurate emissions measurements as needed to support upcoming emissions regulations. The engine dynamometer is equipped with quick-disconnect hardware, a new universal wiring harness and new instrumentation and data collection protocols to allow for rapid removal and replacement of test engines. Currently a 2012 Cummins ISL 8.9-l engine is being used in the engine test cell to evaluate the interactions between a variety of biodiesel blends and advanced diesel engine emission control systems. Additionally, a significant number of chassis dynamometer test programs have recently been executed to evaluate fuel consumption and emission from medium- and heavy-duty advanced technology vehicles and vehicles utilizing bio-fuels.

Engines employing advanced combustion strategies are being aggressively researched and developed by industry because of their potential for enabling high-efficiency, emissions-compliant engines. Sandia National Laboratories (SNL) has two engine labs focused on developing a fundamental understanding of the combustion and emissions characteristics of advanced liquid petroleum-based, bio-derived, and synthetic fuels on the various new combustion strategies for enabling high-efficiency engines. In addition, other engine research capabilities are used as needed for additional supporting fuels research. The first fuels focused engine lab is the Advanced Heavy-Duty Fuels Laboratory. Research in this lab is conducted using a single-cylinder version of a Caterpillar® heavy-duty engine. The second fuels focused lab is the Stratified-Charge, Spark-Ignition (SI) Light-Duty Engine lab. Research in this lab is being conducted in a single-cylinder, direct-injection, light-duty SI engine, also extensively modified to provide optical access into the combustion chamber. In both labs, laser and imaging diagnostic techniques are used to observe combustion and emissions-formation processes through windows in the piston, the upper periphery of the cylinder liner and/or cylinder head. The optical measurements are complemented by heat-release analysis and quantification of engine-out emissions, including NOx, hydrocarbon (HC), CO, CO_2, O_2, and smoke. These added measurements put the results into proper context with those acquired from industry partners and other research laboratories using non-optical prototype and production engines. Such observations are essential for understanding how fuel formulation affects engine efficiency and emissions, for discovering novel fuel-enabled strategies for high efficiency, clean engine technologies, and for creating accurate computer models to aid the development of such engines. Example accomplishments in FY 2012 include: 1) Co-led an international research team that developed and experimentally validated a robust methodology for creating "surrogate" diesel-type fuels containing only eight chemical compounds that have molecular-structure, ignition-quality, volatility, density, and other characteristics similar to those of real-world fuels containing thousands of compounds. 2) Demonstrated that E85 enables injection-timing retard to near TDC for high-efficiency, stratified, spark-ignition combustion that results in ultra-low emissions of NO and PM. The research performed using gasoline and E85 showed that these results were unique to E85. New understandings such as those represented by the example accomplishments above are critical for understanding fuel effects on engine in-cylinder processes and for ultimately enabling the accurate numerical simulation and cost-effective design of high-efficiency engines for current and future fuels.

At Oak Ridge National Laboratory (ORNL), the Fuels, Engines, and Emissions Research Center is a comprehensive laboratory for internal combustion engine technology, specializing in research on paths to higher efficiency, lower emissions, reduced petroleum use, and understanding of fuel and emissions chemistry. Capabilities include catalyst spectroscopy laboratories, bench-top engine exhaust simulators, a range of engine dynamometer cells, and a 48-inch single-roll vehicle chassis dynamometer. In this facility, ORNL has developed several new diagnostic and analytical methods that allow greater definition of fuel combustion species and their spatial and temporal distribution and utilization in the emission control system. Among the recently updated capabilities are:

- Two fully operational General Motors 1.9-L multi-cylinder diesel engines to support research on engine efficiency, emission controls, fuel composition effects on advanced combustion, and methods for expanding high efficiency combustion. One of the engines has been modified to support research on Reactivity Controlled Compression Ignition (RCCI) and gasoline compression ignition combustion.
- Two modified General Motors 2.0-L Ecotec gasoline engines to support research on gasoline direct-injection particulate matter characterization, high efficiency combustion, and renewable fuels.
- A single-cylinder research engine with fully variable hydraulic valve actuation provides a highly flexible research platform for gasoline boiling range fuels research and has been used to explore efficiency with thermo chemical recuperation, ethanol-blend fuels as well as spark-assisted HCCI combustion. This engine is also equipped with a laboratory air handling system for external exhaust gas recirculation and boosted operation.
- A Ford multi-cylinder diesel engine is being used to study bio-fuel effects including exhaust gas recirculation cooler fouling and corrosion issues.
- Two Ford multi-cylinder gasoline EcoBoost engines are being used to study fuel octane opportunities and cold/warm start lubricant and fuel challenges.
- A lean gasoline direct injection multi-cylinder engine (from European BMW 120i vehicle) has been installed and has full custom combustion control with a Drivven-based controller. This platform will be used to support research on lean exhaust aftertreatment.
- A soot-capture and microreactor system, developed at ORNL, is used to assess how the fuel-specific constituents of soot from diesel and gasoline engines affect the oxidation kinetics as seen in soot-filter regeneration.
- A technique for detailed characterization of particulate matter (PM) morphology and size has been developed combining charge-based collection techniques with Transmission Electron Microscopy (TEM); the technique has been proven especially useful for the small and complex PM from GDI engines.

Numerous additional single-cylinder and multi-cylinder engines are also available to support fuels research. Many of these engines have open architecture engine controllers with research performed in close cooperation with on-going advanced combustion and aftertreatment research. Advanced combustion modes under investigation include reactivity controlled compression ignition, premixed charge compression ignition, and high dilution gasoline direct injection.

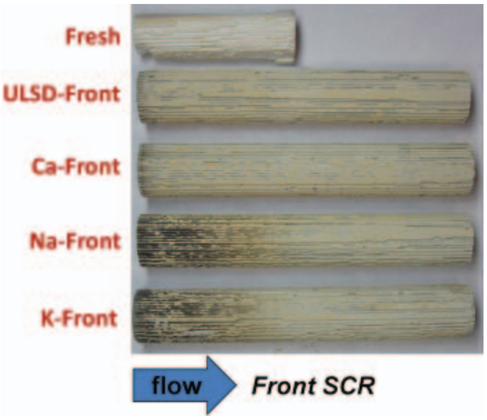
I.2 HIGHLIGHTS OF SIGNIFICANT FY 2012 ACCOMPLISHMENTS

The following presents highlights of the Fuel & Lubricant Technologies project accomplishments in 2012.

Fuels and Lubricants to Enable Efficient Engine Operation While Meeting 2007-2010 Standards

The objective of this subprogram activity is to identify fuel and lubricant properties that facilitate efficient engine operation and durable emissions control devices.

- ORNL is identifying important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology including issues arising from the introduction of renewable fuels such as biodiesel and advanced lubricant additives. In the past year they: showed deactivation of selective catalytic reduction (SCR) catalysts by replacement of Cu with Na and K but not Ca; materials characterization demonstrates first known reported evidence that Na and K found in engine exhaust can exchange with the Cu-metal in the SCR catalyst; and published findings in Catalysis Today and submitted additional findings to Topics in Catalysis and SAE International. (Toops)

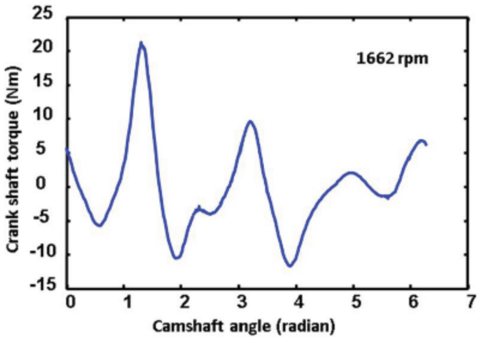


Cores removed from the front SCR catalyst show a dark region in the Na- and K-aged samples (Toops)

- Exhaust gas recirculation system performance when using non-petroleum-based fuels is being quantified by ORNL. They: (1) Showed that extended operation at low Reynolds' number, low-temperature conditions can build significant deposit layers high in fuel-HCs with very little effectiveness loss; (2) Found that removal of deposits occurs at high flow rates that result in impractically high pressure drops; and (3) Determined that spall material is not re-entrained diesel particulate, but rather has different characteristics than typical diesel particles. (Sluder)
- ANL is developing accurate and reliable correlations between benchtop tests and engine tests considering friction and wear performance data. In the past year they: (1) Identified and reviewed critical ASTM International standards and test protocols for benchtop friction, wear, and reliability; (2) Identified existing database(s) on benchtop test protocols, in situ friction measurements, and engine/vehicle economy tests; and (3) Initiated preliminary friction studies using benchtop tests. (Demas)
- ANL is developing and optimizing lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles. In the past year they: (1) Established an empirical connection between the structure of tribochemical surface films formed from additives and their friction properties; (2) Developed multiple analytical

techniques to assess the structure and hence the frictional attributes of tribochemical films; and (3) Initiated the measurement of the mechanical and frictional properties of tribochemical films using the nano indentation technique. (Ajayi)

- ANL is developing lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in non-flex-fuel legacy vehicles. In the past year they: (1) Completed the structural design of time-release low-friction, wear resistant and scuffing prevention additive system; (2) Developed preliminary proof-of-concept test with simple polymeric surfactant encapsulation; and (3) Conducted preliminary friction and wear performance evaluation of proof-of-concept systems. (Ajayi)
- ANL is developing self-replenishing lubricants that would provide reduction in friction and wear comparable to the effects of low-friction solid lubricant coatings. In the past year they dispersed a tungsten (W)-based POM, phosphotungstic acid modified with oleic acid, in polyalphaolefin 10 oil and selected promising W-based POM composition based upon tribological testing. (Demas)
- ORNL is developing oil-soluble ionic liquids as engine oil additives and plans to demonstrate 10% improvement in mechanical efficiency of internal combustion engines. In the past year: A series of quaternary structured ionic liquids are being designed, synthesized, and characterized and base oils and baseline lubricants have been determined and acquired, and complementary tribological bench tests have been determined. (Qu)
- The Massachusetts Institute of Technology (MIT) is investigating low-friction, environmentally friendly and commercially feasible lubricant formulations that significantly improve the mechanical efficiency of modern engines by at least 10%, versus the 2002 level without causing increased wear, emissions or deterioration of the emission-aftertreatment system. In the past year they: (1) Established a research team and specific aims and targets for team members, including industry partnerships with a major engine company and major lubricant oil and additive formulator; (2) Adapted and applied two engine friction simulations based on methodologies developed earlier at MIT to determine lubricant regimes in subject test engine. Established estimates of lubrication regimes in specific engine zones; (3) Acquired test engine and completion of experimental setup, including construction and implementation of a standalone cylinder head (valvetrain) test bench; and (4) Completed initial measurements of valvetrain friction on chosen test engine. (Cheng)



Instantaneous camshaft torque as a function of the cam angle for the test engine (Cheng)

- Ford Motor Company is developing lubricant formulations capable of at least 10% engine friction reduction compared to current GF-5 engine oil technology at the same viscosity grade level most commonly used in the North American market. In the past year they: (1) Acquired 13 modified polyalkylene glycol (PAG)-based engine oils; (2) A number of friction and wear evaluations were completed; and (3) Completed motored engine friction screening tests on two PAG oils and factory fill GF-5 oil at various oil temperatures and engine speeds. (Gangopadhyay)
- MIT is investigating the potential for improved performance and efficiency, and reduced greenhouse gas emissions, of gasoline-fueled vehicles by raising engine compression ratio and boost, through use of alcohols to suppress knock. In the past year they: (1) Established experimental and simulation-based methodology for generating turbocharged engine performance maps for range of different fuels at different compression ratios and boost levels; (2) Developed and demonstrated

fundamentally based and autoignition induction time methodologies for quantifying knock onset brake mean effective pressure limits; (3) Tested range of knock suppressing alcohol (and blended) fuels and defined their high load behavior; and (4) Generated performance maps experimentally, and through modeling, with gasoline and knock-suppressing fuels. (Heywood)

Fuel Property Effects on Advanced Combustion Regimes

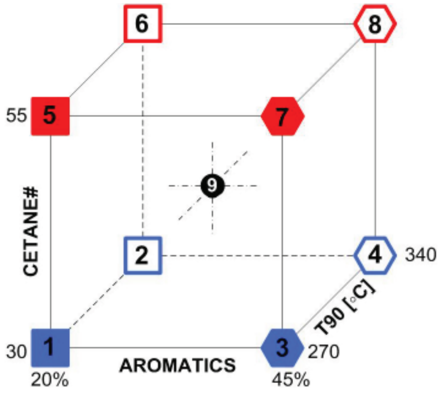
The objective of this subprogram activity is to identify how fuel properties can be used to make combustion more efficient with lower emissions.

ORNL apparatus for washing and polishing biodiesel (Szybist)

- ORNL is obtaining representative samples of new, unique, or emerging fuels and screening with engine and laboratory analytical techniques to continue to add to a database of results and to develop tools for the rapid, efficient screening of new fuels and fuel components. In the past year they: (1) Developed a multi-step process for upgrading pyrolysis oil to be compatible with diesel engines mixed at a 20% blend ratio; (2) Experimentally evaluated pyrolysis oil in a single-cylinder diesel engine; (3) Produced biodiesel that approximate algae and fish oil sources; and (4) Experimentally evaluated thermochemically-derived renewable diesel produced at the University of Maine. (Szybist)
- SNL is facilitating the introduction of renewable and/or unconventional fuels and the advanced engine-combustion strategies for their utilization in a manner that enhances domestic energy security, economic competitiveness, and environmental quality. In the past year they: (1) Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council (CRC) in developing a methodology for formulating diesel surrogates that matched the carbon-bond types, ignition qualities, volatilities, and densities of two real-world diesel fuels; (2) Completed the data-acquisition phase of a large parametric investigation of fuel effects on mixing-controlled combustion using CRC Fuels for Advanced Combustion Engines (FACE) diesel reference fuels; and (3) Conducted a literature review showing how and why raw liquids created from the fast pyrolysis of woody biomass are not suitable as fuels for modern CI engines. (Mueller)
- LLNL is developing detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. In the past year they: (1) Validated chemical kinetic models for methyl palmitate, methyl oleate, and methyl linoleate, which are real biodiesel components; (2) Furthered validation of chemical kinetic model for iso-pentanol, an advanced biofuel; (3) Continued development and validation of a chemical kinetic model for n-pentanol; (4) Developed preliminary model for dimethylcarbonate, a biofuel that can be used to displace conventional diesel fuel; and (5) Supported the FACE fuel effort through project AVFL-18, “Surrogate fuels for kinetic modeling.” (Pitz)
- LLNL is working on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. In the past year they: (1) Developed a methodology that combines experimental engine data, multizone detailed chemical kinetic engine simulations, sensitivity and uncertainty analysis software, and supercomputing resources to improve the predictive capability of advanced fuel chemical kinetic mechanisms for

engine combustion regimes; (2) Applied Converge^{TM}—a parallel engine combustion computational fluid mechanics software package utilizing LLNL's multizone combustion model—to investigate engine operation with alternative fuels; and (3) demonstrated operation of an experimental HCCI engine using an exhaust heat exchanger fueled with ethanol-water mixtures. (Killingsworth)

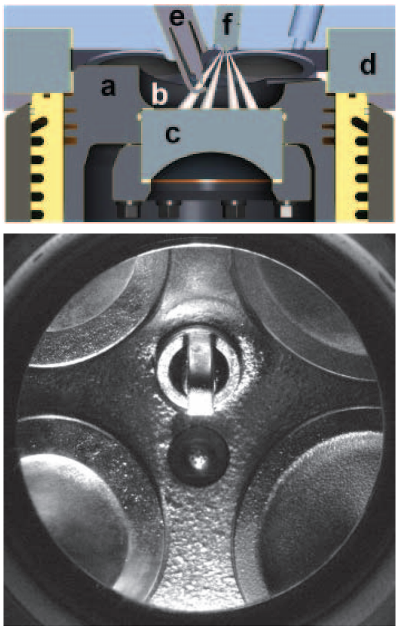
- NREL is designing a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different research and development organizations working on similar and different advanced combustion modes and engine designs. In the past year they: (1) Continued development of Ignition Quality Tester-based experimental and simulation research platform to characterize fuel ignition properties; (2) Supported development and utilization of research Fuels for Advanced Combustion Engines (FACE) to determine relationships between fuel chemistry and engine combustion performance and emissions; (3) Collaborated with other DOE and Canadian national laboratories, along with corporate industrial partners via the Coordinating Research Council; and (4) Utilized a spark-ignition direct-injection single-cylinder research engine facility to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program. (Zigler)



FACE Gasoline Research Fuel Matrix (Zigler)

- NREL is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems. In the past year they: (1) Demonstrated initial engine performance in PCCI and HCCI operation with the FACE diesel fuel matrix; (2) Conducted CRC-sponsored research study on HCCI operation in a light-duty diesel engine with FACE diesel fuels (CRC Advanced Vehicles Fuels and Lubricants [AVFL]-16 project); (3) Expanded effort to include evaluation of advanced alternative and renewable fuels (CRC AVFL-19 project, formerly CRC FACE Advanced Alternatives and Renewable Fuels Team); (4) Applied output of FACE diesel fuels advanced characterization effort to facilitate development of a diesel surrogate with full kinetic model (CRC AVFL-18 project); and (5) Correlated available diesel, PCCI, and HCCI engine data using FACE diesel fuels with key fuel properties. (Zigler)

- SNL is exploring how emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark ignition light-duty engines being developed by the automotive industry. In the past year they: (1) Demonstrated the ability of injection-timing retard with E85 to enable ultra-low emissions of NO and PM; (2) Performed multiple high-speed optical diagnostics of stratified gasoline and E85 combustion, and identified one stochastic in-cylinder phenomenon that correlates with cyclic variability of both flame development and indicated mean effective pressure; (3) Performed a spectroscopic characterization of flame luminosity of the various stages of highly-stratified 85% ethanol in gasoline (E85) combustion; and (4) Combined a spray model and a flame-speed model in



Top: computer-aided design rendering of cross-section of combustion chamber at top-dead center. Bottom: view from below via piston-bowl window with piston at -10°CA position. (Sjoberg)

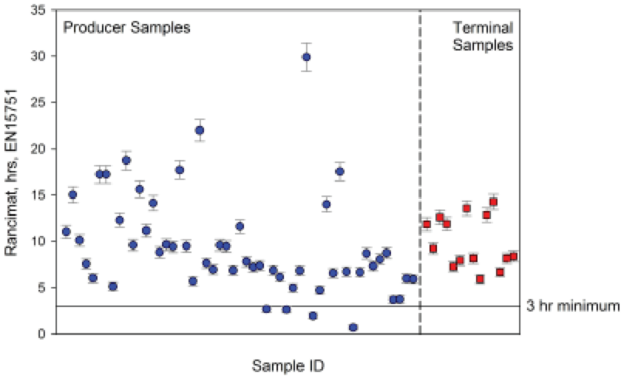
CHEMKIN. Used models to quantify fuel effects, like vaporization cooling, on mixture formation and combustion in various regions of fuel jets. (Sjoberg)

- ORNL is providing experimental engine data with combustion and emissions analysis for selected fuels to support development of the Reaction Design Model Fuels Consortium modeling tools and reaction mechanisms. In the past year they performed a blending study to measure the fuel properties of 86 fuel blends in the gasoline boiling range and operated a series of seven fuel blends under diesel conditions, performed statistical analysis, and reported results to Reaction Design. The fuel blends were made from pure hydrocarbon as surrogate species for kinetic modeling. This project is complete. (Szybist)
- ORNL is investigating the impacts of non-petroleum-based fuels on advanced combustion regimes for diesel and gasoline engines. In the past year they: (1) Characterized the potential of biofuels to enable and expand the operating range of RCCI combustion in a multi-cylinder engine; and (2) Demonstrated that there is a significant opportunity to optimize an engine for high ethanol fuels compliant with the 2011 revision of ASTM D5798. (Szybist)
- ORNL is investigating the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion engine applications. In the past year they: (1) Demonstrated ~30% lower friction from advanced formulation lubricating oils; (2) Small single-cylinder motored and fired engine tests were conducted for IL-additized lubricants. Normal engine behavior was observed during testing and no measurable wear was detected on the piston ring or cylinder liner after disassembly; and (3) Engine exhaust analysis did not detect any IL decomposition products on the particulate matter filter, confirming its ashless feature. (Qu)
- Ford Motor Company is identifying fuel properties that can be used to enable controllable extended lift-off combustion (ELOC) with low NOx. In the past year they: (1) Evaluated mixtures of tri-propylene glycol methyl ether (TPGME) and n-hexadecane with 15% and 50% TPGME; (2) Conducted smoke point lamp experiments to screen different oxygenated compounds for soot formation tendency; (3) Used a grouped chemistry model to develop fuel surrogates of varying cetane number; (4) Investigated modeling oxygenated fuels and obtained necessary fuel properties to adjust inputs to spray and combustion models; and (5) Initiated an experimental plan to characterize ELOC in a controlled engine combustion simulation facility. (Kurtz)

Petroleum Displacement Fuels/Fuel Blending Components

The objective of this subprogram activity is to identify how non-petroleum-based fuels can be used by themselves and in blends to displace petroleum-based fuels.

- NREL is conducting a variety of projects relating to biodiesel and ethanol fuels:
  - They are studying the impact of fuel metal impurities on the long-term durability of emission control systems found in modern diesel engines. In the past year they developed a method for accelerated aging of light-duty catalyst parts which results in full-useful-life exposure to fuel metal impurities and thermal aging. Using this accelerated method four separate exhaust systems from a Ford F250 pickup were aged to the equivalent of 150,000 miles. Each of the four systems was aged with a different fuel; ultra-low sulfur diesel containing no metals, 20 vol% biodiesel in diesel containing Na, B20 containing K, and B20 containing Ca. (Williams)
  - They are documenting the quality of current and emerging biofuels in the United States marketplace. In the past year they collected B100 samples from 14 terminals and 53 producers across the United States and developed a new method based on liquid chromatography with mass spectrometric detection method for monoglycerides. (Alleman)



Oxidation Stability Results of B100 Samples (Alleman)

- They are identifying the cause and mechanism of unexpected cold weather fuel filter clogging that has been observed for some biodiesel blends. In the past year they found that: (1) Saturated monoglyceride (SMG) content has the largest effect on increasing cloud point, regardless of the B100 or diesel fuel; (2) At fixed SMG level, higher levels of biodiesel in the blend lower the cloud point by increasing the solubility of SMG; and (3) Only at the high biodiesel blending level (20 volume percent) was saturated fatty acid methyl ester content significant in increasing CP. (McCormick)

- ORNL is implementing analytical methods for characterizing the combustion products from conventional and advanced combustion in order to further elucidate combustion properties of biofuels and other alternative fuels. In the past year they: (1) Developed a trace detection method for carbonyls, such as formaldehyde and acetaldehyde, which has a detection limit of less than 10 ppb in raw engine exhaust; (2) Developed a thermal analysis of soot utilizing state-of-the-art thermal/pyrolysis gas chromatography–mass spectrometry that has a 10x improvement in sensitivity over conventional solvent extraction methods; and (3) Developed a method for determining the total acid number for a highly polar organic matrix relevant to pyrolysis-derived biofuels. (Lewis)

- ORNL and NREL determined the effects of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on legacy vehicle emissions and emissions durability when aged with a dedicated fuel blend. In the past year they published a final report and several SAE International papers. This project is now complete. (West, ORNL)

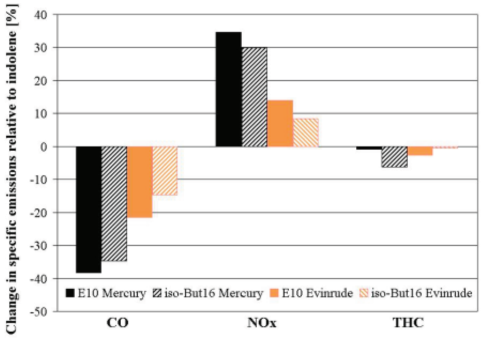
- Pacific Northwest National Laboratory (PNNL) is developing analytical tools to characterize fuels derived from unconventional hydrocarbons, focusing especially on chemistry-based predictive models to support future advanced combustion/emission technologies. In the past year they: completed the ^{13}C and ^{1}H NMR sub-structure analyses and assignments for over 20 diesel and renewable fuels of various origins, and developed new nuclear magnetic resonance (NMR) approaches for identifying structure-property relationships of diesel fuels, including diffusion-ordered spectroscopy, as well as two dimensional NMR techniques, such as single-bond proton-carbon correlation (heteronuclear single quantum

Vehicles on mileage accumulation dynamometers at ETC (top) and SwRI® (bottom) (West) coherence) and multiple-bond proton-carbon correlation (heteronuclear multiple bond correlation) experiments (King)

- PNNL is providing analysis of international alternative fuel use which supports alternative fuel infrastructure development in the United States. In the past year they profiled the development of alternative fuels in Thailand with a concentration on 20% ethanal, 80% gasoline ethanol production and use. (Bloyd)
- PNNL is developing an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. In the past year: (1) Oil price shocks were investigated by extending and applying ATEAM to explore its impacts on the U.S. vehicle fleet and correspondingly the potential for new fuel and vehicle technologies, such as compressed natural gas vehicles and battery electric vehicles and other competitive alternative fuel technologies, to reduce the USA’s vulnerabilities to such changes; (2) Potential market penetration of various fuels including compressed natural gas, liquefied natural gas, liquefied petroleum gas and methanol in light-duty, medium-duty and heavy-duty vehicles was analyzed; (3) Four different methods were explored to compute the early adopter penalty for advanced vehicle technologies to address the diffusion of new technology as the technology becomes more prevalent in the market (4) A list of nine important transportation issues and scenarios were submitted for screening to prepare the series of six technology briefs. Initial study was conducted on the effect of the modification of the Renewable Fuel Standard on the droughts and preliminary results were submitted as a letter to the Environmental Protection Agency; and (5) An online energy information hub Megajoule.org was implemented and expanded as an online database for energy analysts. In addition to improve the user interface and internal structure of Megajoule, introductory materials and new estimates and sources, probabilistic projections obtained from expert elicitations of a series of technologies were added. (Bloyd)
- NREL is measuring the impact of new biomass-derived fuels on gasoline performance properties and light-duty vehicle exhaust emissions. In the past year they found: (1) The effect of isobutanol, 1-butanol, 2-butanol, and blends of these with ethanol on gasoline vapor pressure and anti-knock index (octane number) was quantified over a range of blend levels; (2) At 5.5% oxygen in the fuel (equivalent to 15 vol% ethanol in gasoline, or E15) a blend of 12% isobutanol, 7% ethanol caused no increase in final blend vapor pressure relative to the hydrocarbon blendstock. This blend also exhibited anti-knock index higher by one octane number than the corresponding 5.5% oxygen butanol-only blend; (3) The largest effect on regulated emissions was a reduction in CO from 0.40 g/mile for neat gasoline (E0) to 0.28 g/mile from E15. Isobutanol marginally reduced CO relative to E0. There was no significant effect on NOx; (4) E15 produced the highest unburned alcohol emissions (average of 1.38 mg/mile ethanol). Despite blending at higher concentration than E15, both butanols produced much lower unburned alcohol emissions (0.17 mg/mile 1-butanol, and 0.30 mg/mile iso-butanol); (5) The lower alcohol emissions were offset by higher emissions of carbonyl compounds from the butanol blends. Emissions of butyraldehyde were significantly higher from 1-butanol while emissions of acetone and methacrolein were significantly higher from iso-butanol; and (6) The 12% iso-butanol/7% ethanol blend significantly reduced non-methane organic gases emissions relative to E0 because both carbonyl and unburned alcohol emissions were lower than for blends containing the individual alcohols. (McCormick)
- ANL is taking concepts successfully developed for plug-in hybrid vehicles (also considered a “bi-fuel” vehicle) that estimate in-use customer electric driving fractions and apply them for bi-fuel compressed natural gas/gasoline vehicle assessments. In the past year: (1) A sophisticated analysis spreadsheet was developed that can calculate vehicle costs, home compressor costs, fuel usage, and ultimately, payback periods and net savings based upon a large list of input assumptions; (2) Fuel savings and net costs were analyzed for both a midsized vehicle and a full-sized pickup truck based

upon both driving statistics (total fleet) and usage case scenarios (e.g. short and long commuter case); (3) Analysis shows that significant gasoline savings in both vehicle cases, is appreciated with modest sized tanks (75-100 miles range). However, only the full-sized pickup truck results in net cost savings with current technology costs; and (4) However, if the Advanced Research Projects Agency-Energy goal of $500 for a consumer home refueling appliance is achieved, net cost savings can also be realized for the bi-fuel mid-size passenger car. This project is complete. (Douba)

- ANL is assessing the emissions and operability of gasoline, ethanol, and butanol fuel blends in recreational marine applications. In the past year: (1) Engine lab testing with 10% ethanol in gasoline (E10) and 16 vol% gasoline iso-butanol (iso-But16) showed a 20-40% decrease in CO emissions relative to Indolene for the 4-stroke and 2-stroke direct injection engines. Reduction in CO using E10 was slightly higher compared to the iso-B16 alcohol blend. NOx emissions increased for both engines by 10-30% using alcohol blends. Overall net emissions were similar between the E10 and iso-But16 alcohol blends for each engine technology; (2) In-use vessel testing with Indolene, E10 and iso-But16 showed a 20, 70 and 10% reduction in CO, NO, and total hydrocarbon emissions for 2-stroke engines when using alcohol blends. 4-stroke engines showed a 5-20% reduction in CO emissions but a 10-40% increase in NO emissions. No significant emissions differences between E10 and iso-But16 were found regardless of engine technology; and (3) Friction, wear and scuffing tests suggest that the presence of bio-based components (E10, iso-But16) in the fuel results in a slight friction reduction but a noticeable reduction in scuffing load compared to the baseline case. (Wallner)



Average change in laboratory cycle-weighted emissions for E10 and iso-But16 operation compared to Indolene (Wallner)

I.3 SPECIAL HONORS/RECOGNITIONS

1. J. Qu, P.J. Blau, H. Luo, B.G. Bunting, ORNL Significant Event Award, October 2011.

2. Charles Muller (SNL) was elected to Fellow grade of membership in the Society of Automotive Engineers.

3. Westbrook, C.K., (LLNL) "Recent Advances in Autoignition Kinetics of Automotive Fuels", (invited plenary lecture) COMODIA 2012, Fukuoka, Japan, July 23-26, 2012.

4. Charles K. Westbrook (LLNL): 2008 - 2012 President of the Combustion Institute.

5. S.M. Sarathy (LLNL): Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada, 4/2010 to 4/2012).

6. Invited candidature by the Scientific Secretariat for the 2013 ENI Award to recognize the paper, J. Qu et al. (ORNL), "Anti-Wear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive," ACS Applied Materials & Interfaces 4 (2) (2012) 997–1002.

7. Wallner (ANL):

- In-use testing work featured in an article and video on www.boats.com by Lenny Rudow, http://blog.boats.com/2012/05/butanol-the-next-great-biofuel-for-boats/
- Press release published on www.boatingindustry.com on May 9, 2012, http://www.boatingindustry.com/news/2012/05/09/brp-to-begin-testing-next-generation-biofuel/
- 'Isobutanol Testing, Round Two' published in Boat U.S. Magazine's News From The World Of American Boating in August/September 2012, http://www.boatus.com/magazine/2012/august/BoatUS-Reports-Jurisdictions-Target-Boat-Gatherings.asp

I.4 PATENTS ISSUED

1. Invention Disclosure: 83238953 - 212-0297 Combustion system for leaner lifted flame combustion (LLFC) Strategy. (Kurtz, Ford)

I.5 FUTURE ACTIVITIES

This section describes the activities that will be pursued in each portion of the Fuel & Lubricant Technologies subprogram in the next year.

Fuels and Lubricants to Enable Efficient Engine Operation While Meeting 2007-2010 Standards

Activities in the coming year in this portion of the Fuel & Lubricant Technologies subprogram will focus on how fuel sulfur and lubricating oil additives degrade exhaust catalysts, and how fuel properties can be exploited to optimize emission control system operation.

These projects are focused on how emission control devices can be made more durable and efficient based on conventional fuels, non-petroleum-based fuels, and advanced-petroleum-based fuels.

- ORNL is identifying important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology. In the coming year they plan to collaborate with NREL is moving into a heavy-duty investigation where we will be working with Cummins to investigate the impact of Na with the SCR after the diesel particulate filter. Particular focus will be on the migration of Na from the diesel particulate filter to the downstream SCR. They will also investigate impact of new lubricant additive formulations on the catalytic activity of three-way catalyst, diesel oxidation catalyst, and SCR catalysis (Toops)
- ORNL is quantifying exhaust gas recirculation system performance when using non-petroleum-based fuels. In the coming year they will conduct broad analysis of existing experimental data to draw conclusions about deposit stabilization as a conclusion to the project in FY 2013. (Sluder)
- ANL is developing accurate and reliable correlations between benchtop tests and engine tests considering friction and wear performance data. In the coming year they plan to analyze fired engine tests results through industrial collaboration and correlate results from reciprocating ring-on-liner tests and actual engine tests to produce a predictive associative model. (Demas)
- ANL is developing and optimizing lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles. In the coming year they plan to: (1) Continue the development of comprehensive characterization of tribochemical films, including the chemical composition and phase allotropes; (2) Continue measurements of mechanical properties of tribochemical films with different structure; (3) Explore, develop and optimize other techniques for the production of films with same or similar structure as the tribochemical films from appropriate additives; and (4) Validate the friction performance of tribochemical films derived from various advanced additives in an engine condition. (Ajayi)
- ANL is developing lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in non-flex-fuel legacy vehicles. In the coming year they plan to: (1) Select the most effective functional nano-additives for friction reduction, wear prevention and scuffing prevention from preliminary performance evaluation results; (2) Develop synthesis of time release encapsulation systems. Different condition and environment sensitive encapsulating will be evaluated; (3) Integrate and optimize the various functional additives for blending into appropriate basestock lubricant; (4) Comprehensive tribological performance evaluation of optimized and blended additive system; and (5) Validate the friction and wear performance of new lubricant system in an engine condition. (Ajayi)

- ANL is developing self-replenishing lubricants that would provide reduction in friction and wear comparable to the effects of low-friction solid lubricant coatings. In the coming year they: (1) Conduct Raman spectroscopic analysis of composition of tribofilms formed after tribological testing with self-replenishing lubricants; (2) Optimize chemistry and composition of polyoxometallate using the polarizability/crystal chemical approach to lubricity of oxides as initial guidance; and (3) Test and select organic groups tailored to the intended functionality of the lubricant (friction reduction, viscosity modification, antioxidant, etc.). (Demas)
- ORNL is developing oil-soluble ionic liquids as engine oil additives and plans to demonstrate 10% improvement in mechanical efficiency of internal combustion engines. In the coming year they plan to: (1) Continue designing, synthesizing, and optimizing oil-soluble ionic liquids; (2) Characterize the physical/chemical properties of oil-soluble ionic liquids; (3) Carry out standard additive evaluation for ionic liquids and lubricant formulation; (4) Conduct systematic tribological bench tests and analyses; and (5) Investigate and model the lubrication mechanisms of ionic liquid additives. (Qu)
- MIT is investigating low-friction, environmentally friendly and commercially feasible lubricant formulations that significantly improve the mechanical efficiency of modern engines by at least 10%, versus the 2002 level without causing increased wear, emissions or deterioration of the emission-aftertreatment system. In the coming year they plan to: (1) Develop a database for the effectiveness of specific lubricant attribute (base oil, viscosity modifiers, friction modifiers) as a function of the local operating environment; (2) Develop the lubricant/additives requirement optimized for local operating environment; and (3) Verify optimized lubricant/additive package in various engine operating zones. (Cheng)
- Ford Motor Company is developing lubricant formulations capable of at least 10% engine friction reduction compared to current GF-5 engine oil technology at the same viscosity grade level most commonly used in the North American market. In the coming year they plan to: (1) Explore additional friction benefit through appropriate friction modifier chemistry; (2) Explore wear protection and oil oxidation protection capability improvements through additive chemistry; (3) Complete bench-top friction and wear property measurements of new oil formulations; (4) Analyze tribo-films formed on contacting surfaces to understand friction reduction mechanism(s); (5) Demonstrate friction reduction potential and wear characteristics on selected polyalkylene glycol oil formulations through motored engine component level tests; and (6) Continue motored engine friction evaluations and ASTM sequence tests to demonstrate anti-oxidation and wear protection capabilities and determine optimized polyalkylene glycol formulations. (Gangopadhyay)
- MIT is investigating the potential for improved performance and efficiency, and reduced greenhouse gas emissions, of gasoline-fueled vehicles by raising engine compression ratio and boost, through use of alcohols to suppress knock. In the coming year they plan to: (1) Complete engine performance maps for turbocharged engine with broader range of gasolines, alcohols, alcohol plus water blends at higher compression ratio and boost levels; (2) Initiate engine-in-vehicle simulations to generate vehicle fuel consumption data and knock suppressing fuel requirements with these performance maps; (3) Upgrade our turbocharged engine test facility to operate at higher compression ratio and boost levels; and (4) Combine our engine test data with similar data generated by Cummins, Inc. at higher compression ratio and boost levels. (Heywood)

Fuel Property Effects on Advanced Combustion Regimes

The focus of this portion of the Fuel & Lubricant Technologies subprogram is on how fuels properties affect combustion and how they can be used effectively to enhance combustion modes such as HCCI and HECC where emissions of NOx and PM are extremely low. The pathway to accomplish this is not marked, and several different approaches are being taken. For example, SNL is studying the effects of fuel volatility and composition on transient liquid-phase fuel penetration, wall impingement, emissions, and efficiency under early direct-injection operating conditions with a narrow-included-angle injector nozzle using in-cylinder laser imaging techniques and an optical piston assembly. LLNL is developing detailed chemical kinetic reaction models for components of conventional, advanced petroleum-based and non-petroleum-based fuels. These models will allow quicker combustion analysis using commonly available computing power. NREL is working to correlate advanced ignition parameters with physical properties or compositional measurements of real fuels such as various biodiesels, and oil-sands-derived diesel fuels, in an advanced combustion engine. ORNL is employing statistical techniques to correlate fuel properties with engine operating parameters to identify how engines can compensate for varying fuel properties and still achieve high efficiency and low emissions. A specific effort by ORNL is being conducted to improve engine efficiency with ethanol and ethanol-gasoline fuel blends.

- ORNL is obtaining representative samples of new, unique, or emerging fuels and screen with engine and laboratory analytical techniques to continue to add to a database of results and to develop tools for the rapid, efficient screening of new fuels and fuel components. In the coming year they plan to experimentally evaluate biodiesel-derived fuels. (Szybist)
- SNL is facilitating the introduction of renewable and/or unconventional fuels and the advanced engine-combustion strategies for their utilization in a manner that enhances domestic energy security, economic competitiveness, and environmental quality. In the coming year they plan to: (1) Complete the data analysis for, and draw conclusions from, the large parametric study of the emissions-certification and FACE diesel reference fuels; (2) Conduct engine tests on surrogate and real-world target fuels to more thoroughly assess the success of the surrogate-fuel formulation methodology and to assist in its optimization; and (3) Expand the fuel-effects studies to include oxygenated/renewable fuels of interest, higher injection pressures (≥2,400 bar), and laser-induced incandescence diagnostics to better understand and quantify the production, oxidation, and distribution of soot within the cylinder. (Mueller)
- LLNL is developing detailed chemical kinetic reaction models for components of advanced petroleum-based and non-petroleum-based fuels. In the coming year they plan to: (1) Develop ethanol-gasoline model for large amounts of ethanol and direct-injection spark-ignition engine application; (2) Further validations and improvements for chemical kinetic models for saturated and unsaturated large methyl esters, with particular emphasis on the low-temperature chemistry which is important for engine combustion; (3) Development of reduced surrogate mechanisms for biodiesel (cuphea methyl ester) and long-chain alcohols for use in computational fluid dynamics engine simulations; (4) Develop a low-temperature chemical kinetic model for diethylcarbonate; and (5) Provide technical support for the FACE working group. (Pitz)
- LLNL is working on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. In the coming year they plan to: (1) Develop a robust systematic software tool for refining advanced fuel chemical kinetic mechanisms based on engine experimental data for distribution; (2) Investigate the effects of fuel characteristics on the multidimensional combustion processes in advanced engines; and (3) Quantify the uncertainty of our engine modeling tools to provide an accurate measure of their ability to predict engine behavior as a function of operating condition. (Killingsworth)
- NREL is designing a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different R&D organizations working on similar and different advanced

combustion modes and engine designs. In the coming year they plan to: (1) Continue expanding Ignition Quality Tester-based experimental and simulation research; (2) Collaborate with other DOE and Canadian national laboratories, along with corporate industrial partners via the Coordinating Research Council; and (3) Employ SIDI single-cylinder research engine to study fuel chemistry impacts on advanced combustion, enabling NREL to study span of renewable fuels from fuel production and processing to engine performance and emissions. (Zigler)

- NREL is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems. In the coming year they plan to complete development and characterization of FACE gasoline fuel matrix; apply techniques developed in FACE diesel advanced characterization effort to address paucity of data for advanced alternative and renewable fuels; and continue development of multi-component diesel surrogate with full kinetic model, complementing FACE diesel fuel matrix. (Zigler)
- SNL is exploring how emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection spark-ignition light-duty engines being developed by the automotive industry. In the coming year they plan to: (1) Examine the effects of fuel blend in the E0 to E100 range on exhaust NOx and PM for stratified operation, and evaluate potential implications for flex-fuel vehicles; (2) Examine effects of engine speed and intake air temperature on stratified operation with selected gasoline/ethanol blends; and (3) Apply planar laser induced fluorescence to measure in-cylinder fuel distribution for better understanding of both low-emissions operation and sources of cyclic variability. (Sjoberg)
- ORNL is investigating the impacts of non-petroleum-based fuels on advanced combustion regimes for diesel and gasoline engines. In the coming year they plan to: (1) Investigate the fuel effects on multiple advanced combustion strategies on the same light-duty multi-cylinder engine for direct comparison of the combustion strategies; (2) Investigate fuel-specific impacts of the chemistry occurring when fuel is injected into the negative valve overlap, as is relevant to HCCI and spark-assisted HCCI using the ORNL 6-stroke engine cycle; and (3) Map the efficiency, emissions, and operable load range of gasoline, an ethanol fuel blend, and an iso-butanol fuel blend using conventional spark ignited combustion, spark ignited combustion with high levels of exhaust gas recirculation, lean-burn HCCI, and SA-HCCI. (Szybist)
- ORNL is investigating the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion engine applications. In the coming year they plan to: (1) Investigate the interactions between the IL [P66614][DEHP] and emission catalysts; (2) Work with a lubricant additive company to formulate an engine oil using the IL [P66614][DEHP] as an anti-wear additive; and (3) Conduct high-temperature, high-load full-size engine tests. (Qu)
- Ford Motor Company is identifying fuel properties that can be used to enable controllable extended lift-off combustion (ELOC) with low NOx. In the coming year they plan to: (1) Identify and confirm fuel properties needed to achieve ELOC and evaluate their spray characteristics and optical engine behavior; (2) Validate and use fuel and combustion models to optimize selected fuel properties and identify combustion design changes needed to facilitate non-sooting diesel combustion; and (3) Continue to improve modeling efforts to guide fuel selection and boundary conditions for future engine testing. (Kurtz)

Petroleum Displacement Fuels/Fuel Blending Components

The focus of this portion of the Fuel & Lubricant Technologies subprogram over the next year will be on biodiesel, ethanol, and advanced petroleum-based fuels made from natural gas, and oil sands liquids. The objective is to identify how these fuels affect engine efficiency and emission control device performance by themselves or in blends with conventional petroleum fuels.

- NREL is conducting a variety of projects relating to biodiesel and ethanol fuels:
  - They are studying the impact of fuel metal impurities on the long-term durability of emission control systems found in modern diesel engines. In the coming year they plan to conduct similar accelerated aging experiments on a heavy-duty catalyst system with a much longer full-useful-life requirement of 435,000 miles. (Williams)
  - They plan to continue to work with ASTM International to improve the D6584 method for glyceride determination, and in collaboration with the Coordinating Research Council, survey and report on mid-level ethanol blend quality from so-called blender pumps. (Alleman)
  - For some B100, observation of the polymorphic phase transformation requires a significantly slower heating rate (although still faster than occurs in real world diurnal warming). Ongoing experiments are directed at understanding why this occurs. A related study has been initiated with industry to investigate these issues with real world, as opposed to spiked, samples. (McCormick)
- ORNL is implementing analytical methods for characterizing the combustion products from conventional and advanced combustion in order to further elucidate combustion properties of biofuels and other alternative fuels. In the coming year they plan to conduct analyses with capillary electrophoresis mass spectrometry of inorganic and organic acid anions in exhaust condensates, and evaluate soot derived from non-petroleum-based fuel engine combustion for aromatic acids and anhydrides. (Lewis)
- PNNL is developing analytical tools to characterize fuels derived from unconventional hydrocarbons, focusing especially on chemistry-based predictive models to support future advanced combustion/emission technologies. In the coming year they plan to: (1) Continue to develop structure-property correlations built upon data obtained from current fuel sets; (2) Identify key molecular structure features in unconventional fuels which have the greatest impact on fuel properties and performance; (3) Continue to coordinate the interaction with Natural Resources Canada (CanmetEnergy) on analytical correlation of fuel properties and material compatibility investigations; (4) Continue collaborative work with members of the Coordinating Research Council's Working Group and the alternative and surrogate fuels subcommittees; and (5) Acquire biomass-derived pyrolysis oil samples from disparate sources, having different degrees of upgrading, particularly processed samples with significantly reduced oxygen and acid content, to extend the analysis and correlation chemistry of bio-based fuels. (King)
- PNNL will follow the changes that are occurring in alternative fuel use in Thailand with an emphasis on the issues being encountered with distribution and use of higher ethanol blends of E20 and 85% ethanol, 15% gasoline. (Bloyd)
- PNNL is developing an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies. In the coming year they plan to: (1) Incorporate the estimates for various biomass costs to update biomass supply curves. Compare cellulosic ethanol and other advanced biofuels pathways, including "drop-in fuels" that need less distribution infrastructure. Examine the portfolio effects of uncertainty results from research and development on biofuels; (2) Develop a Web-based ATEAM document using direct links from the ATEAM model to corresponding webpages, and cross links with the guide and make it easier to access and navigate; (3) Develop a series of two to four page technology briefs and a paper demonstrating ATEAM capabilities; and (4) Move the main hosting of Megajoule to another platform to enhancing the visibility by search engines. Expand the dataset with data from both research and collaborating information-sharing resources and continue to improve the user-friendliness and flow of the user interface. (Bloyd)

- NREL is measuring the impact of new biomass-derived fuels on gasoline performance properties and light-duty vehicle exhaust emissions. In the coming year expansion of this work should include testing of these blends in one or more additional cars as well as assessment of evaporative emissions. Future work may also examine the performance of other cellulosic biomass-derived oxygenates such as methyl pentanoate and furan-based compounds. (McCormick)
- ANL is assessing the emissions and operability of gasoline, ethanol, and butanol fuel blends in recreational marine applications. In the coming year they plan to: (1) Conduct end-of-life performance and emissions laboratory tests upon completion of run-time accumulation; (2) Perform laboratory engine testing with focus on engine cold start performance and particulate matter emissions assessment; (3) Extend test matrix to include tri-fuel blend (gasoline/ethanol/butanol) combustion analysis and emissions on laboratory engine as well as tri-fuel blend field evaluation; and (4) Assess the wear mechanisms in samples tested with clean engine oils and oils contaminated with different levels of fuel for E0, E10 and iso-But16 fuels. If possible, wear mechanisms in engine components after teardown will also be evaluated. Attempt to develop a correlation of wear mechanisms in laboratory tested samples and engine tested components. (Wallner)

I.6 SUMMARY

The work being conducted in Fuel & Lubricant Technologies on conventional, non-petroleum-based, and renewable fuels complements the efforts to build advanced engines and fuel cells for use in transportation applications. High-efficiency prime movers such as advanced combustion engines need clean fuels with carefully defined properties to enable fuel-efficient light-duty and heavy-duty vehicles with the attributes that consumers demand. Highly fuel-efficient vehicles with very low emissions are essential to meet the challenges of climate change, energy security, and improved air quality. As the new fiscal year begins, we look forward to on-going and new cooperative efforts with the auto and energy industries to develop new and innovative fuels technologies for use in advanced transportation vehicles that are fuel-efficient, clean, and safe.

Kevin Stork

Technology Development Manager
Fuel & Lubricant Technologies
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II.1 Compatibility of Emerging Fuels and Lubricants on Emissions Control Devices using Accelerated Aging Techniques

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Objectives

- Identify important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology:
  - Includes issues arising from the introduction of renewable fuels such as biodiesel and advanced lubricant additives.
- Develop and implement accelerated poisoning and aging protocols to provide:
  - Rapid evaluations of emissions control devices.
  - Deeper understanding of the mechanisms and chemistry affecting deactivation.
  - Input for modeling of deactivation processes and their impact on performance.
- Develop laboratory experiments to mimic field use:
  - Base protocol on analysis of the application and ways to accelerate.
  - Use extensive materials characterization.
  - Verify results by comparing to high mileage emissions control devices.
- Procedures and techniques developed in this project can also be used to evaluate field durability.

Fiscal Year (FY) 2012 Objectives

- Working with the National Renewable Energy Laboratory (NREL), the Manufacturers of Emission Controls Association (MECA) and Ford to determine if emissions control systems in light-duty vehicles will necessitate a new limitation for the biodiesel specification of less than 5 ppm Na+K and less than 5 ppm Ca.
- Determine extent and mechanism of deactivation caused by Na, K, and Ca in collaboration with Ford, NREL and MECA.

Accomplishments

- Showed deactivation of selective catalytic reduction (SCR) catalyst by replacement of Cu with Na and K but not Ca:
  - Degradation only occurred within the first few inches of the inlet.
  - Vehicle was able to meet the emissions regulations at end of life, but failed 1-2 tests during aging.
- Materials characterization demonstrates first known reported evidence that Na and K found in engine exhaust can exchange with the Cu-metal in the SCR catalyst:
  - Previously observed only through aqueous exchange.
  - Results in CuO formation on the surface of the washcoat.
- Published findings in *Catalysis Today* and submitted additional findings to *Topics in Catalysis* and SAE International.

Future Directions

- Collaboration with NREL is moving into a heavy-duty investigation where we will be working with Cummins to investigate the impact of Na with the SCR after the diesel particulate filter (DPF). Particular focus will be on the migration of Na from the FPD to the downstream SCR:
  - Goal is to determine if a new limitation for the biodiesel specification of less than 5 ppm is necessary.
- Investigate impact of new lubricant additive formulations on the catalytic activity of three-way catalyst, diesel oxidation catalyst (DOC), and SCR catalysis.

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INTRODUCTION

To enable new and emerging fuels to displace petroleum and advanced lubricants to improve efficiency, it is critical to evaluate their compatibility with existing and emerging emissions control devices. This effort applies accelerated aging and poisoning techniques to the investigation of the potential impact of these new formulations on emissions control devices. Efforts are aimed at introducing elements of concern at levels high enough to simulate end of life exposure, and then evaluate the impact on specific emissions control devices. Evaluation will include both emissions control effectiveness and materials characterization.

The emissions control devices that are currently being installed on diesel vehicles do not have rapid aging or poisoning protocols in place to enable the quick assessment of new formulations or designs. The development of these protocols will enable more rapid implementation of new fuel and lubricant formulations and enable improvements in the emissions control devices being developed. In 2010, diesel vehicles can require an oxidation catalyst (DOC), a particulate filter (DPF), and a NOx reduction device. Currently, urea-based SCR is the most-widely adopted solution being employed for NOx control. In past years we have investigated the effects of lube-oil constituent effects on DOCs [1-2], ash accumulation in DPFs [3], and thermal aging of lean-NOx trap [4-7] and SCR catalysts [8-10]. In addition to these deactivation mechanisms that emissions control devices will incur during normal operation with petroleum-based fuel, the implementation of renewable fuel sources, such as biodiesel, introduces additional complications. One of the issues that we are addressing is the concerns that have arisen from the presence of trace levels of Na in biodiesel—current specification is up to 5 ppm. Of particular concern is the deactivation of zeolite-based SCR catalysts, which has been recently reported [9-12]. In studying these processes we are hoping to either alleviate the concerns of diesel vehicle industry or determine the deactivation mechanisms and suggest possible remedies. If the concerns can be alleviated it may be possible to increase the allowable biodiesel blend levels to 20% from the current 5% level.

APPROACH

The investigation of aging mechanisms relies on accelerated techniques with the exact approach depending on the given concern. When necessary a representative engine will be employed but some approaches rely solely on bench flow reactors. In past studies, we employed a 517-cc Hatz single-cylinder diesel engine to either study deactivating effects of additives, generate ash or high temperatures. In the efforts this year we established a collaboration with NREL and Ford Motor Company to investigate the impact of metal impurities—specifically Na, K, and Ca—that are known to exist in biodiesel. The experimental details of this effort can be found elsewhere [13], but essentially NREL employed an accelerated technique to age a set of production exhaust systems from a 2011 Ford F250 to an equivalent of 150,000 miles of thermal aging and metal exposure. These exhaust systems included a DOC, SCR and DPF. Four separate exhaust systems were aged, each with a different fuel; ultra-low sulfur diesel (ULSD) containing no measureable metals, 20% biodiesel in ULSD (B20) containing Na, B20 containing K, and B20 containing Ca. Metals levels were selected to simulate the maximum allowable levels in 100% biodiesel, i.e. 5 ppm. Analysis of the aged catalysts included Federal Test Procedure (FTP) emissions testing with the systems installed on a Ford F250 pickup at NREL, bench flow reactor testing of catalyst cores at Ford, and detailed materials characterization of the aged DOCs and SCRs at ORNL. Additionally, the thermo-mechanical properties of the aged DPFs were also measured in a project funded by DOE's Propulsion Materials program.

At ORNL, the catalysts received from NREL were removed from their metallic canisters, cored and sectioned, as illustrated in Figure 1. Intact cores were sent to Ford while other cores were sectioned and analyzed for changes in material properties compared to the fresh and ULSD-based thermally-aged samples. The techniques that were our focus were inductively coupled plasma techniques for bulk elemental analysis, scanning electron microscope with energy-dispersive X-ray spectroscopy (EDS) for isolated or spot elemental analysis, and electron probe microanalysis (EPMA) for elemental concentration mapping.

RESULTS

The detailed results from this collaborative effort with NREL and Ford are found elsewhere [13], but the highlights from the materials characterization of the DOC and SCR catalysts will be reported here. During aging at NREL the intact exhaust system was periodically evaluated for emissions validation using the FTP cycle. After full-life exposure all of the aged exhaust systems passed the emissions standards; however, the Na- and K-aged samples exceeded the NOx standard at 1-2 points during the aging. The DOC core evaluations at Ford showed that the functionality was largely unaffected, but the K- and Na-aged samples did illustrate some signs of deactivation. Further analysis with the SCR cores revealed that the front of the SCR catalysts (C-F-1 in Figure 1) aged with Na and K were significantly deactivated compared to the Ca- and ULSD-aged samples, and even the front of the rear SCR catalysts

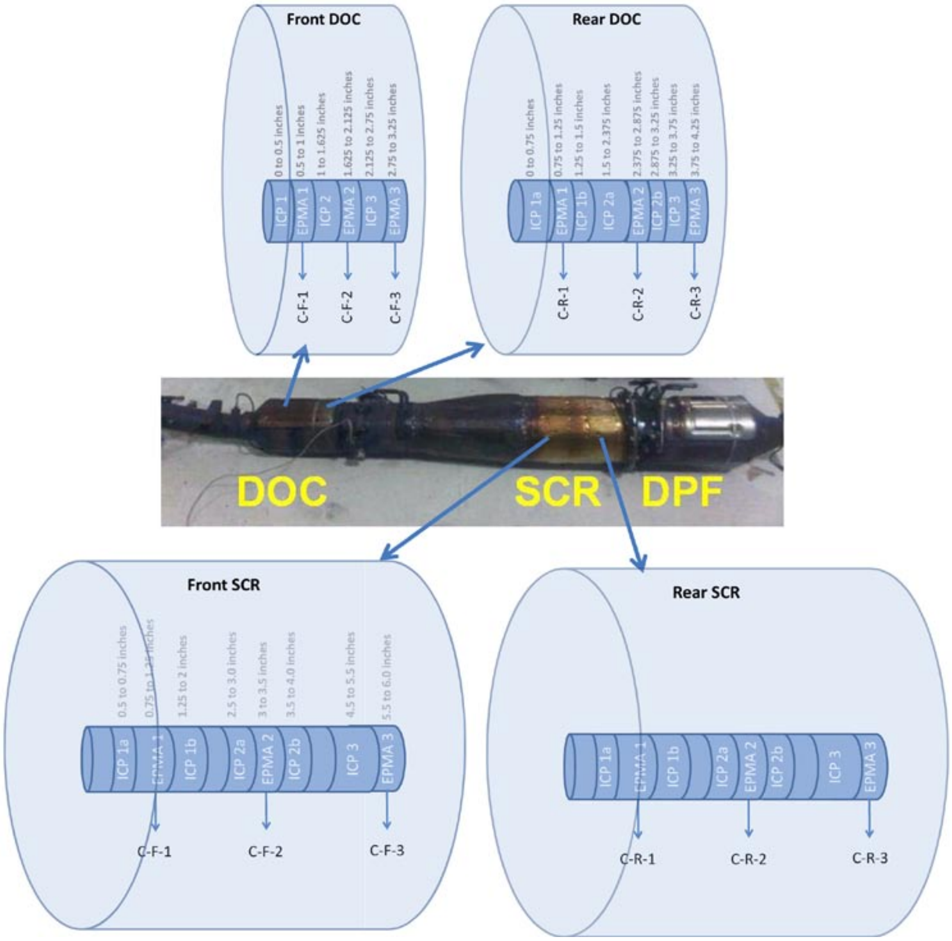


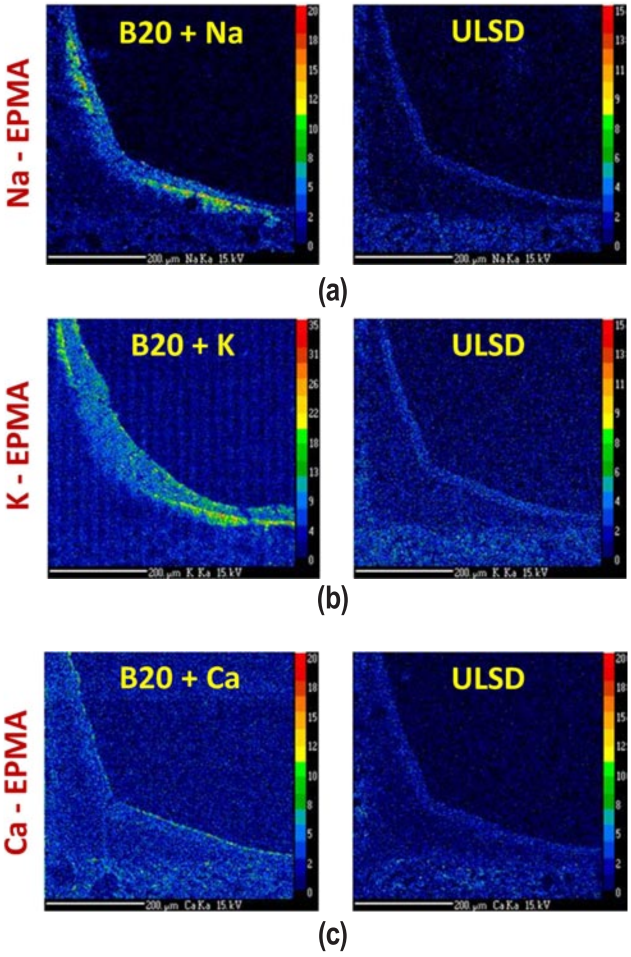
FIGURE 1. Emissions control system that was used in the study and how each device was sectioned for analysis. C refers to a core from the center of the brick, and F and R refer to samples from the front and rear bricks, respectively.

(C-R-1 in Figure 1) aged with Na and K. These findings provided the basis for which sample to focus on in our materials characterization study.

The aged DOCs were initially investigated using EPMA by looking at the cross-section of the catalytic washcoats. The micrographs with elemental mapping for Na, K, and Ca are highlighted in Figure 2 for the first section of the front DOC, C-F-1. This figure clearly shows the elevated levels of the metals of interest when compared to the ULSD case with no metal addition. Comparing the Na and K location and penetration into the washcoat, it can be seen that the interaction is much stronger compared to Ca, which essentially is only present on the surface (Figure 2c). This was repeated for the three sections of both the front and rear DOC catalysts and the quantitative metal analysis is shown in Figure 3 for each metal. This figure illustrates that the Na and K are adsorbed at considerably higher levels for their aging routine and that their concentrations decrease from the inlet to the outlet of the DOC. Bulk analysis of the washcoat for Ca concentrations shows that the Ca-aged sample was not measurably higher than any of the other four samples.

Similarly, the inlet of the front SCR was analyzed with EPMA, C-F-1 (analysis of the remaining sections forthcoming). The EPMA micrographs shown in Figure 4 once again show that the Na and K metals penetrate the entire washcoat, while the Ca interaction is isolated to the surface. Additionally, it can be seen that there is an interesting gradient in the samples as the corner of the washcoat has measurably lower concentrations than the side. This is observed both in the micrographs and the EDS-based elemental analysis of specific locations within the washcoat (bar charts).

Another important aspect of this deactivation is revealed when a comparison is made between the Na or K content and the Cu content. These SCR catalysts consist of a small pore zeolite that has been exchanged with Cu atoms to create a highly stable and active NOx reduction catalyst; recently described in [14]. While it is known

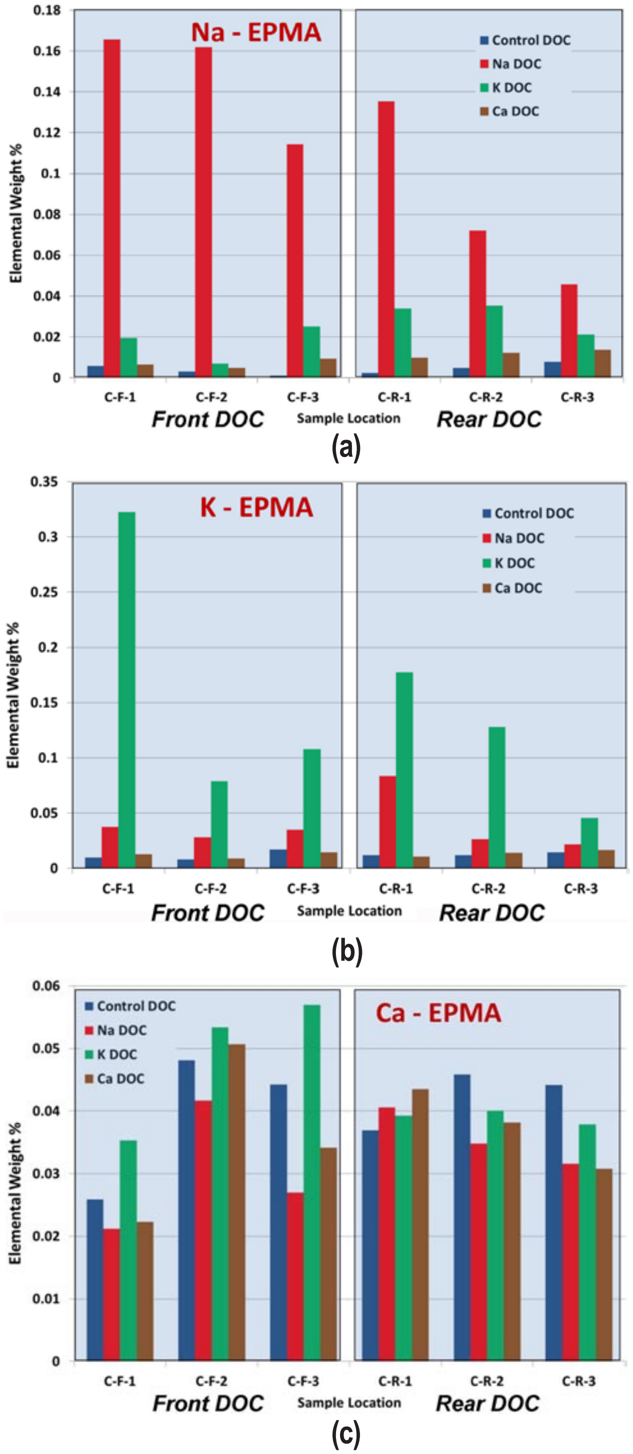


(a)

(b)

(c)

FIGURE 2. (a) Na, (b) K, or (c) Ca EPMA micrographs of the C-F-1 section of the DOC aged with Na, K, or Ca, respectively; results are compared to the DOC from the ULSD-only control case.



(a)

(b)

(c)

FIGURE 3. (a) Na, (b) K, or (c) Ca EPMA-based elemental analysis of each section of the DOC aged with Na, K, or Ca, respectively; results are compared to each of the other aged systems.

that using aqueous chemistry other metals can also be exchanged on these same sites as Cu, it was not known if exhaust-based metals could also do this. The bar charts in Figure 4 are the first known reported evidence that this is indeed possible in exhaust systems. It can be seen that Cu content decreases in the washcoats when Na and K levels increase. To confirm that this was not due to lower concentrations of Si+Al-based zeolite in the spots being analyzed, Al was also included in the analysis, and it was shown to not have a significant variance on the two different areas. The Ca sample also did not show a variance between the two sections. Furthermore, it was noticed that the K and Na samples each had an area of dense particles on the surface of the washcoat that was not observed in the Ca-age or fresh samples, Figure 5. Additional EDS and Raman analysis of these particles revealed them to be CuO particles. Combining these two findings there is ample evidence to indicate that fuel-borne metals, particularly Na and K, can deactivate Cu/zeolite-based SCR catalysts, and they do so by displacing the Cu which results in a layer of CuO on the washcoat surface. Surprisingly, this CuO layer is visible with the unaided eye as can be seen in Figure 6. The deactivation

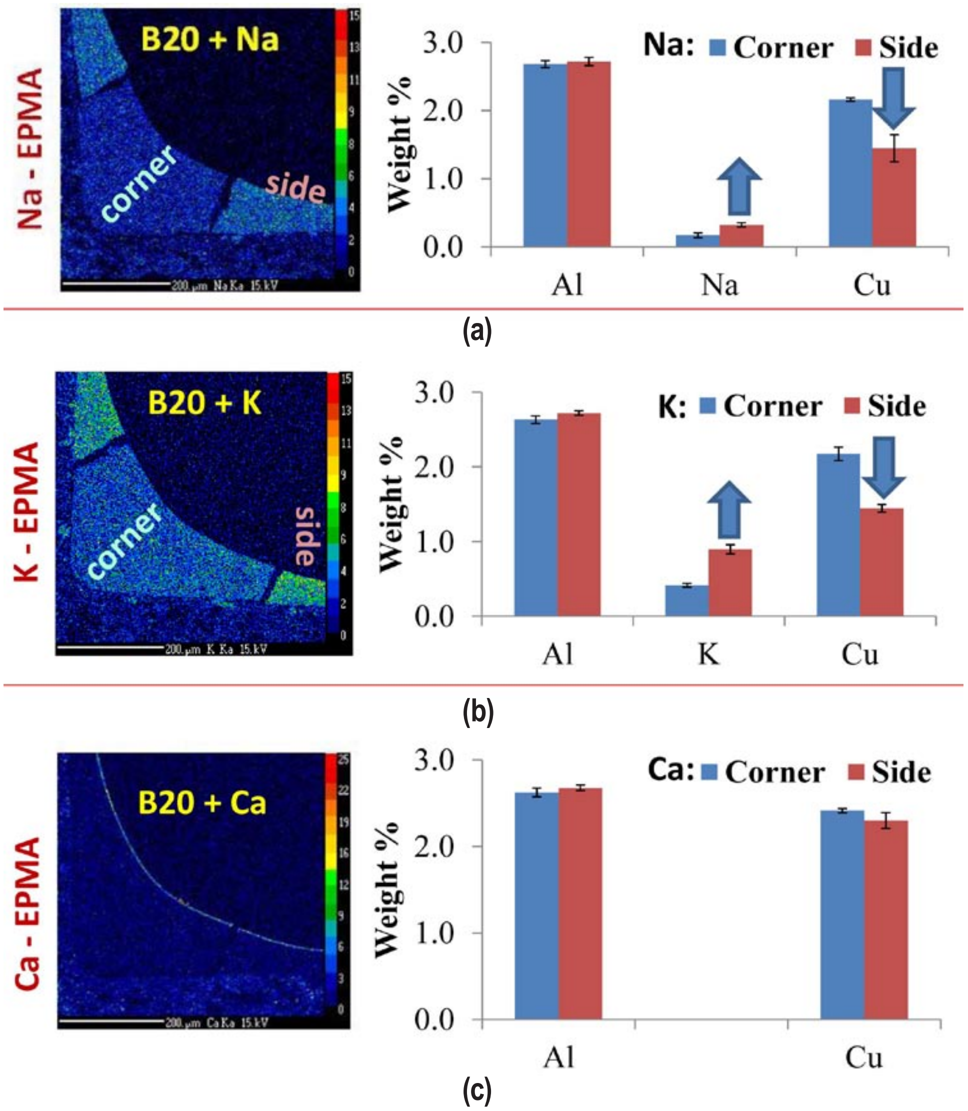


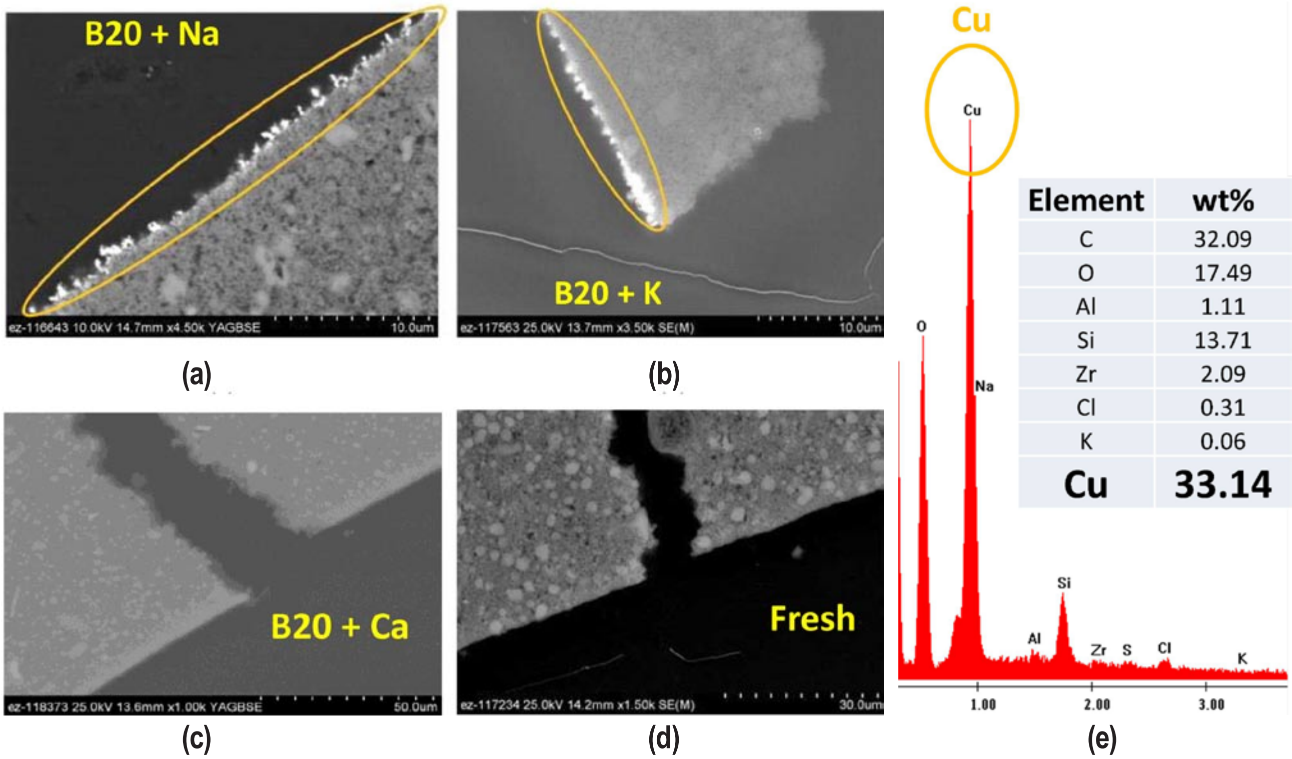
FIGURE 4. (a) Na, (b) K, or (c) Ca EPMA micrographs and the corresponding EDS-based elemental analysis of corner and side portion of the SCR washcoat from section C-F-1. Results show when Na and K levels increase locally, Cu level decreases; not observed with Ca sample.

appears to progress approximately 30-40% into the front catalyst, or 15-20% of the entire SCR system.

It is important to note that although deactivation was observed in this study, under most circumstances the nature of the deactivation would not have a catastrophic effect on emissions compliance, especially if the SCR catalysts were over-sized for the given application. A significant concern that one could have would be that the increase in the CuO content would lead to increased NH_3 oxidation, such that the NH_3 would not be available for SCR at the rear of the catalyst. This does into appear to be the case here, but should be considered in prolonged exposures or more stringent emissions regulations.

CONCLUSIONS

- DOC-Based Conclusions
  - Showed highest collection efficiency of metals; first device in exhaust:
    - Decreasing concentrations from inlet to outlet.
  - Na and K interacted strongly with washcoat and substrate:
    - Ca deposition only on the washcoat surface.
  - Deactivation was not significant.
- SCR-Based Conclusions



Element	wt%
C	32.09
O	17.49
Al	1.11
Si	13.71
Zr	2.09
Cl	0.31
K	0.06
Cu	**33.14**

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

FIGURE 5. Scanning electron micrographs illustrating dense particle formation on the surface of the washcoated SCR when aging with (a) Na and (b) K; particles not observed on the (c) Ca or (d) fresh samples. (e) EDS shows these particles to be CuO-based.

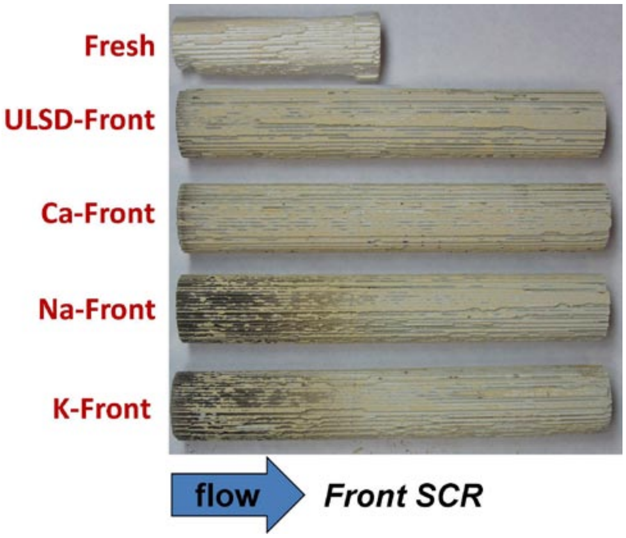


FIGURE 6. Cores removed from the front SCR catalyst show a dark region in the Na- and K-aged samples. Elemental investigation reveals this is not soot but instead the CuO that was shown in Figure 5.

  - Lower concentration of metals observed in SCR samples than DOC samples.
  - Chemical nature of catalysts significantly changed at the inlet of the front brick:
    - Na and K exchanged/displaced Cu from zeolite active centers.
    - Cu_xO formation observed on the surface.
  - Materials characterization shows strong correlation to deactivation which only occurred at the front of the SCR.
- Results presented here and elsewhere [13] suggest the current specification of 5 ppm Na+K is adequate for light-duty applications, as long as the following are true:
  - SCR is appropriately sized to be able to withstand deactivation in front quarter.
  - The biodiesel fuel meets the specification and the petroleum-based fuel does not contain Na and K.

REFERENCES

1. B.G. Bunting, K.L. More, S.A. Lewis Sr., and T.J. Toops, "Phosphorous Poisoning and Phosphorous Exhaust Chemistry with Diesel Oxidation Catalysts", SAE 2005-01-1758 (2005).

2. S. Eaton, K. Nguyen, B.G. Bunting, T.J. Toops, "The Role of Phosphorus and Soot on the Deactivation of Diesel Oxidation Catalysts", SAE 2009-01-0628 (2009).

3. A. Youngquist, K. Nguyen, B.G. Bunting, T.J. Toops, "Development of an Accelerated Ash Loading Protocol for Diesel Particulate Filters", SAE 2008-01-2496 (2008).

4. K. Nguyen, H. Kim, B.G. Bunting, T.J. Toops, C.S. Yoon, "Rapid Aging of Lean NOx Traps by High-Temperature Thermal Cycling", SAE 2007-01-0470 (2007).

5. T.J. Toops, B.G. Bunting, K. Nguyen, A. Gopinath, "Effect of Engine-Based Thermal Aging on Surface Morphology and Performance of Lean NOx Traps", Catalysis Today 123 (2007) 285.

6. N.A. Ottinger, K. Nguyen, B.G. Bunting, T.J. Toops, J. Howe, "Effects of Rapid High Temperature Cyclic Aging on a Fully-Formulated Lean NOx Trap Catalyst", SAE International Journal of Fuels and Lubricants 2:1 (2009) 217; SAE 2009-01-0634.

7. N.A. Ottinger, T.J. Toops, K. Nguyen, B.G. Bunting, J. Howe, "Effect of Lean/Rich High Temperature Aging on NO Oxidation and NOx Storage/Release of a Fully-Formulated Lean NOx Trap", Applied Catalysis B: Environmental 101:3-4 (2011) 486-494.

8. T.J. Toops, K. Nguyen, A.L. Foster, B.G. Bunting, N.A. Ottinger, J.A. Pihl, E.W. Hagaman, J. Jiao, "Deactivation of Accelerated Engine-Aged and Field-Aged Fe-Zeolite SCR", Catalysis Today 151 (2010) 257.

9. D.W. Brookshear, K. Nguyen, T. J. Toops, B.G. Bunting, J. Howe, "Investigation of the Effects of Biodiesel-based Na on Emissions Control Components", Catalysis Today 184 (2012) 205-218; 10.1016/j.cattod.2011.12.001.

10. D.W. Brookshear, K. Nguyen, T. J. Toops, B.G. Bunting, "Impact of Biodiesel-based Na on the Selective Catalytic Reduction of NOx by NH_3 Over Cu-zeolite Catalysts", accepted to Topics in Catalysis.

11. G. Cavataio, H. Jen, D.A. Dobson, and J.R. Warner, SAE 2009-01-2823 (2009).

12. A. Williams, R. McCormick, J. Luecke, R. Brezny, A. Geisselmann, K. Voss, K. Hallstrom, M. Leustek, J. Parsons, and H. Abi-Akar, SAE 2011-01-1136 (2011).

13. A. Williams, J. Burton, R.L. McCormick, T.J. Toops, A.A. Wereszczak, E.E. Fox, M.J. Lance, G. Cavataio, D. Dobson, J. Warner, R. Brezny, D.W. Brookshear, K. Nguyen, "Impact of Fuel Metal Impurities on the Durability of a Light Duty Diesel Aftertreatment System", submitted to SAE.

14. J.-S. McEwen, T. Anggara, W.F. Schneider, V.F. Kispersky, J.T. Miller, W.N. Delgass, F.H. Ribeiro, Catalysis Today 184 (2012) 129.

FY 2012 PUBLICATIONS

1. A. Williams, J. Burton, R.L. McCormick, T.J. Toops, A.A. Wereszczak, E.E. Fox, M.J. Lance, G. Cavataio, D. Dobson, J. Warner, R. Brezny, D.W. Brookshear, K. Nguyen, "Impact of Fuel Metal Impurities on the Durability of a Light Duty Diesel Aftertreatment System", submitted to SAE.

2. D.W. Brookshear, K. Nguyen, T.J. Toops, B.G. Bunting, "Impact of Biodiesel-based Na on the Selective Catalytic Reduction of NOx by NH_3 over Cu-zeolite Catalysts", accepted to Topics in Catalysis.

3. D.W. Brookshear, K. Nguyen, T.J. Toops, B.G. Bunting, J. Howe, "Investigation of the Effects of Biodiesel-based Na on Emissions Control Components", Catalysis Today 184 (2012) 205-218; 10.1016/j.cattod.2011.12.001.

FY 2012 PRESENTATIONS

1. (INVITED) Todd J. Toops, Michael Lance, Andrew A. Wereszczak, D. William Brookshear and Ke Nguyen "Materials Characterization to Investigate Location of Fuel-borne Metals", 2012 Biodiesel Technical Workshop, Kansas City, MO, October 30, 2012.

2. D.W. Brookshear, K. Nguyen, T.J. Toops, B.G. Bunting, W.F. Rohr, "Impact of Biodiesel-based Na on the Selective Catalytic Reduction of NOx by NH_3 over Cu-zeolite Catalysts", 9th International Congress on Catalysis and Automotive Pollution Control (CAPoC9), August 29–31, 2012, Brussels, Belgium.

3. C.S. Sluder, J.E. Storey, T.J. Toops, C.S. Daw, B.G. Bunting, S.L. Lewis, M. Lance, "Fuel Effects on Emissions Control Technologies", 2012 DOE Annual Merit Review, Crystal City, VA, May 14–18, 2012.

4. (INVITED) T.J. Toops, "Characterization Techniques to Investigate Location and Impact of Biodiesel Metals", 2011 Biodiesel Technical Workshop, Kansas City, MO, November 1, 2011.

5. D.W. Brookshear, K. Nguyen, B.G. Bunting, T.J. Toops, "Impacts of Biodiesel on Emission Control Devices", Directions in Emissions and Efficiency Research (DEER) Conference, Detroit, MI, October 2011.

II.2 Non-Petroleum-Based Fuels: Effects on EGR System Performance

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Objectives

- Quantify exhaust gas recirculation (EGR) system performance when using non-petroleum-based fuels.
- Identify fuels or fuel properties that may reduce the effectiveness of the EGR system through problematic deposit formation.

Fiscal Year (FY) 2012 Objectives

- Identify conditions under which plugging, and potentially a fuel-formulation impact are most likely.
- Investigate the potential for deposit removal by flow-induced shear forces.

Accomplishments

- Showed that extended operation at low Reynolds number, low-temperature conditions can build significant deposit layers high in fuel hydrocarbons (HCs) with very little effectiveness loss.
- Found that removal of deposits occurs at high flow rates that result in impractically high pressure drops.
- Determined that spall material is not re-entrained diesel particulate, but rather has different characteristics than typical diesel particles.

Future Directions

- Conduct broad analysis of existing experimental data to draw conclusions about deposit stabilization as a conclusion to the project in FY 2013.

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INTRODUCTION

EGR is an oxides of nitrogen (NO_X)-reduction technology that utilizes engine exhaust recirculated to the engine intake and mixed with fresh air as a means of reducing the combustion temperatures and engine-out NO_X emissions. As the quantity of EGR being used has increased and the conditions where EGR is used have broadened, EGR coolers have come to be a critical component of the EGR system. These coolers reduce the temperature of the EGR gases so that further NO_X reductions are possible. Increasingly stringent NO_X regulations have placed further importance on this approach. Commercial constraints, such as cost and packaging, place emphasis on compact, light-weight designs that are easily manufactured.

Unfortunately, the exhaust gases being cooled in the EGR cooler contain both particulate matter (PM) and chemical species such as unburned HCs and in some cases acids derived from sulfur present in the fuel and nitrogen dioxide (NO_2) produced during combustion. [1-2]. PM will deposit thermophoretically on surfaces where a temperature gradient exists, and when this occurs in EGR coolers the effectiveness of the cooler is degraded, resulting in hotter EGR gases at the cooler exit. HCs and acids may also contribute to this problem by creating an environment less conducive to removal of the PM by aerodynamic forces within the flow stream. This reduction in effectiveness of the EGR cooler is a critical problem because it may result in vehicles falling out of compliance with EPA emissions control durability requirments or, in severe cases, impacting driveability. Thus, manufacturers currently must design the EGR cooler to have more capacity than necessary, leading to increased cost and packaging issues.

Some non-petroleum-based fuels (such as, for example, biodiesel) have unique fuel chemistries and/or combustion behavior that may cause changes in the fouling tendencies of EGR coolers. Most domestic biodiesels, for example, have low vapor pressure relative to diesel fuel, potentially resulting in preferential deposition in the EGR cooler. If this is found to be the case, it represents a very significant technical hurdle that must be overcome if these fuels are to be successful in significant market penetration. The first step toward overcoming this hurdle is to gain an understanding of the scope of the problem.

APPROACH

ORNL has approached this problem from an experimental point-of-view. An engine and sampling system have been established to facilitate studies of surrogate EGR cooler tubes that can be removed and extensively analyzed to examine the nature of the deposits caused by operation with non-petroleum-based fuels. Examination of the deposits can provide insights into the fouling processes with these fuels and possible strategies to mitigate the problem.

RESULTS

Studies to date have shown that EGR cooler deposits are made up primarily of soot. These deposits are highly insulative by nature. However, plugged coolers from the field typically have deposits that are more tar-like and contain larger amounts of condensed species [1]. The conditions under which these types of deposits can form are limited. Since the condensation of large amounts of hydrocarbons are not favored when the deposit increases in temperature, the most likely pathway for these deposits to occur is through the formation of a highly dense deposit that is much more thermally conductive. This situation arises if the rate of deposition of hydrocarbons exceeds that of soot in a volumetric sense for a significant period of time. In such a case, the hydrocarbons create a fluid layer that incorporates the soot in a dense deposit. The soot may act to increase the viscosity of the fluid layer, thus allowing it to become thicker than would otherwise be possible.

Experiments were conducted to examine the potential for creation of deposits with high mass but low effectiveness loss. These experiments focused on low gas velocities with low temperature gradient between the gas and coolant. In such situations, hydrocarbon deposition may dominate over soot deposition since the former is a function of the wall temperature, while the latter is a function of the temperature gradient. Experiments conducted over a period of several days found that high-mass deposits could indeed be formed without substantial loss in thermal effectiveness. Deposits with masses in excess of 100 mg/tube were observed with negligible gain in deposit thermal resistance. The deposits were found to contain substantial amounts of volatile species. Since deposit density is the most important characteristic in determining the deposit thermal conductivity, the deposits must have had a much more dense structure than deposits formed at higher temperatures [1].

Since the deposits formed in this manner do not increase significantly in temperature, volatile species can continue to deposit faster than soot, and hence, these layers can build up over time at a sustained rate. High-temperature deposits, by comparison, typically deposit initially at a high but decreasing rate, since the temperature gradient that drives soot deposition is reduced as the deposit thickens. Thus, deposits formed under cold conditions are much more likely to lead to cooler plugging. To the extent that non-traditional fuel formulations result in less volatile species in the exhaust, they will make plugging more likely. Applications that are likely to experience these conditions include airport shuttles and other low-load duty cycles. Anecdotal evidence from the field supports this hypothesis.

Deposit removal through flow-induced shear force may be one explanation for the observed phenomenon of EGR cooler deposits reaching stabilization. To investigate this hypothesis, several tubes were fouled for 8 hours, and then removed from the fouling apparatus and subjected to air flows to generate deposit removal. Several tubes were analyzed destructively to establish the deposit thickness prior to removal, while others were characterized after deposit removal to examine differences in the deposit. Tubes were subjected to step-wise increases in air mass flow rate while the air exiting the tube was monitored for particle removal using a TSI Engine Exhaust Particle Sizer (EEPS). Figure 1 shows the particle concentration observed at the tube exit versus time. The peak labels show the air mass flow rate (kg/min) corresponding to observed spikes in the particle concentration. Next, several tubes were subjected to an air mass flow rate of 0.090 kg/min for 30 minutes while the particle concentration was again monitored using the EEPS. The tubes were subsequently weighed and the weight combined with the integrated EEPS particle concentration to estimate the mass removal rates at various air flow rates. The results of this analysis are shown in Figure 2. The approximate deposition rates during fouling are shown by the red lines in the figure. The results show that large air mass flow rates are required to produce removal rates that compare with fouling rates. Finally, the shear stress was estimated at each air mass flow rate and examined as a function of the air velocity. Velocities in excess of 40 m/s are needed to produce removal, resulting in apparent shear stresses of 0.03 kPa. Unfortunately, velocities this high produce

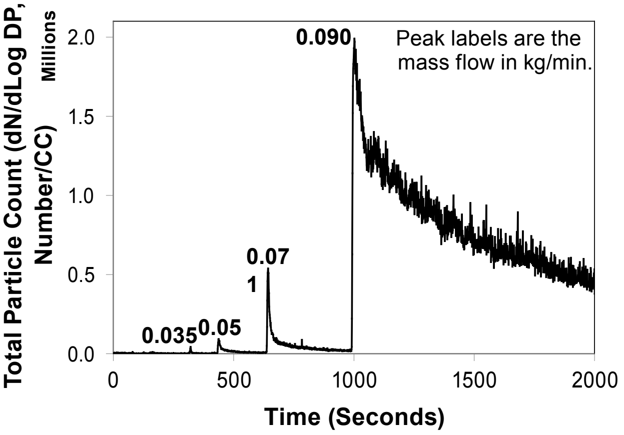

FIGURE 1. EEPS particle count trend during shear-based removal experiment.

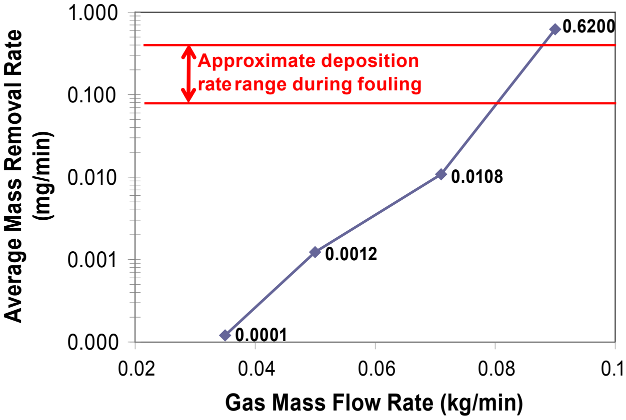

FIGURE 2. Estimated deposit mass removal rates for several air mass flow rates.

high pressure drops, and make it unlikely that removal using only flow-induced shear is effective for practical applications. It is likely that observations of removal in the field result from a combination of flow-induced shear and other forces such as an uplift force induced by curvilinear gas flow paths.

An electrostatic sampling device was used to collect material liberated from the deposits for subsequent analysis by scanning electron microscope. The particles were observed to be quite large compared with typical diesel particles, suggesting that the particles were not simply re-entrained diesel particulate. Rather, the particles appear to be fragments that have been mechanically dislodged from the deposit. Analysis of the particle size data provided by the EEPS also supports this hypothesis, as the particles were observed to be larger than 200 nm. These results suggest that the use of cricital shear-force models for removal that are based on a spherical particle assumption are not accurate for EGR cooler deposits. Figure 3 shows an image of one of the particles.

CONCLUSIONS

- EGR cooler plugging most likely results from low Reynolds' number flows at low gas temperatures. Deposits produced under these conditions are more dense and conductive, and can build up to produce thicker deposits.
- Shear-force based removal does occur in EGR cooler deposits in smooth tubes, but only at velocities that produce excessive pressure losses. Observations of removal in the field likely result from multiple processes that include but are not limited to flow-induced shear.

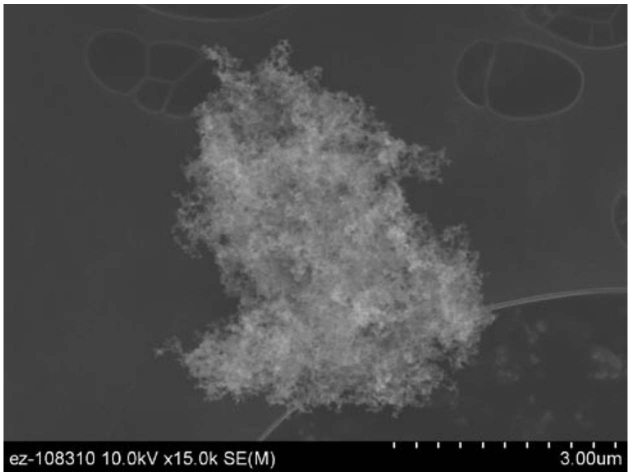

FIGURE 3. Electron microscope image of a particle removed from an EGR cooler deposit by flow-induced shear.

- Particles removed from EGR cooler deposits under the action of flow-induced shear are larger than typical diesel particles and suggest that critical-shear force models using a spherical assumption are not accurate for EGR cooler deposits.

REFERENCES

1. Michael J. Lance, C. Scott Sluder, Hsin Wang, and John M.E. Storey, "Direct Measurement of EGR Cooler Deposit Thermal Properties for Improved Understanding of Cooler Fouling," SAE Technical Paper 2009-01-1461, SAE International, 2009.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Scott Sluder, John Storey, Todd Toops, Stuart Daw, Bruce Bunting, Sam Lewis, and Michael Lance, "Fuel Effects on Emissions Control Technologies," presented at the 2012 DOE Annual Merit Review, May, 2012.

2. C. Scott Sluder, John M.E. Storey, Michael J. Lance, and Teresa Barone, "Removal of EGR Cooler Deposit Material by Flow-Induced Shear," submitted for consideration for the 2013 SAE International Congress and Exposition.

3. C. Scott Sluder, John M.E. Storey, and Michael J. Lance, "Temperature and Thermal Conductivity of Soot Deposits in EGR Coolers: Measurements and Challenges," submitted for consideration for the 2013 Eurotherm Heat Exchanger Fouling and Cleaning Conference.

II.3 Lab-Engine Correlation and In Situ Validation of Fuel-Efficient Engine Lubricant Technologies

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Objectives

- Obtain fuel economy, durability and reliability data obtained from engine tests.
- Develop accurate and reliable correlations between benchtop tests and engine tests considering friction and wear performance data.
- Utilize the protocols, techniques, and knowledge established to work with industry in evaluating candidate solutions under a common set of conditions.

Fiscal Year (FY) 2012 Objectives

Task 1

- Identify benchtop tests that best simulate friction, wear, and failure mechanisms.
- Develop test protocols (load, time, temperature, speed, lubricant, materials, finish, etc.) that replicate the engine environment.
- Develop and validate test rigs that enable in situ measurement of friction (and wear) in fired single-cylinder engines.
- Identify test protocols that can measure the impact of individual tribological technologies on engine fuel economy.
- Develop correlations between engine fuel economy studies/data (auto original equipment manufacturer) and benchtop and rig studies.
- Identify conditions and protocols that best correlate with engine and vehicle studies.

Task 2

- Develop baseline friction, mechanism, and fuel efficiency database for baseline tribological engine systems (fluid/materials/finish – tribo environment).
- Evaluate/assess performance of candidate technologies against baseline database.

Accomplishments

- Established collaborations with academia and industry – Massachusetts Institute of Technology, General Motors/Ford/Chrysler, and oil suppliers.
- Identified and reviewed critical ASTM International standards and test protocols for benchtop friction, wear, and reliability.
- Identified existing database(s) on benchtop test protocols, in situ friction measurements, and engine/vehicle economy tests.
- Initiated preliminary friction studies using benchtop tests.

Future Directions

- Analyze fired engine tests results through industrial collaboration.
- Correlate results from reciprocating ring-on-liner tests and actual engine tests to produce a predictive associative model.

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INTRODUCTION

With the demand for improved vehicle efficiency, utilization of alternative fuels, and implementation of new emission strategies, there is an increasing need to develop advanced tribological systems for engines, drivetrains, and auxiliary systems. However, due to the complexity of tribological phenomena that involve materials, coatings, engineered surfaces, and advanced lubricants and additives, the design of new and improved systems often involves a progression of increasingly more complex and costly research and development activities to demonstrate the technological feasibility and cost-effectiveness of a given approach. For example, the development of an advanced lubricant typically involves benchtop tests that demonstrate the efficacy of an additive to reduce friction and/or improve durability under ideal conditions. Rig tests using coupons obtained from prototypic engine components may then follow to demonstrate the technology will function on real-world materials. The rig tests are followed by single-cylinder tests using fired engines, multi-cylinder engine tests, and eventually, vehicle and fleet studies. As the technology progresses from one stage of test complexity to the next, the results are perceived to be more and more representative of real-world conditions; however, the costs of the tests increase dramatically (upwards of $100K for a Sequence V test). With the complexity and cost of tests increasing as one moves to more representative conditions, there is a great demand to ensure that benchtop tests utilize test protocols that are representative of vehicle conditions such that they can accurately screen technologies in the early stage of development and thus avoid testing technologies that will fail in the full-scale tests.

APPROACH

We intend to use reciprocating test rigs that utilize prototypical engine components to perform benchtop tests under conditions that are representative of vehicle conditions such that they can accurately screen technologies in the early stage of development. Collaborations with academia and industry will be used to determine these conditions and also provide helpful data from an actual engine test for correlation with the laboratory results.

RESULTS

A test method for conducting friction tests of piston ring and cylinder liner materials under lubricated conditions has been identified and reviewed. This test method (ASTM G181-11) [1] covers procedures for conducting laboratory bench-scale friction tests of materials, coatings, and surface treatments intended for use in piston rings and cylinder liners in diesel and spark-ignition engines. The goal of this procedure is to provide a means for preliminary, cost-effective screening or evaluation of candidate ring and liner materials. A reciprocating sliding arrangement [2] is used to simulate the contact that occurs between a piston ring and its mating liner near the top-dead-center position in the cylinder, where liquid lubrication is least effective and most wear is known to occur. Special attention is paid to specimen alignment, running-in, and lubrication condition.

We have performed tests that were approximately three hours long and consisted of an initial ramp-up and ramp-down “speed ramp”, then a three-hour test at a constant speed, followed by a second speed ramp at the end at a specified load. One such test is shown in Figure 1(a). A load of 50 N at a temperature of 130^{o}C was

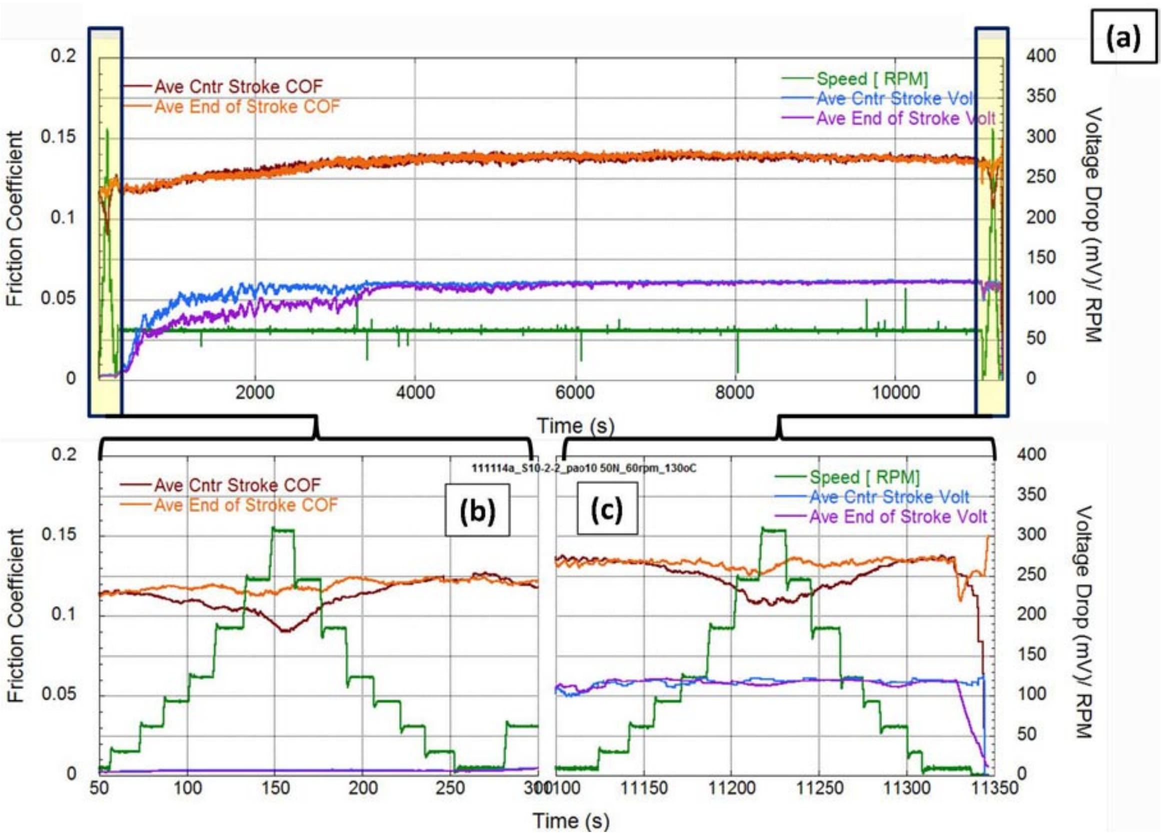

FIGURE 1. (a) Coefficient of friction in 3-hr test using a PAO10 lubricant at 130°C with speed ramps at the (b) start and (c) finish of the test.

used. During the test an average center-stroke coefficient of friction was calculated as well as an average end-of-stroke coefficient of friction. Furthermore, an average center-stroke and end-of-stroke voltage was monitored during the tests. The voltage indicates the formation of an insulating tribofilm at approximately 500 seconds. Figure 1(b) and (c) show details of the friction coefficients during the initial and final speed ramps.

Performing similar tests to the one described above, we developed Stribeck curves for three different liners: plateau honed, slide honed, and fine honed. The experimental results were compared with simulated results obtained from a model [3] that uses the Greenwood-Tripp asperity contact model and the Swift-Steiber (Reynolds) cavitation model to predict the performance of a cylinder liner and piston ring under reciprocating conditions. The experimental data and simulated data are plotted in Figure 2. Each liner has a different boundary friction coefficient: plateau honing, 0.11; slide honing, 0.10; and fine honing, 0.08. These experimental data were used in the simulation program.

The fine-honing liner stops at around 15 cm/s because the stroke length is only 10 cm, half as long as the stroke length of the plateau-honing and slide-honing liners. Each test has a positive and negative direction because of the reciprocating nature of the tests; however, the labels “positive” and “negative” are arbitrary. As evident in Figure 2, the coefficients in the positive direction for the experimental data correlate well with the simulated data for all three liners. The coefficients in the negative direction for the simulated data, however, are too high in all three cases. The coefficients in the negative direction for the experimental data match the positive direction predicted in the slide- and fine-honing plots but not the plateau-honed.

Various additive formulations were also assessed in a laboratory reciprocating test. Figure 3 shows the coefficient of friction as a function of time for various additives blended with polyalphaolefin (PAO) basestock. The data indicate that the use of additives can reduce friction, and the laboratory reciprocating test can be used to rank these additives in terms of tribological performance.

After extensive talks and planning with an industrial partner, we recently established a project to evaluate the test results from reciprocating trials in order to determine the optimum combination of engine oils with a nanocrystal additive. This optimum condition is designed to produce the minimum in friction and wear under the conditions typical of sliding contacts in vehicle engines and drivetrains. We are currently working on dispersion of the nanocrystal additive in base oil, semi-formulated oil, and fully formulated oil. When the synthesis, surface

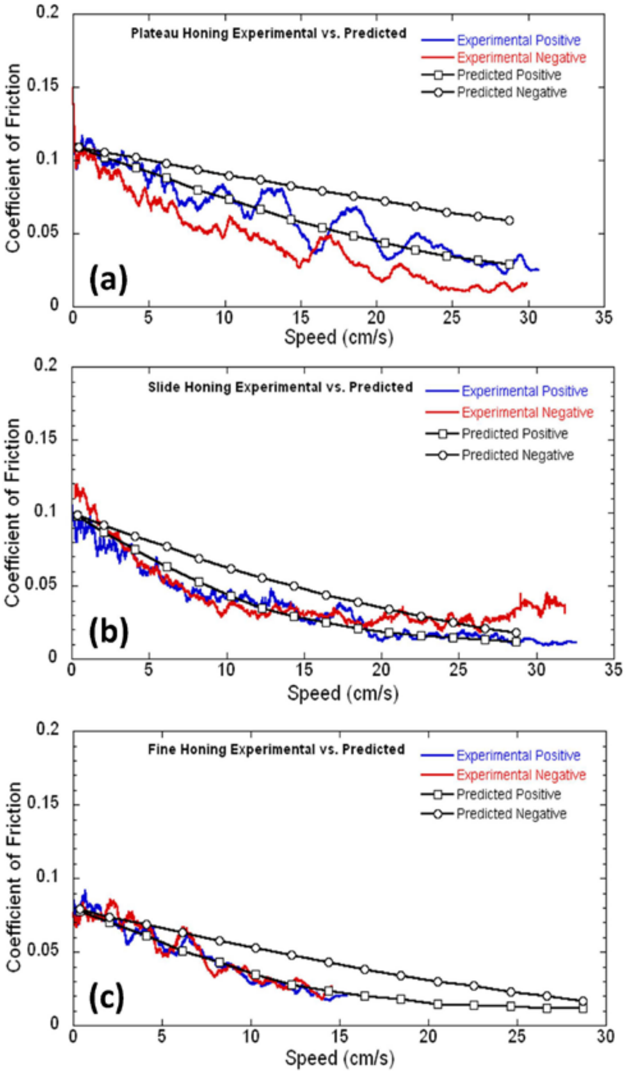

FIGURE 2. Experimental and predicted curves of friction coefficient as a function of speed for three liner finishes: (a) plateau honed, (b) slide honed, and (c) fine honed.

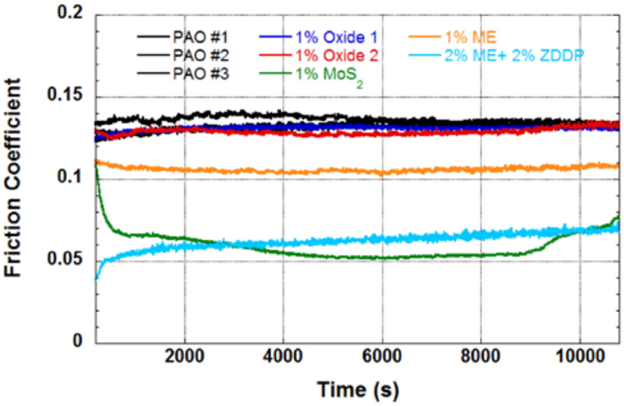

FIGURE 3. Coefficient of friction as a function of time for various additives blended with PAO basestock.

modification, and dispersion are completed, we will tribologically evaluate the formulations and try to gain understanding into the mechanisms of friction reduction.

We also investigated the effect of stroke length on the transitions between lubrication regimes. Tests were performed at stroke lengths of 10 and 30 mm. Figure 4(a) shows a plot of coefficient of friction waveforms as well as a time average of coefficient of friction as a function of cycle number over a range of speeds from 45 rpm to 525 rpm. These tests were conducted at room temperature using 10-mm stroke length and 15.7-N normal load. Figure 4(b) shows a similar plot for tests using 30-mm stroke length and speeds ranging from 15 rpm to 175 rpm. It is apparent that at the smaller stroke lengths there is more noise in the data. However, there are similarities between the waveforms at identical sliding speeds, as shown in Figures 5(a) and 5(b). (Note that the sliding speed is identical at 10 mm/360 rpm and 30 mm/120 rpm.) Therefore, a longer stroke length is more favorable in terms of higher fidelity friction data.

CONCLUSIONS

- A test method for conducting friction tests of piston ring and cylinder liner materials under lubricated conditions has been identified and reviewed.
- Experimental data obtained in benchtop tests showed reasonably good agreement with simulation data.
- Additives to PAO basestock reduced friction.
- Longer stroke length is more favorable in terms of higher fidelity friction data.

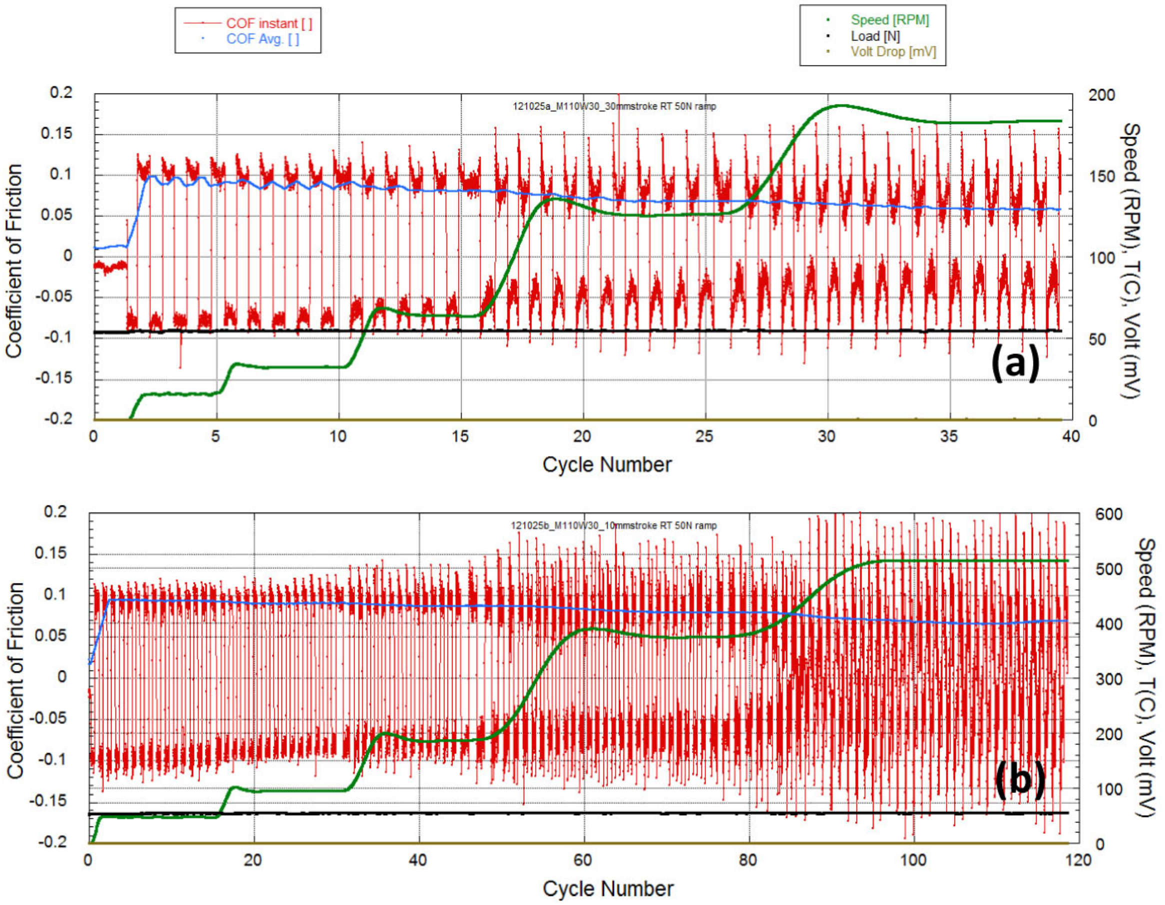

FIGURE 4. Coefficient of friction waveforms as well as a time average of coefficient of friction as a function of cycle number over a range of speeds from (a) 45 rpm to 525 rpm and (b) from 15 rpm to 175 rpm. Tests conducted at room temperature using 10-mm stroke length and 15.7-N normal load.

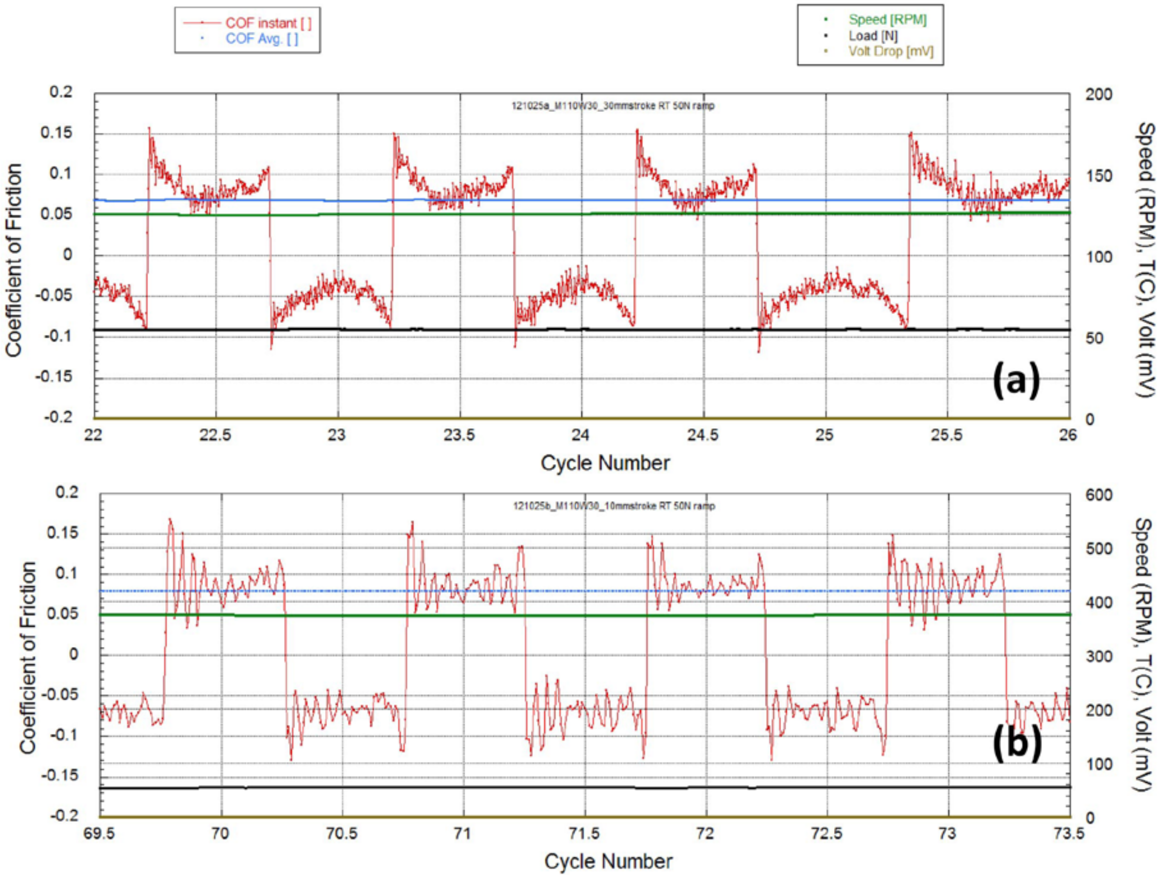

FIGURE 5. Coefficient of friction waveforms as well as a time average of coefficient of friction as a function of cycle number over a range of speeds from (a) 45 rpm to 525 rpm and (b) from 15 rpm to 175 rpm. Tests conducted at room temperature using 10-mm stroke length and 15.7-N normal load.

REFERENCES

1. American Society for Testing and Materials. Standard test method for conducting friction tests of piston ring and cylinder liner materials under lubricated conditions. ASTM G181-11, DOI: 10.1520/G0181-11.

2. Demas, NG, Erck, RA, Fenske, GR. Tribological evaluation of piston skirt/cylinder liner contact interfaces under boundary lubrication conditions. *Lubrication Science* 22(3), 73-87 (2010).

3. Profito, FJ, Zachariadis, D, Tomanik, E. One dimensional mixed lubrication regime model for textured piston rings. Proceedings of 21st Brazilian Congress of Mechanical Engineering (2011).

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Presentation to Steve Przesmitzki at Argonne National Laboratory, November 27, 2012.

2. Demas, NG, Erck, RA, Fenske, GR, Progress Report, October 12, 2012.

II.4 Advanced Lubrication Additives for Improved Fuel Efficiency

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Objectives

- Develop better understanding of the nature (structure), composition and the mechanisms of formation of tribochemical surface films.
- Investigate various methods of production of low-friction tribochemical surface films.
- Determine the pertinent properties and tribological performance attributes of tribochemical surface films.
- Validate performance in both bench top testing and engine environments.

Fiscal Year (FY) 2012 Objectives

- Identify conditions to produce tribochemical films with different frictional behavior from known additives.
- Characterize the structure and properties of tribochemical films with different frictional behaviors.
- Commence measurement of some pertinent properties of the tribochemical films.

Accomplishments

- Established an empirical connection between the structure of tribochemical surface films formed from additives and their friction properties. This will enable lubricated interface friction reduction by as much as 50%.
- Developed multiple analytical techniques to assess the structure and hence the frictional attributes of tribochemical films.
- Initiated the measurement of the mechanical and frictional properties of tribochemical films using the nano indentation technique.

Future Directions

- Continue the development of comprehensive characterization of tribochemical films, including the chemical composition and phase allotropes.
- Continue measurements of mechanical properties of tribochemical films with different structure. This will enable the establishment of correlation between the structure and properties of the film and ultimately the frictional properties.
- Explore, develop and optimize other techniques for the production of films with same or similar structure as the tribochemical films from appropriate additives.
- Validate the friction performance of tribochemical films derived from various advanced additives in an engine condition.

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INTRODUCTION

A majority of critical components in engines and transportation vehicle sub-systems are oil lubricated. Significant improvement in efficiency, and hence fuel consumption in transportation vehicles can be achieved through effective and sustainable friction reduction in lubricated components and systems. Satisfactory performance of these components and systems in terms of low friction, reliability and durability is achieved through a combination of materials, surface finish and lubricant oil formulation technologies often using an Edisonian trial-and-error approach. In order to achieve and maintain low friction in lubricated components of an engine without sacrificing reliability and durability, the trial and error approach to lubrication is inadequate and certainly inefficient. Departure from this approach; and effective and adequate friction reduction will require a fundamental understanding of both boundary lubrication and surface failure mechanisms.

Oil lubricants usually contain various performance additives to meet specific requirements. For example, anti-wear additives provide protection against wear, while friction modifiers are designed to control friction. These additives react with the surface material during oil lubricated sliding and/or rolling contact to form tribochemical surface films. Design and engineering of these tribochemical surface films is the key to friction reduction while maintaining reliability and durability. The main goal of the current project is the development and optimization of lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles.

APPROACH

In order to fully take technological advantage of this low-friction tribochemical surface layer, better understanding of the nature, the composition, the mechanism of the formation and durability of the film is required. The initial goal of this proposed effort is to develop this understanding. The overall goal is to develop the in situ generated, low-friction surface layer film technology to point of commercialization. This will involve controlled method of production, properties and performance optimization for a variety of pertinent components. Detailed modeling and validation studies (benchtop and engine tests) will also be performed.

The approach for this project will involve two key components (1) the development and optimization of the low-friction tribochemical film generation and (2) the validation of performance through engine testing at Massachusetts Institute of Technology. Briefly, this will involve the following tasks:

- Low-friction tribo film deposition technique development.
- Detailed characterization of the composition, and structure of the tribo film using combination of various analytical techniques.
- Detailed characterization of nano-mechanical properties of the tribo films.
- Tribological performance evaluation of the tribo film by a variety of bench top friction and wear testing.

RESULTS

Tribochemical films were produced from a variety of additives and combination of additives using a reciprocating line contact of 52100 steel roller sliding on different hardened alloy steel material as well as cast iron material flat. These are the most commonly used materials for lubricated components in vehicles. In terms of friction reduction, which is the focus of the present project, some additives were identified that exhibited duality in their friction behavior under boundary lubrication regime, depending on the operating contact conditions. More specifically, the operating temperature has a significant effect. Figure 1 shows the effect of temperature on the boundary friction behavior for a model additive showing frictional duality under isothermal test conditions. At low temperatures of 10° and 25°C, the boundary friction coefficient was about 0.09. At 75°C, however, the friction coefficient decreased to values as low as 0.03. At higher temperature of 125 and 150°C, the boundary friction increased back the lower temperature values. This is a significant finding, for the typical boundary friction for current commercial lubricant is usually between 0.10 and 0.12. When tested under continuously varying temperature, the model additive still displays the frictional duality as shown in Figure 2.

Structural analysis of the high- and low-friction tribochemical films from this model additive showed there is a clear correlation between the structure of the film and their friction behavior. The films are sometimes amorphous, sometimes crystalline and sometimes a mixture. This is also a significant finding, which will enable the engineering of low-friction additives and tribochemical films. In view of the important role of

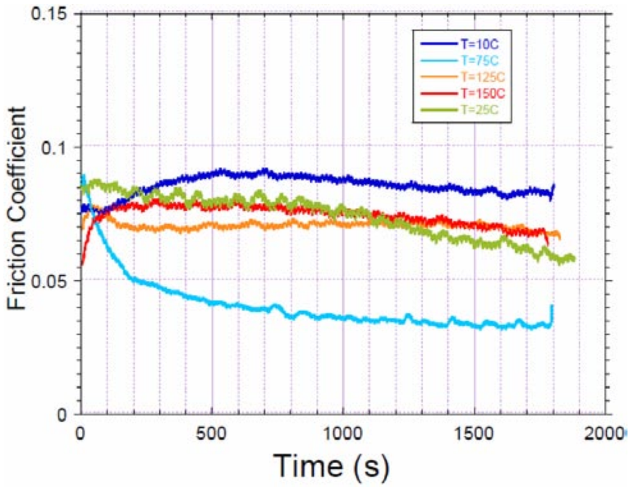

FIGURE 1. Boundary lubrication regime friction for model additive under isothermal test condition.

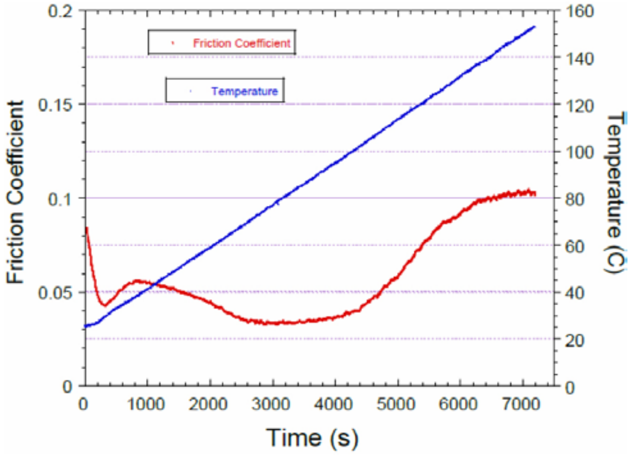

FIGURE 2. Boundary lubrication regime friction for model additive under continuously varying temperature test conditions.

temperature in the tribochemical film phase formation or transformation, mechanisms and the kinetics of this film phase change will be further explored in future work. This will enable effective selection of low-friction additive for a particular application in addition to the development and optimization of lubricant additive for low-friction attributes.

The dual friction behavior in Figure 2 is however not typical for all low-friction tribochemical films. It is true only for films in which phase transformation or phase change occurs. Figure 3 shows the frictional behavior for a tribochemical film formed from a different low-friction additive. Although some transitions were observed in the friction as the temperature increases, no phase transition occurred in this film according to structural analysis of the film. The friction remained low, as low as 0.03, which is remarkable for boundary lubrication regime. Again the typical boundary regime friction for current state-of-the art lubricant is about 0.10. The three transitions observed are most likely the result of change in mechanical properties of the films. This will be investigated later in the project. At this point, suffice to say that there is a plausible and proven pathway for sustainable friction reduction under boundary lubrication regime through the engineering of the tribochemical surface films.

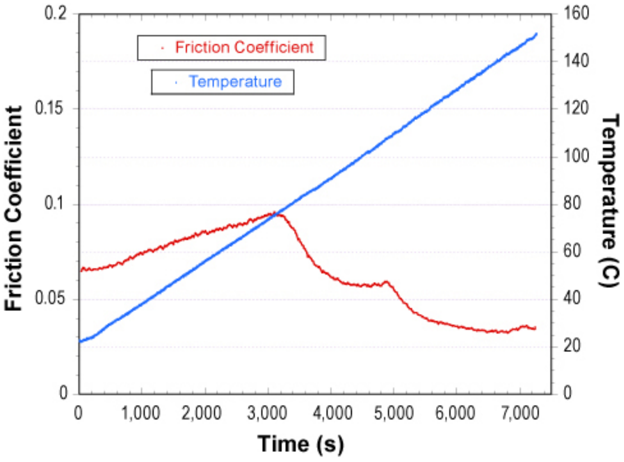

FIGURE 3. Boundary lubrication regime friction for another model additive under continuously varying temperature test conditions showing consistently low friction.

CONCLUSIONS

Although this is the first year of this project, a foundational discovery was made for the design, formulation and engineering of lubricant additives to provide sustainable friction reduction under the boundary lubrication regime. Structural analysis of tribochemical films formed from additives by a several techniques showed the films could be amorphous, crystalline and/or a mixture of both. The friction behavior under boundary lubrication regime was observed to be connected to the structure of the films. Two model additives with different structure as a function of temperature were evaluated; and their friction behavior are consistent with our finding. Preliminary indications also suggest that the mechanical properties of the films may equally have a noticeable effect on friction. Future work will be devoted to further clarification of the key factors that govern tribochemical films formation, structure, properties and friction.

II.5 Fuel Efficient Lubricants for Legacy Vehicles

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Objectives

- Design and develop novel lubricant additive package that can provide friction reduction while ensuring reliability and durability of legacy vehicles.
- Conduct comprehensive tribological performance evaluation in terms of friction, wear and scuffing for the new additive system(s).
- Develop mechanistic understanding of how the new additives function.
- Optimize the additive systems for different lubricated components and systems in transportation vehicles.
- Validate performance in both bench top testing and engine environments.

Fiscal Year (FY) 2012 Objectives

- Design functional additives in terms of friction reduction, wear prevention, scuffing prevention, and thermal dissipation using nano-particulate approach.
- Design time-release architecture and capability for the various nano-additives by appropriate encapsulation.
- Synthesize the new time-release functional additive systems.
- Conduct preliminary tribological performance evaluation of prospective nano additive systems.

Accomplishments

- Completed the structural design of time-release low-friction, wear-resistant and scuffing prevention additive system.
- Preliminary proof-of-concept test with simple polymeric surfactant encapsulation.
- Preliminary friction and wear performance evaluation of proof-of-concept systems.

Future Directions

- Select the most effective functional nano additives for friction reduction, wear prevention and scuffing prevention from preliminary performance evaluation results.
- Develop synthesis of time release encapsulation systems. Different condition and environment sensitive encapsulating will be evaluated.
- Integrate and optimize the various functional additives for blending into appropriate basestock lubricant.
- Comprehensive tribological performance evaluation of optimized and blended additive system.
- Validate the friction and wear performance of new lubricant system in an engine condition.

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INTRODUCTION

Significant fuel savings, and the consequent reduction in emissions can be achieved by improving the fuel efficiency and the use of non-petroleum-based fuels in legacy vehicles currently on the U.S. roads. Currently, there are estimated 250 million vehicles on the U.S. roads and less than 10 million of them are flex-fueled models. Currently, about 95% of fuels for these vehicles come from petroleum, about 70% of which is imported. Thus, any meaningful petroleum-based fuel savings will result in reduction of oil importation and increase national energy security. DOE has several on-going programs to develop new vehicle technologies that are more fuel efficient or use non-petroleum fuels in order to reduce oil importation. When fully implemented, (which will be several years down the road) these programs will no doubt reduce petroleum usage for transportation vehicles. Substantial fuel savings and reduced use of petroleum oil can be achieved in the near-term if the fleet of the current legacy vehicles could be made more efficient without expensive retrofit. An approach most likely to succeed is the development of lubricant that can reduce engine friction compared to the currently available ones. Also, the use higher levels (> current 10%) of ethanol bio-based fuel in the current legacy gasoline engines will require engine lubricant that can protect the engine components from expected accelerated wear. Thus, an innovative approach to develop engine lubricants for friction reduction below the current levels, and protection of engine component surfaces from accelerated wear when higher levels of bio-based fuels are used in the legacy vehicle is expected to result in substantial reduction in petroleum use in the near-term. The current proposed seeks to develop lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in non-flex-fuel legacy vehicles.

APPROACH

The main goal of this effort is to develop and deploy novel lubricant additives package that can provide sustainable friction reduction in existing legacy vehicle engines over extended time duration. The additives will package will also be designed with the attribute of mitigating the detrimental impact of the use of higher levels of non-petroleum fuels in the legacy vehicles. In the present effort, the nano particles will be specifically designed and functionalized and designed to reduce friction, and neutralize corrosive chemical species from the combustion of bio-based fuels. The nano particles will be engineered to perform these functions in a controlled released manner, similar to the time release of pharmaceutical agents. Layered nano particles with friction reducing core and pressure sensitive shell will be designed and synthesized. Under high contact pressure of boundary lubrication regime, wherein the friction is high, the particle shell will decomposed making available the friction reducing core. In such system, the additives will only be used as needed for friction reduction. Similarly, layered nano particles will be designed and synthesized with a basic core (to neutralize acid) and pH sensitive shell. When corrosive and acidic combustion by products accumulate in the engine oil, the shell layer will be removed, making available the core to neutralize the acid. Again, the additive will be activated only when needed. Formulating engine oils with these two engineered nano particulate additives will enable sustained friction reduction and the use of higher levels of bio-based (ethanol) fuels in current legacy vehicles without compromising their performance, reliability and durability. Lubricants are also act to dissipate frictional heat generated at sliding contact interface. Additives that can increase heat removal from tribological contact interface, especially under severe contact conditions will enhance the reliability and durability of the surface. Such additive exhibits an extreme pressure action. Layer nano particles will be designed and synthesized to increase dissipation of heat from tribological contact interface.

RESULTS

Additives are added to engine lubricants to improve three major functions, namely friction reduction, wear prevention and scuffing prevention. The current state-of-the-art lubricant additive technologies rely on reactive chemicals to perform these functions. In the current project, new approach of lubricant additive development will be undertaken using nanotechnology to enable time release agents for friction, wear reduction and scuffing prevention.

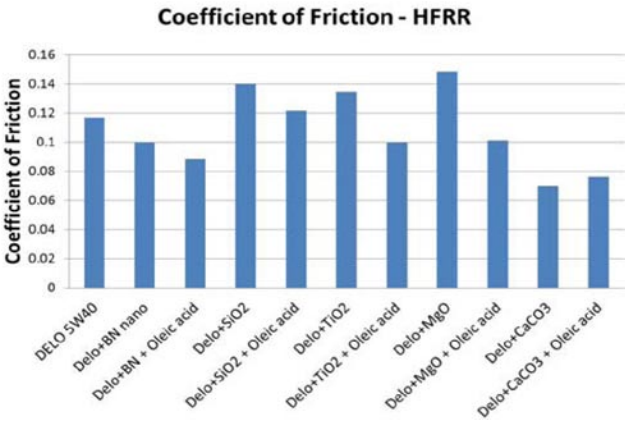
During the first year of this new project, efforts were devoted to the design of adaptive nano-particulate architectures capable of friction reduction, wear reduction, scuffing prevention and heat dissipation over extended period of time. Friction-reducing additive systems include polymer encapsulated soft metal nano particles – Ag and Cu are the starting soft metals choice. In later dates, other soft metals will be explored. Other low-friction architecture includes appropriately encapsulated layered structure solid lubricants; graphite, MoS_2, h-BN are the starting point. For wear resistance additives, the approach is to mitigate the root cause of accelerated wear which is build up of acidic combustion bye products in the lubricant, especially with the use of increased amount of bio-based fuel. The additive architecture for this function consists of basic core with appropriate surface layer. The starting materials for this class of additives are $CaCO_3$, $Al(OH)_3$, $Mg(OH)_2$. These particles will be encapsulated with appropriate surface layer(s). Finally for the scuffing prevention or extreme pressure action, a particulate system that enhances thermal dissipation is needed. A system consisting of Zn core and SiO_2 surface layer which has been shown to increase thermal dissipation is again the starting point for the additive function.

The low-friction additive architecture based soft metal (Ag, Cu) nano-particulate system covered with polymeric layer has been synthesized and blended into engine oil lubricant. Friction and wear testing of this formulation is in progress. The thermal dissipation formulation has been synthesized as well.

Initial tribological performance evaluation of some of the candidate nano particulate additives, with and without encapsulation for time release as the contact severity and contact condition changes was conducted. As a proof of concept, the nano particles tested were encapsulated with oleic acid; a common surfactant. Two types of friction and wear tests were conducted, namely (1) reciprocating ball-on-flat for both friction and wear measurements; (2) 4-ball test, primarily for wear measurement under severe contact conditions.

Figure 1 shows the average friction coefficient during reciprocating friction and wear tests. The lubricant used was DELO 5W40 engine oil. The various nano additives with and without encapsulation were added at 0.1% concentration to the oil.

The fiction results showed that addition of nano additives alone sometimes reduces friction compared



HFRR - high frequency rotating rig

FIGURE 1. Average friction coefficient during reciprocating ball-on-flat sliding.

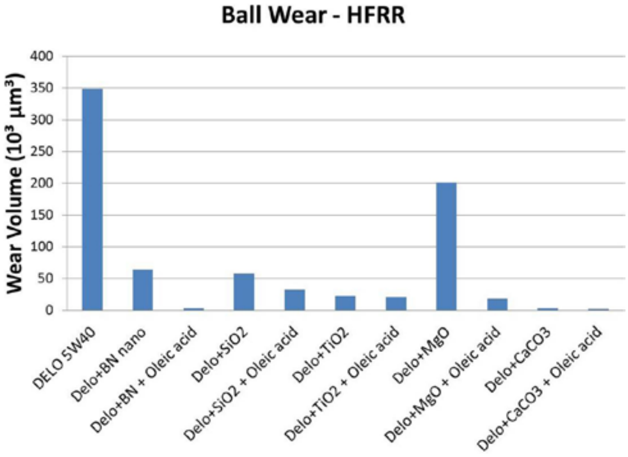


FIGURE 2. Ball wear in reciprocating ball-on-flat tests with different lubricant additives.

to the baseline oil, and sometimes the friction increased. However, for all the particles tested thus far, encapsulation reduced friction compared to particles alone without encapsulation. The impact of the nano particulate additives is much more pronounced on wear. Figure 2 shows the wear on the ball samples tested with various lubricants after 1 hour of reciprocating sliding against the flat. All the nano particulate additives results in substantial reduction in wear. Encapsulation of particles resulted in less wear than without. The most dramatic reduction in wear with encapsulation was observed in both BN and MgO particles, while encapsulation had minimal effect on wear in TiO_2 and $CaCO_3$ particles. Surface analysis of the various samples is on the way to elucidate these wear observations.

Under more severe sliding contact conditions of 4-ball test, nano particulate additives reduced wear compared to the base oil, except for $CaCO_3$ (Figure 3). Encapsulation resulted in substantial wear reduction, especially for the $CaCO_3$ particles. Again, surface analysis and characterization is on the way to elucidate these results.

CONCLUSIONS

Functional lubricant additives based on nano particulate systems that can reduce friction, wear and susceptibility of sliding surfaces to scuffing were identified. As a proof of concept for time-release in formulated lubricants, the particles were encapsulated with polymeric surfactant and their tribological performance evaluated. Preliminary friction and wear test results showed that the current project's concept of time-release lubricant additives is indeed viable and very promising.

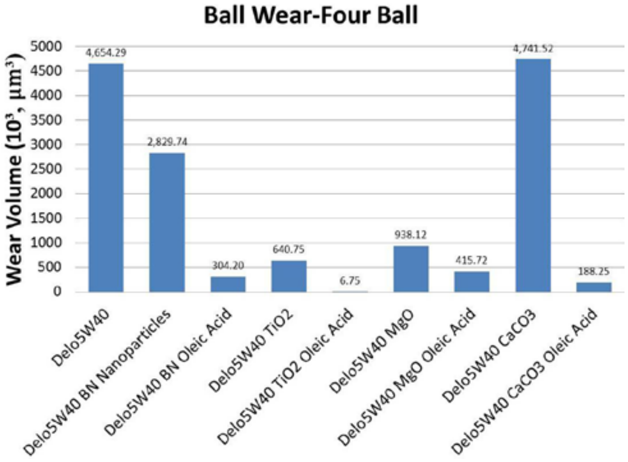


FIGURE 3. Wear in various lubricants after 4-ball wear testing.

II.6 Self-Replenishing Smart Lubricants

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Objectives

- Develop self-replenishing lubricants that would provide reduction in friction and wear comparable to the effects of low-friction solid lubricant coatings.
- Optimize smart lubricants that would provide a cost-effective drop-in solution applicable to any existing system.

Fiscal Year (FY) 2012 Objectives

- Synthesis of organic-modified polyoxometallate (POM) that is well dispersed in lubricant oils.
- Friction and wear testing of new formulations of self-replenishing lubricants.

Accomplishments

- Dispersed a tungsten (W)-based POM, phosphotungstic acid modified with oleic acid, in polyalphaolefin (PAO) 10 oil.
- Selected promising W-based POM composition based upon tribological testing.

Future Directions

- Raman spectroscopic analysis of composition of tribofilms formed after tribological testing with self-replenishing lubricants.
- Optimization of chemistry and composition of POM using the polarizability/crystal chemical approach to lubricity of oxides as initial guidance.
- Tests and selection of organic groups tailored to the intended functionality of the lubricant (friction reduction, viscosity modification, antioxidant, etc.).

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INTRODUCTION

The modern challenges for improved wear, friction, and performance of mechanical moving components could be met by lubricants that reversibly adjust to operating conditions by replenishing mechanisms. The smart lubricants we propose to develop combine benefits of both solid and liquid lubrication, and have the potential to offer significant environmental and tribological benefits, higher efficiencies, and extended life of components. An emerging technology is nanolubricants (dispersion of 10-100 nm particles in liquid lubricant), some of which have demonstrated reduction in friction and wear of moving parts.

This work aims to develop, characterize, and optimize self-replenishing nanolubricants that would provide reduction in friction and wear comparable to the effects of low-friction solid lubricant coatings in the cost-effective form of a drop-in solution that would be applicable to any existing system. Dispersed into the liquid, new low-friction additives will provide higher efficiencies than direct nanoparticle dispersions, improved heat dissipation, and superior stability in solution. They also represent environmentally friendly alternatives to the metal dichalcogenides widely used as solid lubricants. The successful completion of this work will have a significant impact on the fuel efficiency of legacy vehicles addressing the DOE mission in energy security.

APPROACH

The novel approach to lubricant additives we propose to follow draws on the concepts and mechanisms that were proven to work in solid lubricants and extends them to formulations in the liquid phase. Modified with organic groups, POM additive (polyatomic transitional metal ions, 1-20 nm in size) dispersed into base oil will provide self-assembly of strongly charged macromolecular oxide layers on moving surfaces and will result in tribochemical film formation. The extreme efficiency of the proposed self-replenishing lubricant will be provided by the monolayer self-assembly of POM on various surfaces, which results from the conjugated electronic structure of macromolecules. As the POM layer wears off, a tribofilm will further develop, reacting with POM fragments and elements of the shearing surfaces while minimizing friction. The interface of the tribofilm and solution will be continuously replenished by POMs from the bulk of the lubricant. Additional friction reduction mechanisms include repulsion of moving surfaces through the acquired surface charge and shear of organic groups on POMs. The contribution of the additional mechanisms will be stronger as the gap between the moving surfaces closes.

RESULTS

A W-based POM, namely, phosphotungstic acid $H_3PW_{12}O_{40}$ (PW12) modified with oleic acid (OA), was dispersed in PAO10 (see Figure 1). To disperse PW12 in PAO, modification with an appropriate surfactant was required. Since PAO has one unsaturated C=C bond, OA was selected as the surfactant since it has a similar unsaturated structure.

Our initial approach was partially successful. It was speculated that larger than macromolecular crystals of PW12 coated with OA surfactant had formed during re-crystallization. We are exploring other techniques of dispersing PW12 in PAO10 by using a stronger surfactant, as well as two-phase exchange reaction between ethanol and PAO, since these two phases do not mix, and ethanol can provide a macromolecular solution of PW12 without re-crystallization of powders.

The PW12 lubricant was tribologically tested in a reciprocating test rig at 100°C, utilizing cast iron liner segments against a steel ring with a CrN coating. The results are shown in Figure 2. A test of PAO10 has been plotted as a baseline. The friction coefficient of PAO10 was approximately 0.13. With the addition of PW12, only a small reduction in friction was achieved. When functionalized graphene (fcG) was added to the mixture, the friction was lowered by approximately 18%.

In these preliminary tests we are trying to identify the mechanisms and chemistries that show the most promise with regard to friction and wear reduction. The easy way to conduct such screening is by testing the effects of nanoparticle additives with various chemistries. Since the most common transition metals in POMs are W and Mo, we have tested these easily available nanoparticle additives to identify the most promising POM chemistry for further development.

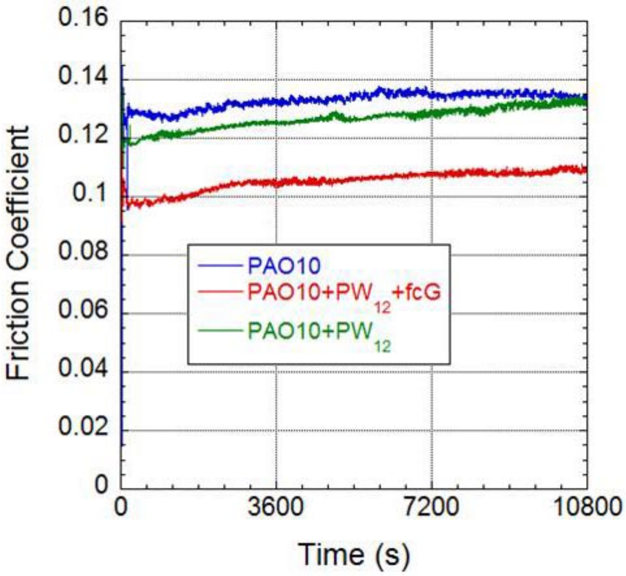

FIGURE 2. Coefficient of friction as a function of time for PW12 dispersions in PAO10.

Tests using MoS_2, WS_2, and h-BN additives with and without the surfactant octadecane thiol (ODT) were also performed. We would like to understand how these solid lubricants behave when suspended in oil and draw on some of the benefits from them to select a macromolecule that will provide the same tribological benefits but also additional mechanisms for friction reduction. The results are shown in Figure 3. Four PAO10 tests have been plotted to demonstrate repeatability. The additives MoS_2, WS_2, and h-BN were mixed with the lubricant at 0.5 wt% and 2 wt%. In the case of MoS_2, lower friction was achieved when the concentration was higher. While the results were influenced by the concentration of MoS_2, h-BN exhibited similar results at the two concentrations. The use of ODT surfactant provided beneficial results at the lower concentration for both MoS_2 and WS_2; however, when used in the higher concentration with MoS_2 it offered no benefit.

The cast iron liners were examined after testing. The results are shown in Figure 4. Mild corrosion was evident on the unworn surface of the cast iron after testing with

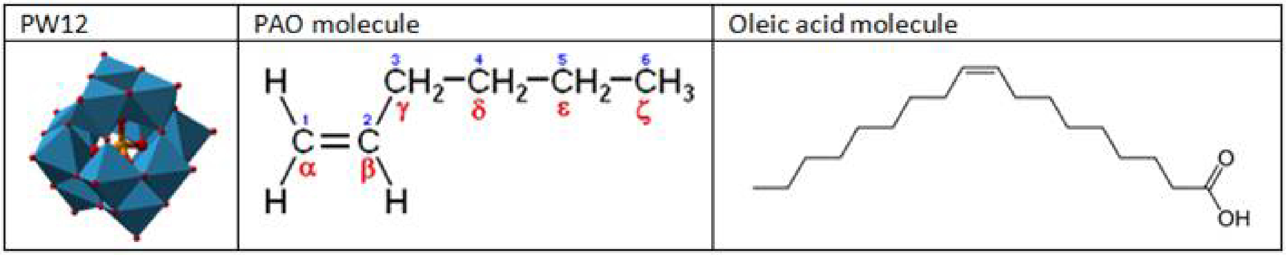

FIGURE 1. Structure of PW12 and chemical formulas of PAO and oleic acid.

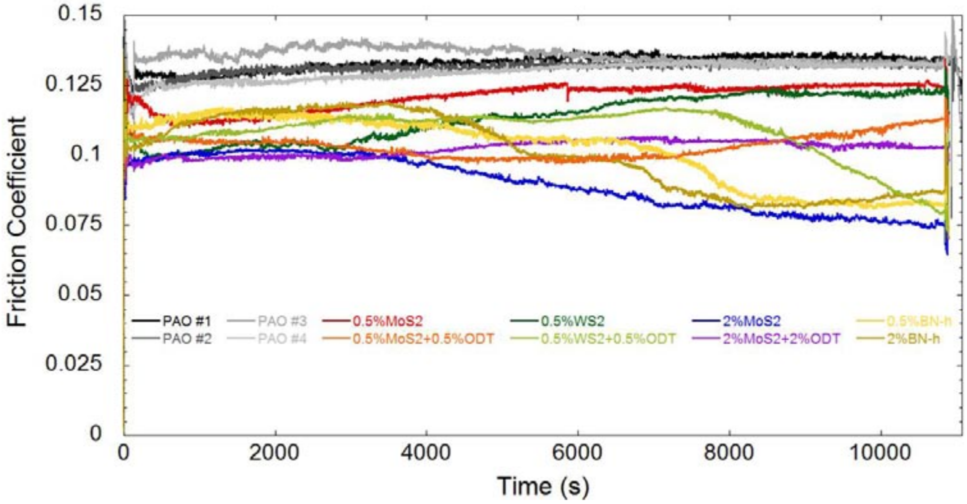

FIGURE 3. Coefficient of friction as a function of time for various additives in PAO10 + PW12.

PAO10 + PW12. It is not certain whether oleic acid or PW12 was responsible. It is interesting to note that corrosion is only evident outside the wear track. Within the worn area, the formation of a tribochemical film is evident. It has a blue appearance under the microscope, as seen in Figure 4. The formation of a tribochemical film is evident for MoS_2, WS_2 with and without ODT, and h-BN. Some type of transfer layer with a brown hue is evident on the surface of the liner tested with PW12 + fcG. We are continuing to look into the concentration effects of nano-additives and the tribological mechanisms for formulations that show lower friction.

CONCLUSIONS

- Tribological testing indicated promising results for PAO10 + PW12 + fcG.
- Tungsten-based additive shows slightly better performance than Mo-based additive.
- Achieving a good dispersion appears to be very important for friction reduction.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Presentation to Steve Przesmitzki at Argonne National Laboratory, Nov. 27, 2012

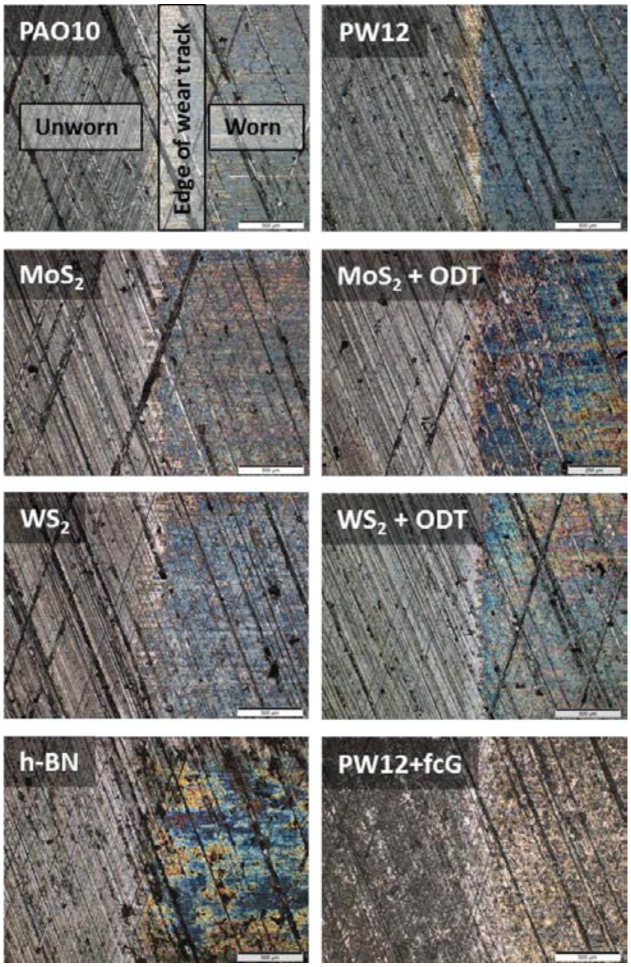

FIGURE 4. Photomicrographs of cast iron liner surface after testing showing the formation of tribofilms.

II.7 ORNL-Shell: Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency

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Objectives

- Develop oil-soluble ionic liquids as engine oil additives.
- Demonstrate 10% improvement in mechanical efficiency of internal combustion (IC) engines.
- Explore potential advantages and disadvantages of this new category of additives through systematic lab experiments, modeling, engine dynamometer tests, and field tests.

Fiscal Year (FY) 2012 Objectives

- Start design, synthesis, and characterization of a series of oil-soluble ionic liquids (ILs) with various molecular structures.
- Design tribological bench tests for various lubrication regimes experienced in engine bearing components.

Accomplishments

- A three-year Cooperative Research and Development Agreement (CRADA) between ORNL and Shell Global Solutions was signed on July 23, 2012.
- A series of quaternary structured ILs are being designed, synthesized, and characterized.
- Base oils and baseline lubricants have been determined and acquired, and complementary tribological bench tests have been determined.

Future Directions

- Continue designing, synthesizing, and optimizing oil-soluble ILs.
- Characterize the physical/chemical properties of oil-soluble ILs
- Carry out standard additive evaluation for ILs and lubricant formulation.
- Conduct systematic tribological bench tests and analyses
- Investigate and model the lubrication mechanisms of IL additives

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INTRODUCTION

For an IC engine, 10~15% of the energy generated in automobile engines is lost to friction. Automotive companies and lubricant suppliers have been looking for advanced lubricants that enhance fuel efficiency and engine durability. Developing effective additive packages in combination with a balancing lubricant viscosity has proven to be the most successful and cost effective route.

In this project, ILs are proposed as a new class of multi-functional (anti-wear and friction modifier) lubricant additives to reduce the boundary friction and allow the use of lower-viscosity engine oils to improve the engine mechanical efficiency. ORNL's previous work [1,2] has made a major breakthrough to develop a group of ILs that are fully miscible in hydrocarbon oils. These oil-soluble ILs have demonstrated non-corrosiveness, high thermal stability, and effectiveness in reducing boundary friction and wear. In the proof-of-concept bench tests, these IL additives made the low-viscosity base oils perform as well as the more viscous, fully formulated engine oils in both friction and wear perspectives [1,2]. This proposed effort jointly with the world-leading lubricant supplier Shell will further develop IL additives specifically for engine lubrication.

APPROACH

The work scope of this ORNL-Shell joint project includes: (1) design, synthesis, and optimization of oil-soluble ILs; (2) characterization of physical/chemical properties of ILs; (3) standard additive evaluation for ILs and lubricant formulation; (4) tribological bench tests and analyses; (5) investigation and modeling of lubrication mechanism of IL additives; (6) instrumented single-cylinder motored engine tests; (7) instrumented single-cylinder fired engine tests with emission analysis; (8) multi-cylinder fired engine fuel efficiency dynamometer tests (ASTM D 7589 Sequence VI); and (9) initial field tests.

ORNL leads this project with main responsibilities for IL design and synthesis, tribological bench tests, materials and surface analysis, lubrication mechanism modeling, single-cylinder engine tests, and emission analysis. Shell is responsible for evaluation of IL additives, lubricant formulation, part of tribological bench testing, and initial field testing.

RESULTS

Base oil and baseline lubricants are determined to be Shell synthetic gas-to-liquid (GTL) 4 cSt and three versions of Shell GTL-based 5W30 engine oils: fully-formulated, without anti-wear additives and friction modifiers. Shell has provided one gallon of each oil to ORNL. Several groups of ILs with three-dimensional quaternary structures have been designed and synthesized at ORNL and selected oil-miscible ILs have been provided to Shell. For example, two candidate ILs are shown in Figure 1. Both have demonstrated >10 wt% solubility in Shell GTL 4 cSt base and fully-formulated 5W30 engine oils without color change or precipitates. The oil-solubility, density, viscosity, thermal stability, and corrosivity of candidate ILs are being evaluated. Storage stability tests of the oil-IL blends are being conducted at Shell.

An IC engine contains multiple bearing interfaces: piston rings and cylinder bores, valve guides, cams and tappets, fuel injector pumps and plungers, transmission gearing, and face seals, which experience various lubrication regimes from boundary, mixed, elastohydrodynamic, to hydrodynamic lubrication, as illustrated in Figure 2.

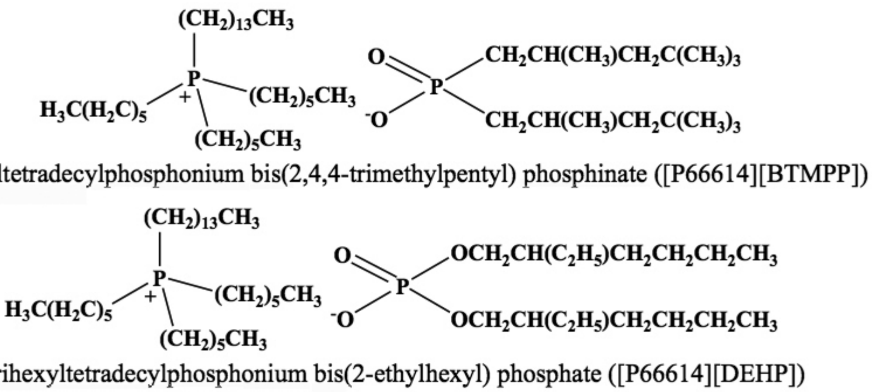

FIGURE 1. Two candidate ionic liquids with high solubility in Shell GTL base and engine oils.

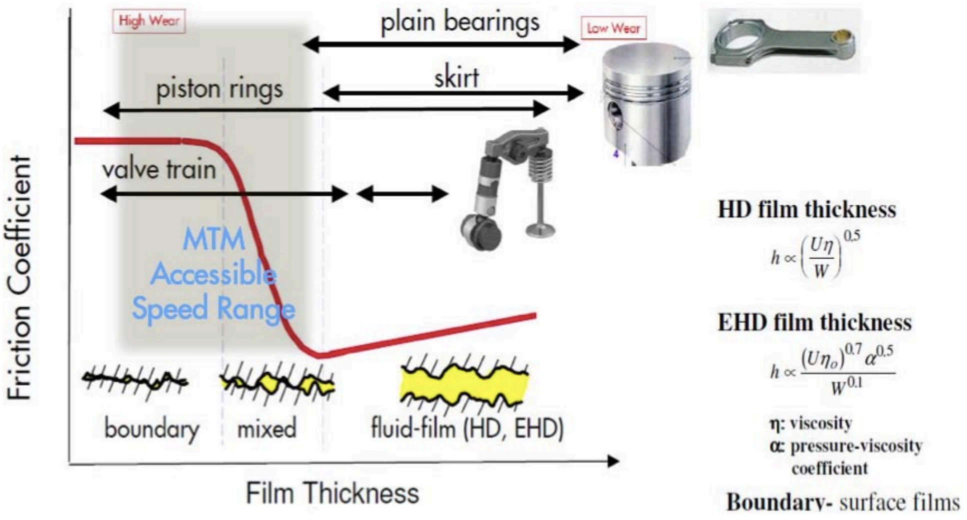

FIGURE 2. Illustration of lubrication regimes and example engine bearing interfaces.

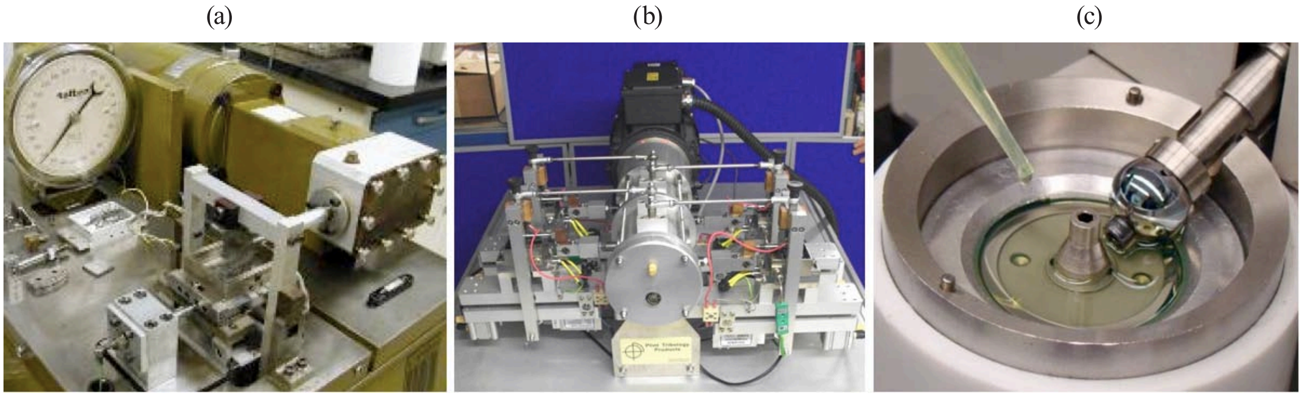
(a) (b) (c)

FIGURE 3. Tribometers: (a) Plint TE-77, (b) Plint TE-90, and (c) PCS MTM.

The team has determined complementary tribological bench tests:

- For boundary lubrication experienced at the top ring reversal region between piston ring and cylinder liner: (1) high contact stress ball-on-flat reciprocating sliding (modified ASTM G 133) with bearing steel ball against grey cast iron flat using Plint^{TM} TE-77 and TE-90 tribotesters (see Figures 3a and 3b). Test specimens have been designed, machined, and shared between ORNL and Shell. Test parameters and test matrices are being finalized; and (2) moderate contact stress cylinder-on-flat reciprocating sliding with steel cylinder against grey cast iron flat.
- For elastohydrodynamic and mixed lubrication experienced by the engine journal bearings and cams/followers: ball-on-disc unidirectional rolling-sliding to generate Stribeck curves using PCS Instruments^{TM} Mini Traction Machine (MTM2, see Figure 3b). A truncated Stribeck approach has been designed by Shell to simulate the multiple lubrication regimes at the piston ring-cylinder liner interface, as shown in Figure 4.

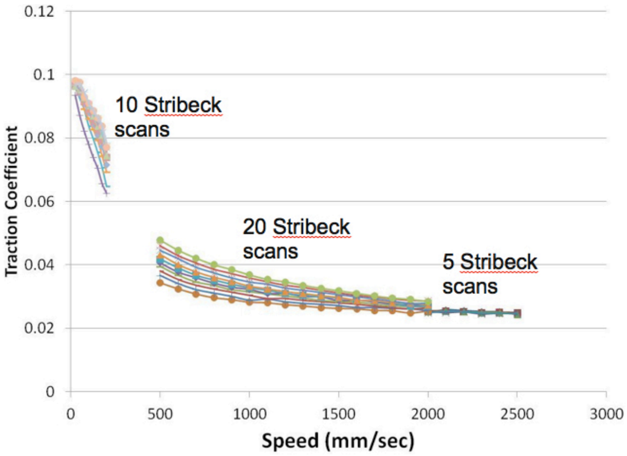

FIGURE 4. Truncated Stribeck curves for piston ring liner simulation.

CONCLUSIONS

In FY 2012, ORNL and Shell signed a three-year CRADA to execute this joint project that officially started on July 23, 2012. Although only two months into the project, good technical progress has already been made in ionic liquids synthesis and characterization, base lubricants selection, and tribological tests design.

REFERENCES

1. J. Qu, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Anti-Wear Performance and Mechanism of an Oil-Miscible Ionic Liquid As a Lubricant Additive,” *ACS Applied Materials & Interfaces* 4 (2) (2012) 997–1002.

2. B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Oil-Miscible and Non-Corrosive Phosphonium-Based Ionic Liquids as Candidate Lubricant Additives,” *Wear* 289 (2012) 58–64.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. J. Qu, B.L. Papke, H. Luo, C. Chen, P.J. Blau, H. Gao, B.G. Bunting, S. Dai, “Oil-Miscible Phosphonium- and Ammonium-Phosphate Ionic Liquids as Potential Ashless Anti-Wear Lubricant Additives,” Abstract submitted to the *STLE 68th Annual Meeting & Exhibition*, May 5-9, 2013, Detroit, MI.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. J. Qu, P.J. Blau, H. Luo, B.G. Bunting, ORNL Significant Event Award, October 2011.

II.8 Lubricant Formulations to Enhance Engine Efficiency in Modern Internal Combustion Engines

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Objectives

- To investigate low-friction, environmentally friendly and commercially feasible lubricant formulations that significantly improve the mechanical efficiency of modern engines by at least 10%, versus the 2002 level without causing increased wear, emissions or deterioration of the emission-aftertreatment system.
- To develop such lubrication system via modeling and measurements of actual film thicknesses, lubricant and additive species composition changes, and other thermal, mechanical, and lubricant conditions due to oil species depletion via vaporization (volatility), inadequate oil supply (starvation), and excessive degradation (thermal, acid contamination) locally and globally in the engine.
- To demonstrate such system in an engine.

Fiscal Year (FY) 2012 Objectives

- Develop overall project plan and interface with industrial partners for lubricant and engine development.
- Model lubricating effect for sub-system development (valvetrain and reciprocating parts).
- Set up experimental engine with separate block and head lubrication system.
- Measurement of valvetrain friction on chosen test engine.

Accomplishments

- Established research team and specific aims and targets for team members, including industry partnerships with a major engine company and major lubricant oil and additive formulator.
- Adapted and applied two engine friction simulations based on methodologies developed earlier at MIT to determine lubricant regimes in subject test engine. Established estimates of lubrication regimes in specific engine zones.
- Acquired test engine and completion of experimental setup, including construction and implementation of a standalone cylinder head (valvetrain) test bench.
- Completed initial measurements of valve train friction on chosen test engine.

Future Directions

- Develop a database for the effectiveness of specific lubricant attribute (base oil, viscosity modifiers, friction modifiers) as a function of the local operating environment.
- Based on the above, develop the lubricant/additives requirement optimized for local operating environment.
- Verification of the optimized lubricant/additive package in various engine operating zones.

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INTRODUCTION

Friction losses in reciprocating internal combustion engines occur primarily in the following areas: (i) the power cylinder (piston and rings), (ii) valvetrain components (cam, tappets, rods), and (iii) crank bearings and (iv), to a smaller extent, accessories. Their relative contributions to friction vary among engines. Estimates vary, as widely reported [1-4], and decrease in the order presented above, with power cylinder components contributing to close to half of the total friction. The lubrication regimes at the various components are also generally understood: bearing (hydrodynamic), valvetrain (mostly boundary), and piston/ring-liner lubrication mostly in hydrodynamic mode except near the end strokes where piston sliding speed is near zero at which mixed or boundary contacts occur. Most friction power loss occurs at mid-stroke due to the large sliding speed [1-4].

APPROACH

A three-phase project is planned to study the lubricant formulation requirements to achieve maximum friction improvement while limiting adverse effects. A combination of modeling and experiments will be performed, and we will correlate lubricant behavior (film thickness, supply and depletion, degradation, oil/additive species and contaminant concentrations) with friction, wear, and base-oil and additive formulations.

In Phase 1, we seek to determine ideal formulations for engine subsystems. These are the best formulations that would apply to individual engine sub-systems, which operate in different lubrication regimes, without significant adverse effects such as increased oil consumption/emissions, wear, or sulfur, phosphorus, ash by-products. Two major subsystems are the power-cylinder components and the valve train subsystem components. In Phase 2, compromises and tradeoffs for composite formulations for the overall engine system are considered. The "ideal" formulations for each subsystem serve as starting points from which an intricate process of formulation for an optimal composite lubricant that works for all components can be developed. Phase 3 entails a proof of concept. The candidate formulation will be used in an actual operating engine to identify the friction improvements in the overall engine and in the various subsystems.

RESULTS

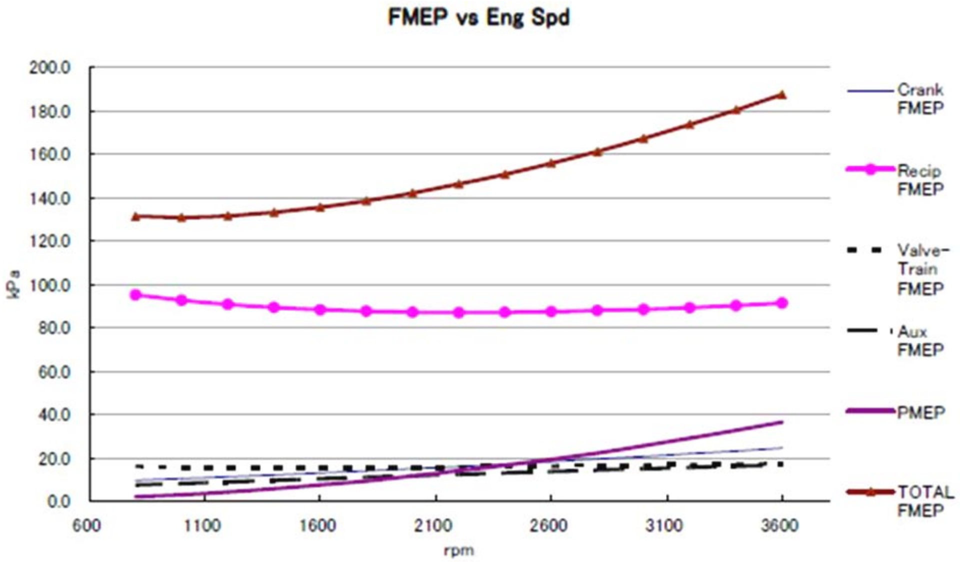
Results to date are limited to analytical model results and some preliminary experimental tests. Using models with methodologies developed at MIT to predict behavior of the chosen test engine, a greater understanding of lubricant regimes in the candidate engine is available.

The friction mean effective pressure (FMEP) for the various engine components and the total value for the selected test engine is shown in Figure 1 as a function of speed. The reciprocating component is dominant; the valvetrain, crank, and auxiliary components are substantial. The relative magnitude determines the weighting of the lubricant optimization when a single lubricant is used for the whole engine.

The team conducted limited tests on a dedicated cylinder head test bench constructed for this purpose. This preliminary data was used to size camshaft sensors for the main engine test bench, as well as validate initial model results for the valvetrain and characterize the general lubrication environment in the valvetrain. The test station is capable of resolving instantaneous camshaft torque as demonstrated in Figure 2. Upgrades are underway to improve the torsional stiffness of the apparatus to provide greater resolution of valve and injector events.

CONCLUSIONS

The focus of the project has considerable relevancy in the current energy environment. It is timely to evaluate all possible approaches to improve engine efficiency, especially from lubricant-formulation technology that can be readily implemented. Development of lubricant specifications and standards has always been an enormous undertaking. This study will aid industry by



PMEP – pumping mean effective pressure

FIGURE 1. Total FMEP and values of the individual components as a function of engine speed using model described in Ref. [5].

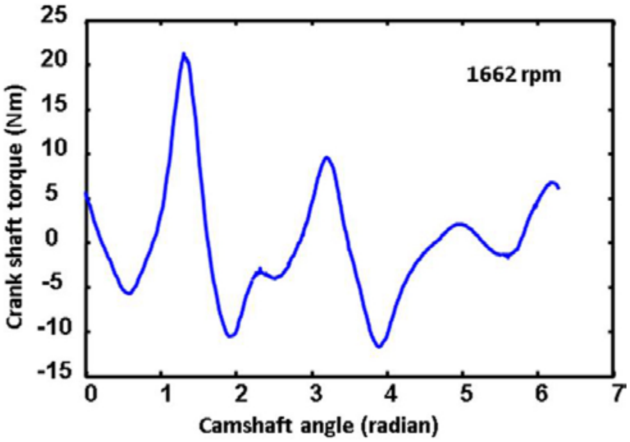


FIGURE 2. Instantaneous camshaft torque as a function of the cam angle for the test engine.

providing additional options for incorporating current knowledge of lubricant technology into formulation design. Because the project is not yet completed, final conclusions cannot be drawn. The project is scheduled for completion in 2014, at which time more results will be available.

REFERENCES

1. Takata, R. and Wong, V.W., "Effects Of Lubricant Viscosity On Ring/Liner Friction In Advanced Reciprocating Engine Systems", ASME Paper ICEF2006-1526, Proceedings of ASME Internal Combustion Engine Division 2006 Fall Technical Conference, November 5–8, 2006, Sacramento, California, USA.

2. Mansouri, S.H., and Wong, V.W., "Effects of Piston Design Parameters on Piston Secondary Motion and Skirt-Liner Friction," SAE Paper # 2004-01-2911, Society of Automotive Engineers, Warrendale, PA

3. Moughon, L., Wong, V., "Effects of Lubricant and Piston Design on Reciprocating Engine Friction," Paper ASME-ICEF2005-1343, Proceedings of the ASME Internal Combustion Engine Division 2005 Fall Technical Conference, September 11–14, 2005, Ottawa, Canada

4. Audette, W.A. III, and Wong, V.W., "A Model for Estimating Oil Vaporization from the Cylinder Liner as a Contributing Mechanism to Engine Oil Consumption," SAE paper 1999-01-1520, SAE International Spring Fuels and Lubricants Meeting, Dearborn, MI, May 3–6, 1999, SAE Trans., Vol. 108, 1999.

5. Sandoval D., and Heywood J. B., 2003, An Improved Friction Model for Spark-Ignition Engines, SAE paper 2003-01-0725, SAE International, Warrendale, PA.

II.9 Development of Modified Polyalkylene Glycol High VI High Fuel Efficient Lubricant for Light-Duty Vehcile Applications

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NETL Project Manager: Nicholas D'Amico

Subcontractors:
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- Dow Chemical Company, Midland, MI

Objectives

- Formulate new modified polyalkylene glycol (PAG)-based engine oils.
- Evaluation fundamental material properties with respect to the new lubricant formulations.
- Complete testing to understand intrinsic lubricant properties, their contributions to engine efficiency, and to determine performance characteristics in sliding and rolling friction and wear.
- Analyze lubricant additive-derived anti-wear films using surface sensitive analytical tools.
- Understand performance characteristics in motored and fired engines through specially designed test rigs.
- Estimate vehicle fuel economy and potential impact on emissions.

Fiscal Year (FY) 2012 Objectives

- Formulate prototype PAG oils and measure basic physical properties and evaluate modified PAG oils for initial friction and wear characteristics.
- Analyze surface films formed at tribological contacts of existing and new oil formulations.
- Initiate component level friction and wear evaluation.
- Select PAG formulations and characteristics to carry forward to next project phase.

Accomplishments

- Dow Chemical Company (Dow) provided 13 PAG oils throughout 2012. The oils were formulated with varying molecular structures and physical properties based on initial friction and wear data. Dow also provided PAG oil formulations with improved miscibility with mineral oils and completed a round robin test to assess variability in high-temperature high-shear viscosity (HTHS) measurements.
- Argonne National Laboratory (ANL) completed a number of friction and wear evaluations. Cylinder-on-flat reciprocating rig tests results showed a number of PAG oil formulations with lower friction and wear than factory-fill GF-5 oil. Block-on-ring test rig results indicate the scuffing load carrying capability of various PAG oil formulations differ and are not as high as factory-fill GF-5 oil. Pin-on-disk test results also showed a few PAG formulations with significantly lower friction coefficient and lower wear than factory-fill GF-5 oil.
- Ford Motor Company (FMC) completed motored engine friction screening tests on two PAG oils and factory-fill GF-5 oil at various oil temperatures and engine speeds. The PAG oil showed significant friction improvements over the GF-5 oil at all temperatures and all engine speeds.

Future Directions

- Explore additional friction benefit through appropriate friction modifier chemistry.
- Explore wear protection and oil oxidation protection capability improvements through additive chemistry.
- Complete bench top friction and wear property measurements of new oil formulations.
- Analyze tribo-films formed on contacting surfaces to understand friction reduction mechanism(s).
- Demonstrate friction reduction potential and wear characteristics on selected PAG oil formulations through motored engine component level tests.
- Continue motored engine friction evaluations and ASTM sequence tests to demonstrate anti-oxidation and wear protection capabilities and determine optimized PAG formulations.

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INTRODUCTION

The intent of this project is to develop lubricant formulations capable of at least 10% engine friction reduction compared to current GF-5 engine oil technology at the same viscosity grade level most commonly used in the North American market.

With most commercial engine oils, engine friction can be reduced by lowering oil viscosity. However, viscosity reduction creates concern for engine component durability due to reduced oil film thickness and variable cam timing device performance dependent on a minimum lubricant pressure. The use of friction modifiers have been shown to improve fuel economy, but their limitations and propensity for deposit formation leaves room for further improvement. PAG-based engine oils could represent an entirely new engine oil technology and its friction reduction capability could lead to 1-1.5% fuel economy improvement.

APPROACH

The project team consists of technical personnel from FMC, Dow and ANL. The project is led by Arup Gangopadhyay (FMC), Mr. John Cuthbert and Mr. Daniel Zweifel (Dow) and Dr. Ali Erdemir (ANL). All three partners will have key roles in achieving the project objectives. FMC is the prime contractor and will provide technical direction to ensure all engine component and multi-cylinder engine friction tests and chassis roll dynamometer tests are completed. Dow will be instrumental in providing new lubricant formulations and completing physical property testing. ANL will be responsible for bench-top friction testing, wear testing and surface analytical characterization techniques.

The project will begin with creating new formulations and performing laboratory bench testing to develop a fundamental understanding of friction, wear, and lubricant film forming characteristics to identify low-friction mechanisms. The team will then conduct component, motored engine and vehicle level testing to assess engine valvetrain friction, piston ring cylinder bore friction and motored engine friction. The engine friction data will be used to estimate PAG fuel economy benefits and the results validated with chassis roll dynamometer tests. Engine component durability will also be demonstrated through ASTM Sequence IVA and ASTM IIIG tests.

RESULTS

Lubrication Formulations

Several types of lubricant formulations have been developed. Base, fully formulated, and modified PAG oils have all undergone various physical, friction, wear and engine testing. Base and fully formulated oils were used to establish a solid foundation for comparison against PAG formulations. A number of PAG oils were formulated with a range of high temperature high shear and kinematic viscosities, viscosity index, and degree of miscibility with mineral oils. The test results have and will continue to be used throughout this project to improve oil friction reduction capabilities.

A round robin test was also conducted regarding HTHS measurement variability. Commercially available GF-5 5W-20 oils were sent to two outside laboratories with known HTHS value of 2.6 mPa.s. Three oil samples were evaluated and the values from both laboratories were within 0.05 mPa.s, which is little higher than the ASTM specification but found satisfactory for the purpose of this investigation.

Friction and Wear Evaluations

Figure 1 shows friction and wear results obtained from pin-on-disk tests under boundary lubrication condition at 80°C. The friction and wear results for various PAG oils are compared against factory-fill GF-5 oil, base oil and fully formulated oil. Generally and as expected, base oil showed higher friction and wear than fully formulated GF-5 oil, with the exception of PAG oil 97011 (97011.00 is base oil and 97011.01 is fully formulated oil).

Figure 2 shows friction and wear results obtained from high frequency reciprocating tests under boundary lubrication condition at 80°C. In general the results are similar to pin-on-disk tests. Both tests showed some of

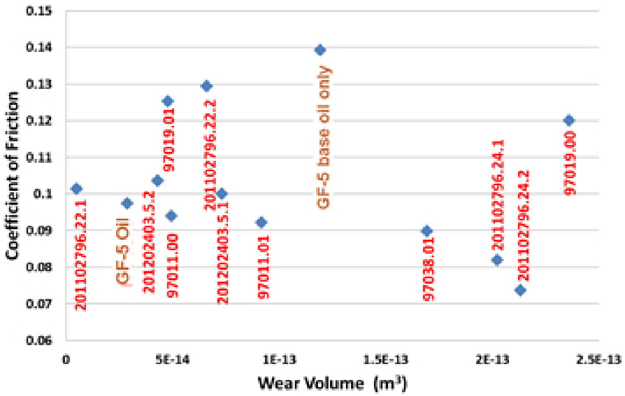

FIGURE 1. Pin-On-Disk Friction and Wear at 80°C

(a)

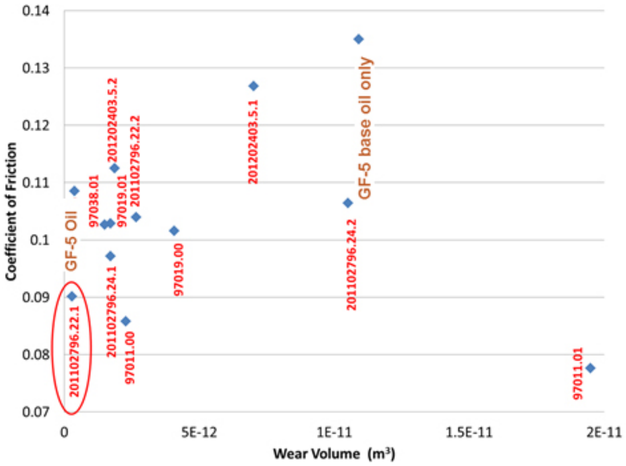

FIGURE 2. High Frequency Reciprocating Friction and Wear at 80°C

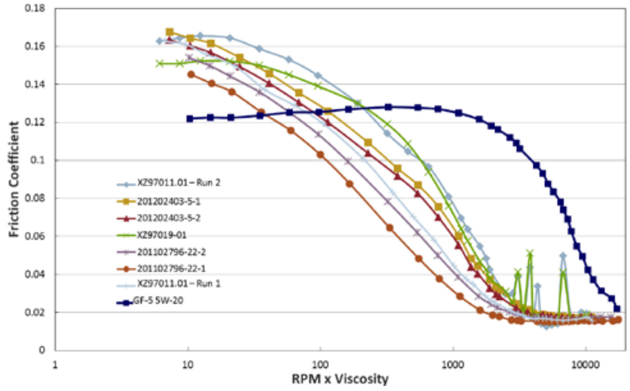

FIGURE 3. Friction Coefficients of PAG and GF-5 Oils at 100°C as a Function of Sliding Speed

the PAG oils exhibiting lower friction and lower wear than GF-5 oil.

Figure 3 compares friction coefficients of various PAG oil formulations with factory fill GF-5 oil as a function of sliding speed under boundary and mixed lubrications conditions at 100°C. All PAG oils showed higher friction coefficients than GF-5 oil at low speed (boundary condition) but lower friction coefficients than GF-5 oil at higher speed (mixed lubrication condition).

Engine Testing

Motored engine friction tests were conducted with PAG and GF-5 oils at 40°C, 80°C, and 100°C. Three tests were conducted at each temperature with very good repeatability. Figures 4-6 presents the results and shows improved friction over GF-5 oil for PAG oils 97011.01 and 97019.01. As the temperature increased, the critical tribological contacts on the engine operated under more boundary lubrication conditions and an inflection point was observed at 100°C and engine speeds lower than 1,000 RPM, a classical Stribeck curve characteristic. PAG oil 97019.01 consistently showed lower friction than GF-5 oil at all temperatures and at all speeds.

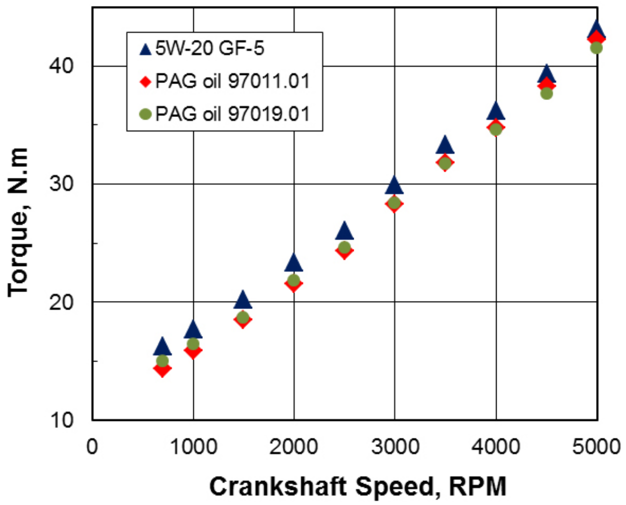

FIGURE 4. Motored Engine Friction at 40°C

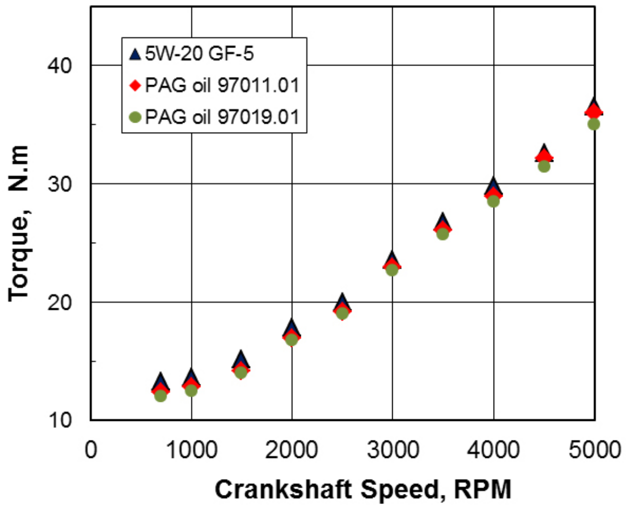

FIGURE 5. Motored Engine Friction at 80°C

ASTM Sequence VID test for fuel economy evaluation is in progress using PAG oil 97011.01 and 97019.01. The test is conducted on a General Motors 3.6-L engine at defined speed load conditions while maintaining oil temperatures at 35°C, 65°C, and 115°C. The test consists of six stages and the fuel economy index is computed based on weighting factors at each stage. The fuel economy improvement is compared against baseline SAE 20W-30 oil after 16 hours and after 96 hours of oil aging. Detailed data is not yet available.

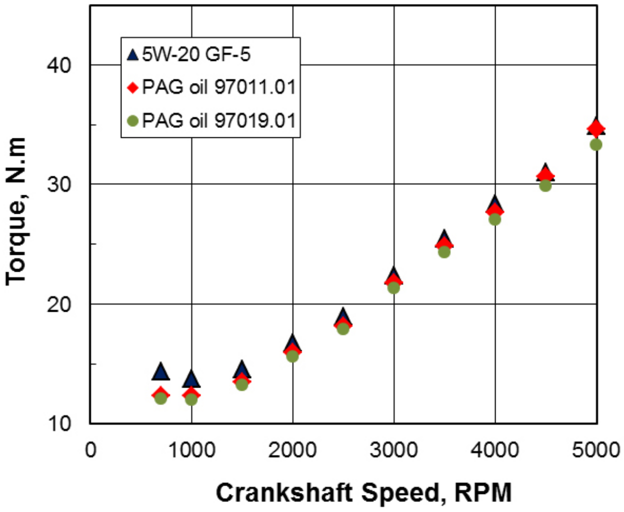

FIGURE 6. Motored Engine Friction at 100°C

CONCLUSIONS

- Under boundary lubrication, a few PAG oils showed lower friction and wear than GF-5 oils. The friction and wear characteristics of PAG oils were dependent upon their chemistry.
- Under mixed lubrication condition, the friction coefficients of PAG oils were different depending on their chemistry but were lower than GF-5 oil under the conditions investigated.
- Motored engine tests showed two PAG oils 97011.01 and 97019.01 exhibited lower friction than GF-5 oil particularly at low speed range and various engine oil temperatures.

II.10 High Compression Ratio Turbo Gasoline Engine Operation Using Alcohol Enhancement

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DOE Technology Development Manager:
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NETL Project Manager: Nicholas D'Amico

Subcontractor:
Cummins, Inc., Columbus, IN

Objectives

Investigate potential for improved performance and efficiency, and reduced greenhouse gas emissions, of gasoline-fueled vehicles by raising engine compression ratio and boost, through use of alcohols to suppress knock.

- Through engine tests and modeling in a turbocharged engine, develop performance maps as a function of compression ratio and boost level.
- Determine the knock-suppressing characteristics of ethanol-gasoline, ethanol-water, methanol-gasoline fuel blends near wide-open-throttle engine operation.
- Use engine simulations to produce performance maps to quantify the above factors at higher compression ratio and boost levels.
- Assess engine-in-vehicle gasoline fuel consumption improvement potential and cost, and consumption of knock-suppressing alcohol-based fuel, using this high efficiency, high specific power, "knock free" engine concept.

Fiscal Year (FY) 2012 Objectives

Complete set of experiments in turbocharged Ecotec gasoline engine with initial set of knock-suppressing alcohol fuels; develop and test engine simulation capability.

- Establish criteria for defining wide-open-throttle operation incorporating knock and maximum-pressure limits, and spark retard.
- Generate engine performance maps (normalized torque versus engine speed) for set of knock suppressing fuels.
- Demonstrate that up to knock onset (which depends on fuel octane rating) that engine performance and efficiency are independent of fuel.
- With engine simulation code GT Power, extend such performance maps to higher compression ratio and boost levels.

Accomplishments

- Established experimental and simulation-based methodology for generating turbocharged engine performance maps for range of different fuels at different compression ratios and boost levels.
- Developed and demonstrated fundamentally based and autoignition induction time methodologies for quantifying knock onset brake mean effective pressure (bmep) limits.
- Tested range of knock suppressing alcohol (and blended) fuels and defined their high load behavior.
- Generated performance maps experimentally, and through modeling, with gasoline and knock-suppressing fuels.

Future Directions

- Complete engine performance maps for turbocharged engine with broader range of gasolines, alcohols, alcohol plus water blends at higher compression ratio and boost levels.
- Initiate engine-in-vehicle simulations to generate vehicle fuel consumption data and knock suppressing fuel requirements with these performance maps.
- Upgrade our turbocharged engine test facility to operate at higher compression ratio and boost levels.
- Combine our engine test data with similar data generated by Cummins, Inc. at higher compression ratio and boost levels.

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INTRODUCTION

The objectives of this project are to quantify the potential for improving the performance and efficiency of gasoline engine technology by use of alcohols to suppress knock. Knock-free operation is obtained by direct injection of a second “anti-knock” fuel such as ethanol, which suppresses knock when, with gasoline, knock would occur. This enables use of higher compression ratios, increased turbocharging boost, and engine downsizing. This project combines engine testing and computer simulation to quantify the potential for improving the efficiency of gasoline spark-ignition engines, and the resulting engine-in-vehicle fuel consumption reductions.

APPROACH

Our approach is to generate engine performance maps with compression ratios and boost levels significantly higher than current values, with various knock suppressing fuels (such as ethanol) used at high-load to prevent the occurrence of engine knock with gasoline. Experiments and simulations will be used to develop these maps. Knock onset limits will be defined experimentally and through induction-time integral and fundamental kinetic autoignition modeling. These performance maps will be used in engine-in-vehicle simulations (PSAT) to quantify the reductions in vehicle gasoline consumption so realized, and the amount of the different knock-suppressing fuels required for different driving cycles. The knock-suppressing fuels to be examined are ethanol, ethanol-gasoline blends, ethanol-water blends, and methanol.

RESULTS

Experimental work in our turbocharged direct-injection General Motors (GM) Ecotec gasoline engine test facility has focused on producing the experimental data needed to generate engine performance maps with gasoline and knock-suppressing fuels. The computer simulation tools for engine combustion analysis (GT-Power), and for knock-onset calculations (CHEMKIN), have been used to interpret and expand the experimental database. These simulations are being used to generate performance maps and knock onset limits for engine designs with higher compression ratios and boost levels. A methodology for quantifying the amount of anti-knock fuel needed to suppress gasoline-fueled knock has been developed.

An important goal in 2012 was to compare fuel conversion efficiencies and determine the knock onset limits for different fuel blends using direct fuel injection. Fuel conversion efficiencies of gasoline at different load conditions and speeds for the 85% ethanol in gasoline (E85), Research Octane Number (RON)96 and RON91 gasoline, and 25% ethanol in gasoline (E25) have been compared. Up to about two-thirds maximum load, the maps are essentially the same, a result we use to construct a “universal efficiency map.” The knock onset limit for these fuels has been determined to assess how the performance of the engine is limited by knock.

Figure 1 shows the bmep versus engine speed performance map for E85 with the standard version of this 2-liter direct-injection turbocharged GM Ecotec engine. With E85, this engine is not knock limited. However, above 2,000 kPa bmep, spark retard is required above about 2,000 rev/min to avoid sustained operation above our engine’s maximum pressure limit. The knock-limited bmep for RON96 gasoline is at about 1,300 kPa; for E25 it is at 1,800 kPa. Above these limits, fuels with higher octane ratings are needed to suppress knock.

Figure 2a shows the brake fuel conversion efficiency versus load at constant engine speed (2,500 rev/min) for RON96 gasoline and E85, up to the knock onset limit. At close to maximum brake torque spark timing, the efficiency vs. load behavior of these two fuels (with substantially different octane ratings and knock onset limits) is essentially the same.

A computer model of our test engine has been set up in the engine simulation code GT-Power so we can model engine behavior. The Rassweiler-Winthrow method of analysis of cylinder pressure data was used to generate burn rate information on the different fuels used. Performance maps have been developed at maximum for best torque (MBT) spark timing, or as close to MBT timing as we could achieve given maximum pressure and knock limits.

Brake efficiency values from experiment and simulation have been compared. Figure 2(b) shows

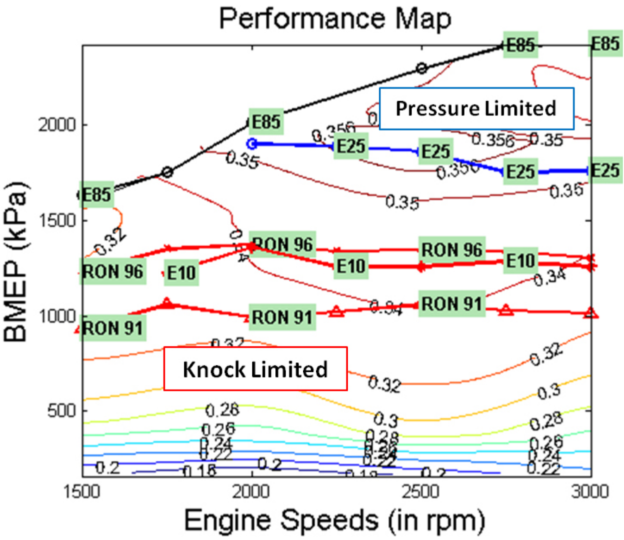
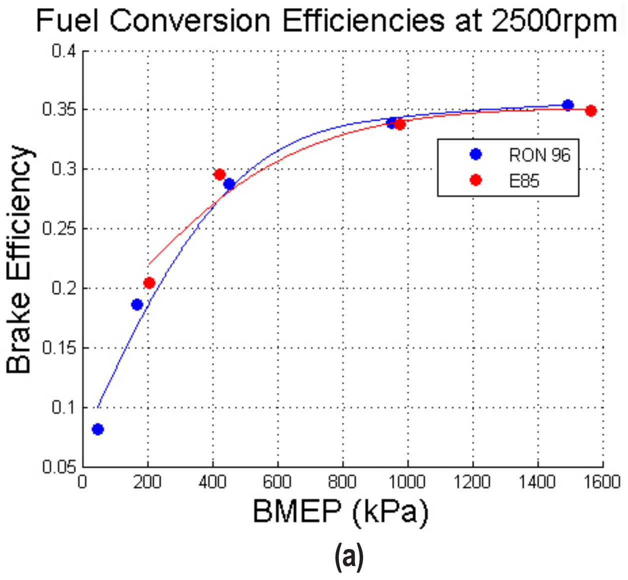
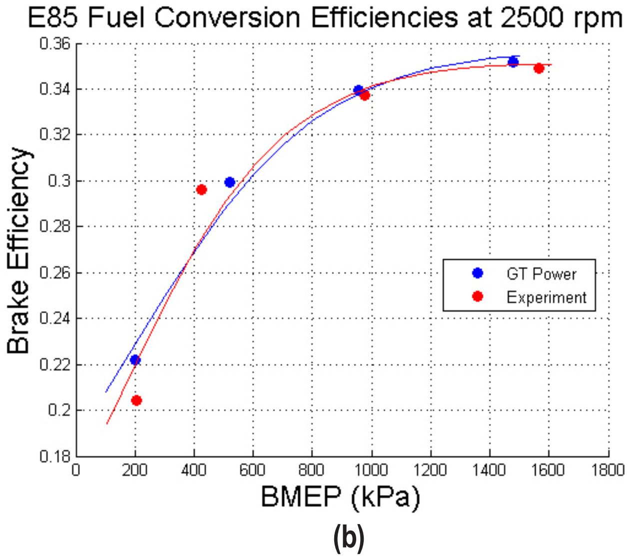


FIGURE 1. Turbocharged engine performance map: bmep as a function of engine speed showing engine peak pressure constraint, and knock onset limits for RON91, RON96, E19, E25, E85, at MBT spark timing.



(a)

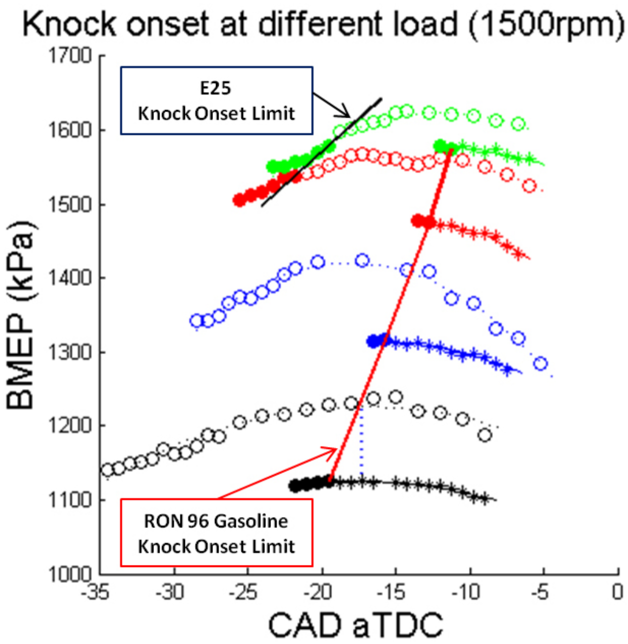


(b)

FIGURE 2. Engine brake fuel conversion efficiency as a function of load (bmep): (a) for RON96 and E85 fuels, at 2,500 rev/min; (b) brake fuel conversion efficiency as a function of load at 2,000 rev/min, E85 fuel, engine experiments and GT-Power simulation.

one such comparison. The difference is modest. We now use this calibrated version of GT-Power to develop performance maps at higher engine compression ratios and boost levels for use in the Phase II vehicle simulation work. We are using the Livengood and Wu induction time integral model combined with the Douaud and Ezyat autoignition correlation to predict knock occurrence. Also, chemical kinetics autoignition calculations are showing useful potential as knock predictors.

Empirically, see Figure 3, knock onset spark timing (knock limited spark advance) as a function of engine load, at given speeds, scales almost linearly. Note that RON96 gasoline limits spark advance: MBT spark timing cannot be realized at these conditions. For E25, the knock limit at these conditions is over advanced beyond MBT spark timing so is not a constraint.



CAD - crank angle degree; TDC - top-dead center

FIGURE 3. Knock onset spark timing from spark sweeps at different engine loads (manifold air pressures) at 1,500 rev/min, RON96 and E85 fuels.

In Phase II, we plan to increase the compression ratio and the engine's boost level to further explore the engine and engine-in-vehicle fuel efficiency improvement potential. Currently the base turbocharged engine studied at our facility has compression ratio of 9.2. Our collaborators at Cummins Research and Technology Center have a single-cylinder engine that can be operated at compression ratios of up to 14. To be able to compare our data and their data at the same compression ratio, we have decided to upgrade our engine to a compression ratio of 11.5. We would then have two compression ratio levels at which to compare results.

CONCLUSIONS

- The brake efficiency contours on our turbocharged engine's performance map, up to each fuel's knock onset bmep, are independent of fuel type.
- Blends of gasoline with increasing amounts of ethanol, and continuing with E85-water mixtures, substantially enhance knock suppression through higher fuel chemical octane and evaporative charge cooling.

- Fundamentally based and empirical autoignition analysis tools show promise as predictors of knock onset.
- Project data to date supports the prospects for substantial improvements in vehicle fuel consumption through application of this “knock-free” gasoline engine concept.

FY 2012 PUBLICATIONS/PRESENTATIONS:

This project has not yet reached the stage where publications, etc., beyond DOE Quarterly Progress Reports are appropriate.

III.1 Fuel Effects on Advanced Combustion Engines

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Kevin Stork

Objectives

- Obtain representative samples of new, unique, or emerging fuels and screen with engine and laboratory analytical techniques. Continue to add to a database of results and develop tools for the rapid, efficient screening of new fuels and fuel components.
- Continue to utilize statistical analysis tools to study fuel effects on engine control and engine performance.
- Determine extent that kinetic mechanisms can be reduced for efficient computational fluid dynamics (CFD) calculation while still showing fidelity to fuel changes.
- Continue to build alliances with industry, universities, or other labs which will advance an understanding of fuel chemistry and property effects on combustion and engine performance and help disseminate DOE research results.

Fiscal Year (FY) 2012 Objectives

- Upgrade commercially available pyrolysis oil through hydrotreating, separation processes and filtration to make it suitable to evaluate in an engine.
- Experimentally evaluate pyrolysis oil-derived diesel fuel in a single-cylinder engine.
- Evaluate biodiesel fuel blends derived from algae and fish oil.
- Build and strengthen partnerships with industry and universities by experimentally evaluating fuels, sharing data, and other collaborations.

Accomplishments

- Developed a multi-step process for upgrading pyrolysis oil to be compatible with diesel engines mixed at a 20% blend ratio.
- Experimentally evaluated pyrolysis oil in a single-cylinder diesel engine.
- Produced biodiesel that approximate algae and fish oil sources.
- Experimentally evaluated thermochemically derived renewable diesel produced at the University of Maine.

Future Directions

There are a number of outstanding commitments from this project that will be completed in FY 2013, including the experimental evaluation of the biodiesel-derived fuels.

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INTRODUCTION

Understanding the relations between fuel properties and engine performance and efficiency is among the greatest needs expressed by engine, automobile, and fuel companies. This is especially true as fuels continue to diversify and increased world trade and international business requires engines and vehicles that can operate anywhere in the world, regardless of country of origin. Fuel formulation and quality have a substantial impact our ability to fully optimize engine performance and efficiency, for both conventional and high efficiency engine operating regimes. Fuel composition impacts whether engines will operate at all and also influences the combustion rate, control, cycle-to-cycle consistency, and emissions. Although non-petroleum-based fuels are emerging and will play a larger role in future fuels, the bulk of diesel and gasoline fuels will continue to be derived from conventional and unconventional petroleum crude for the foreseeable future. As such, this research is focused on gaining a broad understanding of chemistry and property effects for petroleum, non-petroleum, and blends in a variety of engine platforms.

APPROACH

The primary goal of this research is to study the effects that fuel formulation and emerging fuels have on conventional and advanced combustion regimes. This includes identifying challenges or incompatibilities with the emerging fuels, as well as identifying fuel-specific behavior that can be exploited for improved emissions or increased efficiency. Fuel samples for experimental evaluation in this project are obtained through collaborations with other laboratories, universities, industry, or are synthesized in-house. The fuels evaluated this year include renewable pyrolysis oil derived fuel through collaboration with the University of Georgia, renewable thermochemically derived fuel through collaboration with SeaChange Group LLC and the University of Maine, and biodiesel derived from algal oil and fish oil were synthesized in-house for evaluation.

Fuels research for this project is mainly conducted on an air-cooled single-cylinder engine platform that is capable of being configured for conventional direct injection diesel operation or homogeneous charge compression ignition combustion. It is also capable of evaluating fuel performance with a minimal volume of fuel. This engine platform is well understood, with a great deal of historical data for comparison, as well as an available engine mesh for CFD and kinetic modeling.

RESULTS

Renewable Pyrolysis Oil

Pyrolysis oil was obtained by ORNL from Honeywell's UOP. The raw pyrolysis-derived fuels were upgraded by the University of Georgia under subcontract using a multiple-step autoclave hydrotreating with a variety of catalysts. More than 30 experimental upgrading runs were performed to determine the best catalyst and conditions for upgrading. Once the upgrading process was finalized, a number of batches were run to produce approximately 1 liter of fuel which was sent to ORNL, shown in Figure 1.

The hydrotreated fuel had to be upgraded even further onsite at ORNL because of its high levels of suspended solids, low pH, and high levels of emulsified water. A process was developed to simultaneously neutralize the acid and separate the water using a 2-phase extraction. This resulted in fuel with low oxygen and low cetane number. The pyrolysis oil was evaluated in the experimental engine in a 20 vol% blend, and its performance was consistent with its low cetane number. A chromatogram of the 20 vol% pyrolysis oil fuel blend is shown in Figure 2.

Algal and Fish Oil Biodiesel

Biodiesel methyl esters were synthesized from oils that were derived from algal and marine sources. Initial attempts at obtaining pure algal oil from an algal oil manufacturer were unsuccessful, so commercial food grade oil was chosen instead. Udo Oil is a blend of algal and plant-based oils and Omega-3 comes from fish. In both cases, manufacturers report a triacylglyceride profile that includes a significant fraction of long highly unsaturated fatty acid chains, as well as the more common C16 and C18 components as seen in soy-based biodiesels.

FIGURE 1. Pyrolysis oil after upgrading at the University of Georgia.

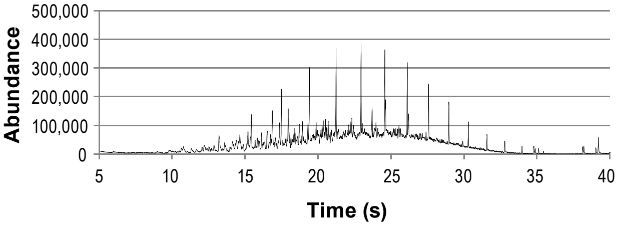

FIGURE 2. Chromatogram of the 20 vol% pyrolysis oil in diesel fuel experimentally evaluated at ORNL.

Before processing, the acid number was measured in the oil samples using ASTM method D664. The acid number of the Udo Oil was significantly higher than that of the Omega-3 oil, so the Udo Oil was treated with a homogeneous acid esterification step using a Parr reactor, shown in Figure 3, to reduce its acidity. The esterification was carried out at 65°C for 2 hours at a stirring rate of 600 rpm. The esterified Udo Oil was rinsed with methanol until the acidity of the rinses was less than 0.01 M. Both oils were then taken through a homogeneous base-catalyzed transesterification process, at 65°C for 10 minutes. The reaction time was chosen based on results from earlier experiments where slow degradation of the biodiesel product could be observed at reaction times longer than 10 min. Most of the conversion

FIGURE 3. ORNL apparatus for washing and polishing biodiesel.

occurred in the first two minutes of the reaction. The product was separated from the glycerine layer and washed repeatedly with dionized water to neutral pH, pH<8.0. The methyl esters were dried on Na_2SO_4 and polished on a column of SiO_2 to remove residual impurities.

Approximately 1 liter of biodiesel has been produced from both the Udo-Oil and the Omega-3 oil. In FY 2013 the experimental measurements of the fuel properties will be completed, including measuring the fatty acid methyl ester profile, viscosity, and acid number. In addition, the fuels will be evaluated experimentally using the ORNL Hatz single-cylinder diesel engine.

Thermochemically Derived Fuels

The thermochemically derived fuel was produced at the University of Maine and SeaChange Group LLC using thermal deoxygenation (TDO), a non-catalytic process with demonstrated potential for the production of low oxygen content feedstock oil from biomass. The primary step within the TDO process is a single-step decomposition reaction that converts calcium-neutralized biomass hydrolyzate to crude hydrocarbons at 450°C under an ambient pressure inert atmosphere. Using this technique, the production of highly deoxygenated crude hydrocarbons can be produced with process yields of over 20 wt% biomass feedstock. The resulting TDO oil has low oxygen (<4 wt%), low total acids (<1.5 mg KOH/g oil) and a higher heating value of over 40 MJ/kg. TDO crude oil boiling point distribution spans from 85 to 585°C.

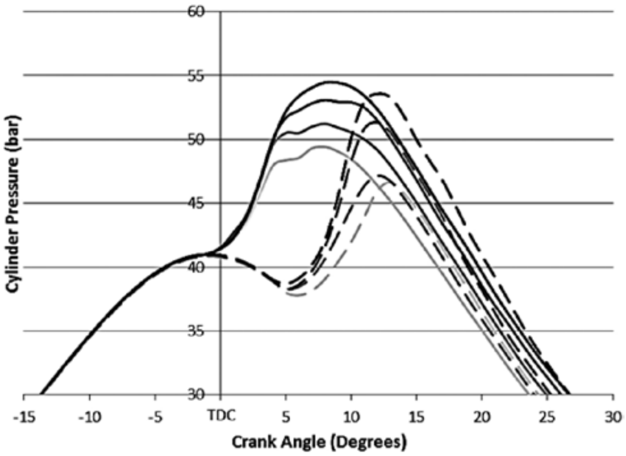

FIGURE 4. In-cylinder pressure trace comparison of an ultra-low sulfur diesel fuel (—) and TDO oil (---) blended to 50/50 vol%. Engine speed: 1,800 RPM, darker line shading signifies higher engine loads.

The purpose of this research effort is to determine the combustion quality of TDO-derived fuel products in a diesel engine. ORNL, in collaboration with the University of Maine and SeaChange Group LLC, has evaluated two TDO-derived fuels in a single-cylinder diesel engine. The fuels were supplied by the University of Maine and consisted of two blends; 1) a straight run TDO oil blended to 50/50 vol% with ultra-low sulfur diesel and 2) a 100% TDO distillate obtained by TDO distillation fractionation. The fuels were found to be operable in stock diesel engine configurations with the addition of intake air heating. The fuels were operated at a fixed engine speed and combustion behavior was characterized over a load sweep. The fuels showed performance consistent with a low cetane number fuel at all loading conditions. This resulted in combustion timing delay and an increase in most engine out emissions as detailed in Figure 4.

This data will be used by the University of Maine and SeaChange Group LLC to refine processing steps in the production of TDO fuels and represents a baseline dataset for the ongoing development.

CONCLUSIONS

Significant progress was made in FY 2012 to evaluate emerging renewable fuels in the diesel boiling point range. This included developing a multi-step process to upgrade to upgrade a commercial pyrolysis oil to make it compatible with diesel engines, producing biodiesel from fish oil and algae oil, and experimentally evaluating a thermochemically derived diesel fuel. Relative to previous years, the emphasis in FY 2012 had a greater emphasis on developing the fuel. Specifically this refers to the multi-step upgrading process developed for the pyrolysis oil and the production of the biodiesel.

Both the pyrolysis oil and the thermochemically derived fuel had very low cetane number, which can most likely be attributed to the derivative aromatic molecules from the larger lignin structures from the biomass.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Bruce Bunting, "Petroleum Infrastructure, Fungibility, Compatibility," 4th International Conference on Sustainable Automotive Technologies, ICSAT2012, Melbourne, AU.

2. Bruce Bunting, "Recent Trends in Emerging Transportation Fuels and Energy Consumption," 4th International Conference on Sustainable Automotive Technologies, ICSAT2012, Melbourne, AU.

3. Bruce Bunting and Alison Boyd, "Pyrolysis Oil Properties and Chemistry Related to Process and Upgrade Conditions for Pipeline Shipment," ORNL/TM-2011/518, January 2012 (note that this study and report was funded by DOE OBP).

III.2 Fuel Effects on Mixing-Controlled Combustion Processes in High-Efficiency Compression-Ignition Engines

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Kevin Stork

Objective

Facilitate the introduction of renewable and/or unconventional fuels and the advanced engine-combustion strategies for their utilization in a manner that enhances domestic energy security, economic competitiveness, and environmental quality. Specifically, provide:

- A fundamental understanding of fuel composition and property effects on mixing-controlled combustion strategies by formulating and studying well-characterized reference fuels made from pure compounds as well as commercial blending stocks.
- High-quality experimental data for analysis and model development to facilitate rapid and cost-effective computational engine optimization for evolving fuels.
- Unbiased assessments of proposed new fuel candidates based on their end-use characteristics.

Fiscal Year (FY) 2012 Objectives

- Develop a methodology for formulating surrogate diesel fuels (made from eight or fewer pure compounds) that have compositional, ignition-quality, volatility, density, and other characteristics similar to those of real-world diesel fuels containing thousands of compounds.
- Acquire high-quality experimental data on the mixing-controlled combustion characteristics of a set of reference fuels created from real-world blending stocks and encompassing significant variations in ignition quality, aromatic content, and 90 vol% distillation temperature.
- Conduct a literature review to assess the feasibility of using raw liquids from the fast pyrolysis of woody biomass as fuels for modern compression-ignition (CI) engines.

Accomplishments

- Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council (CRC) in developing a methodology for formulating diesel surrogates that matched the carbon-bond types, ignition qualities, volatilities, and densities of two real-world diesel fuels to within 5 mol%, 4%, 2%, and 4%, respectively, on average.
- Completed the data-acquisition phase of a large parametric investigation of fuel effects on mixing-controlled combustion using CRC Fuels for Advanced Combustion Engines (FACE) diesel reference fuels #1A, #2A, #6A, and #8A, as well as a 2007 #2 ultra-low-sulfur diesel (ULSD) emissions-certification fuel.
- Conducted a literature review showing how and why raw liquids created from the fast pyrolysis of woody biomass are not suitable as fuels for modern CI engines.

Future Directions

- Complete the data analysis for, and draw conclusions from, the large parametric study of the emissions-certification and FACE diesel reference fuels.
- Conduct engine tests on surrogate and real-world target fuels to more thoroughly assess the success of the surrogate-fuel formulation methodology and to assist in its optimization.
- Expand the fuel-effects studies to include oxygenated/renewable fuels of interest, higher injection pressures (≥2,400 bar), and laser-induced incandescence diagnostics to better understand and quantify the production, oxidation, and distribution of soot within the cylinder.

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INTRODUCTION

This project is focused on the DOE goal of overcoming technical barriers to the utilization of new renewable and/or unconventional fuels in advanced reciprocating engines. The technical barriers are largely due to insufficient data and fundamental understanding of how fuel composition and property changes affect engine efficiency, emissions, and performance. Hence the research regularly involves formulating well-characterized reference fuels and testing them under tightly controlled engine operating conditions using simultaneous laser-based/optical and conventional diagnostics, coupled with detailed data analysis. A surrogate fuel (i.e., a fuel composed of a small number of pure chemical compounds and formulated to match selected properties of a real-world "target" fuel) is an example of such a well-characterized reference fuel. Surrogate diesel fuels have been a primary focus of work during the current reporting period, as described below, and mixing-controlled CI combustion strategies are of particular interest due to their inherently high efficiencies and ease of control.

APPROACH

A working group was formed under the auspices of CRC to create, apply, and verify the success of a methodology for formulating diesel surrogate fuels that accurately match the compositional, ignition-quality, volatility, and density characteristics of their respective target fuels. This effort was led by the principal investigator and a senior fuel scientist from Chevron, and included participation from other energy companies, U.S. national and Canadian federal laboratories, and engine manufacturers. The collaborative team brought to bear the broad and specialized skill set required to achieve the research objectives, as described below.

For the study of the FACE and emissions-certification #2 diesel reference fuels under mixing-controlled CI combustion conditions, the primary experimental apparatus used was a single-cylinder version of a modern-technology, heavy-duty, 4-stroke, direct-injection, CI engine that has been modified by Sandia to provide extensive optical access to the combustion chamber [1]. Detailed, critical analysis of the comprehensive dataset from optical and conventional diagnostics can provide an enhanced understanding of fuel effects on in-cylinder mixing and combustion processes.

RESULTS

This report summarizes some of the key results from the diesel surrogate-fuel formulation study, the full details of which are available in [2]. Some results from the literature review on using raw liquids from the fast pyrolysis of woody biomass as fuels for CI engines [3] also are presented. The results from the parametric reference-fuel study will be discussed in the FY 2013 report for this project after analysis of the extensive dataset has been completed.

Diesel Surrogate Fuels

The first step in creating a surrogate fuel is to select the real-world "target" fuel that the surrogate is to emulate. Two reference #2 ULSD target fuels were used in this study: an emissions-certification fuel from Chevron Phillips Chemical Co., denoted CFA; and FACE Diesel Fuel #9 Batch A, denoted FD9A. The target fuels were characterized using a suite of advanced analytical techniques, the results from one of which are shown in Figure 1.

After one or more target fuels have been identified, the target-fuel properties that are to be matched by the surrogate are selected. In this study, it was decided to match target-fuel compositional characteristics, ignition quality, volatility, and density. The compositional characteristics matched in the study were 11 distinct carbon-bond types that were quantified using ^{13}C (carbon-13) and ^{1}H (proton) nuclear magnetic resonance spectroscopy (measurements and analysis conducted at CanmetENERGY). The 11 carbon-bond types (CTs) are shown in Figure 2. CTs were matched because they are expected to yield the best correlation with engine emissions characteristics such as sooting propensity, provided the palette compounds have representative carbon numbers, as discussed below. The ignition quality, volatility, and density of each target and surrogate fuel were quantified using standardized test methods, including the derived cetane number (DCN) [5], the advanced distillation curve (ADC) [6], and [7], respectively.

The next step in formulating surrogate fuels is to select the surrogate palette, i.e., the set of pure compounds that will be blended together to create each

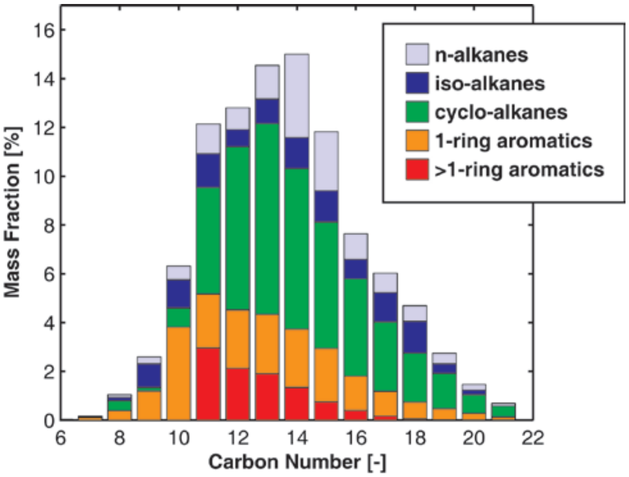

FIGURE 1. Breakdown of hydrocarbon classes by the number of carbon atoms in a given molecule (i.e., the carbon number) for the CFA target fuel. Data were obtained using gas chromatography with field ionization mass spectrometry (GC-FIMS) and paraffins, iso-paraffins, olefins, naphthenes, and aromatics (PIONA) analyses conducted at CanmetENERGY [4].

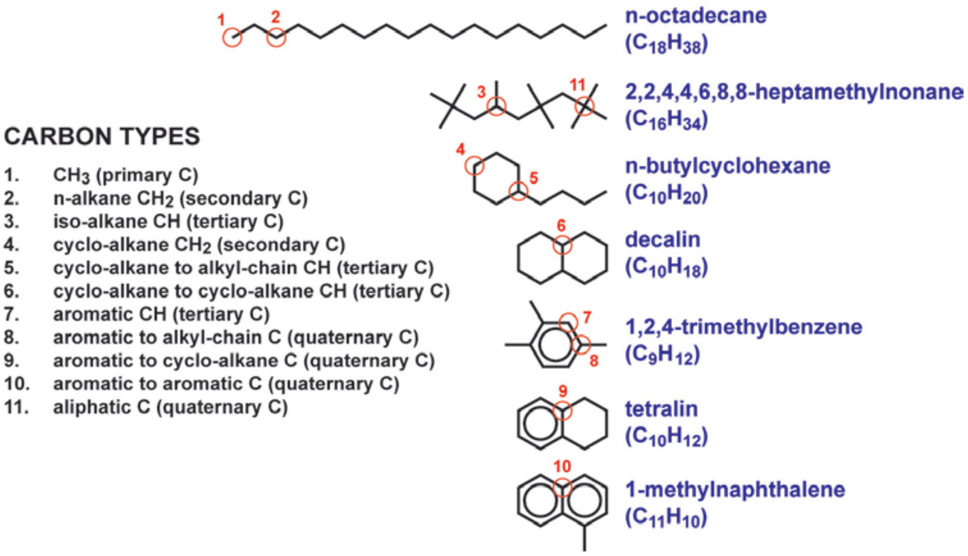

FIGURE 2. Carbon classification system used to match compositional characteristics between target and surrogate fuels. The 11 CTs are listed on the left, and an example of each CT is circled and labeled in red in the molecular-structure diagrams on the right.

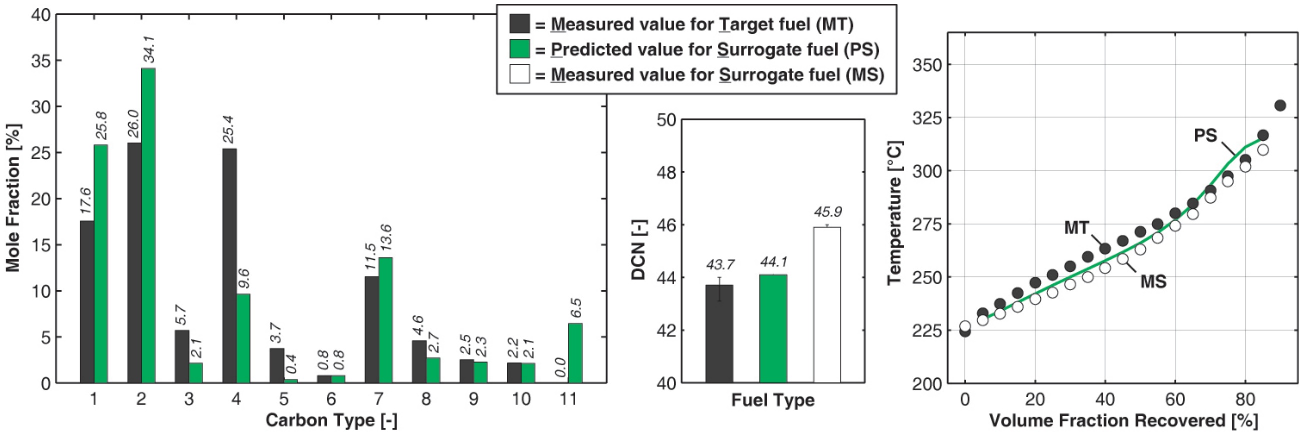

FIGURE 3. Comparison of CFA target- and surrogate-fuel characteristics. Left-hand plot compares compositional characteristics as quantified by CT mole fractions; center plot compares ignition qualities as quantified by DCN; and right-hand plot compares volatility characteristics as quantified by the ADC.

surrogate fuel. Ideally each palette compound would be representative of a class of compounds found in the target fuel, with an appropriate carbon number as determined by GCFIMS/PIONA or a similar technique, and each would have a chemical-kinetic oxidation mechanism available so that its combustion kinetics can be computationally simulated. The surrogate palette used in this study contains compounds with carbon numbers and molecular structures that represent each of the major hydrocarbon families found in market diesel fuels, including: n-alkanes, iso-alkanes, cyclo-alkanes, aromatics, and naphtho-aromatics. Seven of the eight palette compounds are shown on the right side of Figure 2. The eighth palette compound was a second n-alkane, which was omitted from the figure for brevity.

With the surrogate palette established, the next step was to identify and run an optimization code to determine the "recipe" for the surrogate, i.e., how much of each palette compound should be included in the surrogate to achieve the desired matching of target-fuel properties. The optimization code used in the study was a regression model developed at the National Institute of Standards and Technology [8].

Once each surrogate composition was determined, the pure palette compounds were blended together to produce the surrogates, and each surrogate was tested to determine the extent to which the target-fuel properties were matched. Figure 3 shows some results from these comparisons. When averaged over both

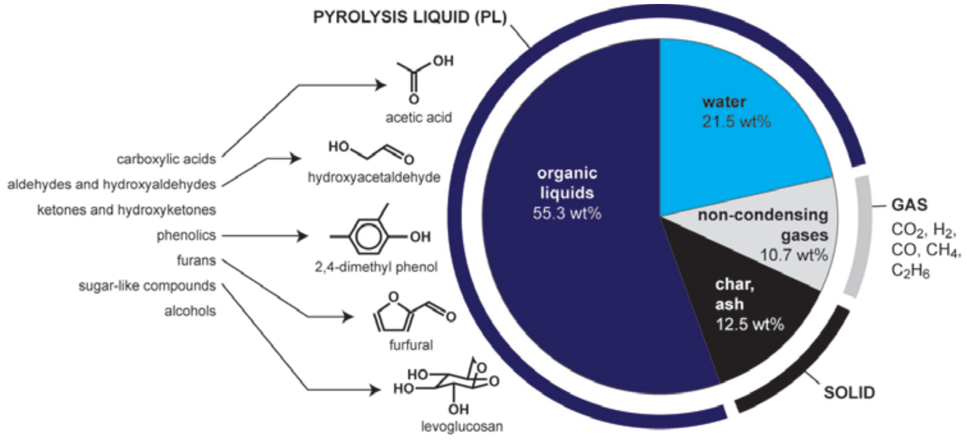

FIGURE 4. The fast pyrolysis of woody biomass produces products in solid, liquid, and gaseous phases. A significant fraction (15-30 wt%) of the liquid phase is water. Other PL components include hydrophilic and hydrophobic organic oxygenates, including acids, aldehydes, ketones, phenolics and other alcohols, furans, and sugar-like compounds.

target fuels, the CTs, ignition qualities, ADC points, and densities were matched to within 5 mol%, 4%, 2%, and 4%, respectively. Furthermore, although they were not explicitly matched, other measured properties of the surrogates showed excellent agreement with their corresponding target-fuel values. For example, molar carbon-to-hydrogen ratios agreed to within 3%, net heats of combustion agreed to within 1%, and smoke points agreed to within the 2-mm repeatability of the test method [9]. Based on these results, it is concluded that the surrogate-formulation methodology developed was highly successful.

Raw Pyrolysis Liquids as Fuels for CI Engines

Another significant effort during this reporting period was to summarize the peer-reviewed literature regarding the use of raw pyrolysis liquids (PLs) created from woody biomass as fuels for modern CI engines. Due to word-limit constraints for this report, only a brief synopsis is presented here; full details are available in [3].

PL-based fuels are of interest because they could provide a number of energy-security, environmental-quality, and economic benefits. A typical product distribution from fast pyrolysis of woody biomass is shown in Figure 4. The chemical composition of a fuel determines its properties, and the properties of a fuel determine its end-use characteristics. Comparing Figure 4 to Figure 1, it is evident that PL composition is profoundly different from #2 ULSD composition. For example, PLs are composed almost entirely of oxygenated compounds and water, while #2 ULSD in the U.S. generally contains neither of these in significant proportions. The differences in end-use characteristics resulting from these compositional differences lead to a number of problems that ultimately preclude the use of raw PLs in modern CI engines, including inadequate stability, incompatibilities with common fuel-system materials, poor ignition quality, high viscosity, and undesirable water/solids/energy contents.

CONCLUSIONS

- A rigorous methodology was developed, validated, and is now available for creating surrogate fuels that accurately match the compositional, ignition-quality, volatility, density, and other characteristics of real-world #2 ULSD fuels.
- A detailed evaluation of the peer-reviewed literature regarding the use of PLs created from woody biomass conclusively indicates that they are not suitable as fuels for modern CI engines without post-processing to improve their end-use characteristics.

REFERENCES

1. Mueller, C.J., Martin, G.C., Briggs, T.E., and Duffy, K.P., “An Experimental Investigation of In-Cylinder Processes under Dual-Injection Conditions in a DI Diesel Engine,” SAE Technical Paper 2004-01-1843, *SAE Trans.* **113**(3):1146-1164, 2004.

2. Mueller, C.J., Cannella, W.J., Bruno, T.J., Bunting, B., Dettman, H., Franz, J., Huber, M.L., Natarajan, M., Pitz, W.J., Ratcliff, M.A., and Wright, K., “Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics,” *Energy Fuels* **26**(6):3284-3303, 2012.

3. Mueller, C.J., "The Feasibility of Using Raw Liquids from Fast Pyrolysis of Woody Biomass as Fuels for Compression-Ignition Engines: A Literature Review," SAE Technical Paper Offer No. 13PFL-0301, SAE 2013 World Congress & Exhibition, *submitted*, 2012.

4. Alnajjar, M., Cannella, W., Dettman, H., Fairbridge, C., Franz, J., Gallant, T., Gieleciak, R., Hager, D., Lay, C., Lewis, S., Ratcliff, M., Sluder, S., Storey, J., Yin, H., and Zigler, B., "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels," Coordinating Research Council Report: FACE-1, 2010. Online source, http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/index.html.

5. ASTM Standard D6890-10a, Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber. ASTM International, West Conshohocken, PA, 2010.

6. Bruno, T.J., Ott, L.S., Lovestead, T.M., and Huber, M.L., "Relating Complex Fluid Composition and Thermophysical Properties with the Advanced Distillation Curve Approach," *Chemical Eng. Tech.* **33**(3):363-376, 2010.

7. ASTM Standard D4052, Standard Test Method for Density, Relative Density, and Api Gravity of Liquids by Digital Density Meter. ASTM International, West Conshohocken, PA, 2009.

8. Huber, M.L., Lemmon, E.W., and Bruno, T.J., "Surrogate Mixture Models for the Thermophysical Properties of Aviation Fuel Jet-A," *Energy Fuels* **24**:3565-3571, 2010.

9. ASTM Standard D1322-08, Standard Test Method for Smoke Point of Kerosine and Aviation Turbine Fuel. ASTM International, West Conshohocken, PA, 2008.

FY 2012 PUBLICATIONS

1. Mueller, C.J., Cannella, W.J., Bruno, T.J., Bunting, B., Dettman, H., Franz, J., Huber, M.L., Natarajan, M., Pitz, W.J., Ratcliff, M.A., and Wright, K., "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *Energy & Fuels* **26**:3284-3303, 2012, doi: 10.1021/ef300303e.

2. Mueller, C.J., "The Feasibility of Using Raw Liquids from Fast Pyrolysis of Woody Biomass as Fuels for Compression-Ignition Engines: A Literature Review," SAE Technical Paper Offer No. 13PFL-0301, SAE 2013 World Congress & Exhibition, *submitted*, 2012.

3. Polonowski, C.J., Mueller, C.J., Gehrke, C.R., Bazyn, T., Martin, G.C., and Lillo, P.M., "An Experimental Investigation of Low-Soot and Soot-Free Combustion Strategies in a Heavy-Duty, Single-Cylinder, Direct-Injection, Optical Diesel Engine," *SAE Int. J. Fuels Lubr.* **5**(1):51-77, 2011, doi:10.4271/2011-01-1812.

4. Fisher, B.T. and Mueller, C.J., "Effects of Injection Pressure, Injection-Rate Shape, and Heat Release on Liquid Length," *SAE Int. J. Engines* **5**(2):415-429, 2012, doi:10.4271/2012-01-0463.

5. Mueller, C.J., Cannella, W.J., and Kalghatgi, G., "Fuels for Engines and the Impact of Fuel Composition on Engine Performance," Encyclopedia of Automotive Engineering, Wiley, *submitted*, 2012.

6. Mueller, C.J., "Experimental Investigation of Fuel Effects on Low-Soot Combustion Strategies in a Direct-Injection, Optical Diesel Engine," *Proc. of DOE Advanced Engine Combustion and Fuels Program Review*, DOE Office of Vehicle Technologies Annual Report, 2011.

7. Mueller, C.J., Pitz, W.J., and Mehl, M., "Surrogate Fuels Match Properties of Real-World Gasoline and Diesel Fuels," *U.S. DRIVE Highlight Report to Congress*, 2012.

FY 2012 PRESENTATIONS

1. Mueller, C.J., "Status Update on AVFL-18/18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling," Coordinating Research Council Advanced Vehicles, Fuels and Lubricants Committee Meeting, The Marshall House, Savannah, GA (January 19, 2012).

2. Mueller, C.J., "Caterpillar/Sandia Collaborative Research: Summary of CY11 Activities," Caterpillar Engine Research Division Meeting, Caterpillar Technical Center, Mossville, IL (January 25, 2012).

3. Mueller, C.J., "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," Advanced Engine Combustion Working Group Meeting, Sandia National Laboratories, Livermore, CA (February 14, 2012).

4. Fisher, B.T., "Effects of Injection Pressure, Injection-Rate Shape, and Heat Release on Liquid Length," SAE International Congress and Exposition, Detroit, MI (April 25, 2012).

5. Mueller, C.J., "Fuels and Combustion Strategies for High-Efficiency Clean-Combustion Engines," DOE Office of Vehicle Technologies Annual Merit Review Meeting, Washington, DC (May 15, 2012).

6. Mueller, C.J., "Status Update on AVFL-18/18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling," CRC Advanced Vehicles, Fuels and Lubricants Committee Meeting, Knoxville, TN (May 31, 2012).

7. Mueller, C.J., "Future Diesel Trends: 2020/2030," invited panelist in Fusfeld Key Expert Panel, sponsored by Phillips 66, Framingham, MA (June 15, 2012).

8. Mueller, C.J., "The Feasibility of Pyrolysis Liquids from Woody Biomass as Fuels for Compression-Ignition Engines: A Literature Review," Advanced Engine Combustion Working Group Meeting, Southfield, MI (June 19, 2012).

9. Mueller, C.J., "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," Multi Agency Coordination Committee for Combustion Research (MACCCR) – 5th Annual Fuels Research Review, Sandia National Laboratories, Livermore, CA (September 19, 2012).

SPECIAL RECOGNITION

Elected to Fellow grade of membership in the Society of Automotive Engineers

III.3 Chemical Kinetic Modeling of Advanced Transportation Fuels

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Objectives

- Develop detailed chemical kinetic reaction models for components of non-petroleum based fuels. These fuel models include components from vegetable-oil-derived biodiesel, oil-sands derived fuel, alcohols and next-generation biofuels.
- Develop detailed chemical kinetic reaction models for mixtures of non-petroleum and petroleum-based components to represent real fuels.
- Reduce detailed chemical kinetic models for use in multidimensional engine simulation codes that can be used to optimize engine efficiency and reduce pollutant emissions.

Fiscal Year (FY) 2012 Objectives

- Further validations and improvements for chemical kinetic models for saturated and unsaturated large methyl esters.
- Develop a chemical kinetic mechanism for isomers of pentanol.
- Further validation and improvements of the iso-pentanol mechanism.
- Develop reduced mechanisms for alternative fuel surrogates to be used in multi-dimensional computational fluid dynamics (CFD) simulations of advanced engine combustion.
- Provide technical support for the Fuels for Advanced Combustion Engines (FACE) working group.

Accomplishments

- Validated chemical kinetic models for methyl palmitate, methyl oleate, and methyl linoleate, which are real biodiesel components.
- Further validation of chemical kinetic model for iso-pentanol, an advanced biofuel.
- Development and validation of a chemical kinetic model for n-pentanol.
- Developed preliminary model for dimethylcarbonate, a biofuel that can be used to displace conventional diesel fuel.
- Supported the FACE fuel effort through project AVFL-18, “Surrogate fuels for kinetic modeling.”

Future Directions

- Develop ethanol-gasoline model for large amounts of ethanol and direct-injection spark-ignition engine (DISI) application.
- Further validations and improvements for chemical kinetic models for saturated and unsaturated large methyl esters, with particular emphasis on the low temperature chemistry which is important for engine combustion.
- Development of reduced surrogate mechanisms for biodiesel (cuphea methyl ester) and long-chain alcohols for use in CFD engine simulations.
- Develop a low-temperature chemical kinetic model for diethylcarbonate.
- Provide technical support for the FACE working group.

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INTRODUCTION

Development of detailed chemical kinetic models for non-petroleum-based fuels is a difficult challenge because some of these fuels contain components that have not been considered in the past. Also, non-petroleum-based fuels are usually blended with petroleum-based fuels like diesel and gasoline so that these blends have the same complexity as conventional fuels with hundreds to thousands of fuel components. It is important to develop detailed chemical kinetic models for these fuels since the chemistry models can be reduced and used in engine simulation codes to optimize engine designs for maximum efficiency and minimal pollutant emissions. Additionally, chemical kinetic models can be used separately to interpret important in-cylinder experimental data and gain insight into advanced engine combustion processes such as reactivity controlled compression ignition and DISI lean-burn engines.

APPROACH

Detailed chemical kinetic models are developed to represent the various components in non-petroleum-based fuels. These non-petroleum-based fuels include biodiesel, alcohol fuels, algal-derived fuels and other advanced bio-derived fuels. Since these non-petroleum-based fuels are usually mixed with petroleum-based fuels in the marketplace, detailed chemical kinetic models are also developed for petroleum-based components such as cycloalkanes and aromatics. The components' models are assembled into mixture or "surrogate" models to represent advanced fuels. Model calculations are carried out with these combined reaction mechanisms to compute ignition, soot precursor formation, and oxides of nitrogen (NOx) formation under practical engine conditions. The mechanisms are then reduced for use in multidimensional CFD codes for simulating engine combustion. These chemistry-enabled CFD engine codes can be used to optimize engine design for new fuels for the best performance and engine efficiency, and for minimum pollutants.

RESULTS

Biodiesel fuel derived from large methyl esters that can be made from vegetable and animal feedstocks and from algae. Methyl esters are both saturated and unsaturated methyl esters and both types of compounds need to be included in a surrogate fuel chemistry model for biodiesel. In FY 2010-11, we developed a chemical kinetic model for the five primary methyl esters in most biodiesel fuel. Unfortunately, experimental data on these methyl esters were not available at that time for model validation because of experimental challenges in handling low vapor pressure fuels. With the development of new experimental techniques, experimental data under shock tube conditions became available in FY 2012. Using these new data, we validated the mechanisms for three of these methyl esters: methyl palmitate, methyl oleate, and methyl linoleate. In Figures 1 and 2, the predicted ignition properties of two unsaturated methyl esters (methyl oleate and methyl linoleate) are compared with the new experimental data [1] at 3.5 and 7 atm. Initial comparisons of modeling results and the new data identified the need to improve estimates of the rate constants for methyl ester decomposition. With these improved estimates, the good agreement in Figure 1 for methyl oleate and the reasonable agreement in Figure 2 for methyl linoleate were obtained. Also, we are using new, unpublished, shock-tube data from Rensselaer Polytechnic Institute to validate the methyl palmitate mechanism. The agreement between results from the mechanism and experiments was reasonable. More experimental data is expected to become available in FY 2013 and we will continue to validate and improve these mechanisms as needed based on these new data, with particular attention to the low temperature chemistry regimes which are important for engine combustion.

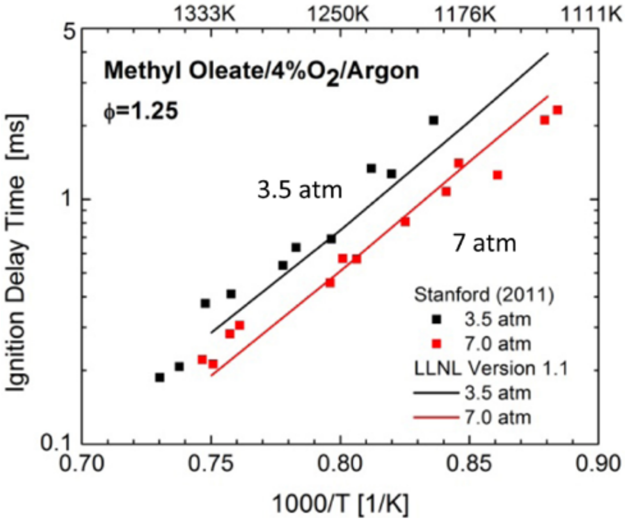


FIGURE 1. Comparisons of ignition delay times from the LLNL chemical kinetic model (lines) and experimental measurements (symbols) [1] in a shock tube using methyl oleate, an actual methyl ester in soybean-derived biodiesel. The fuel/O_2 equivalence ratio (ϕ) is 1.25 and the reflected-shock pressures are 3.5 and 7 atm.

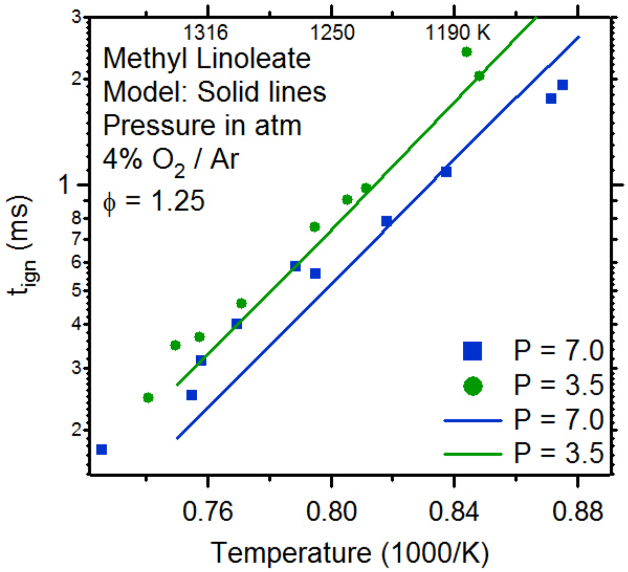
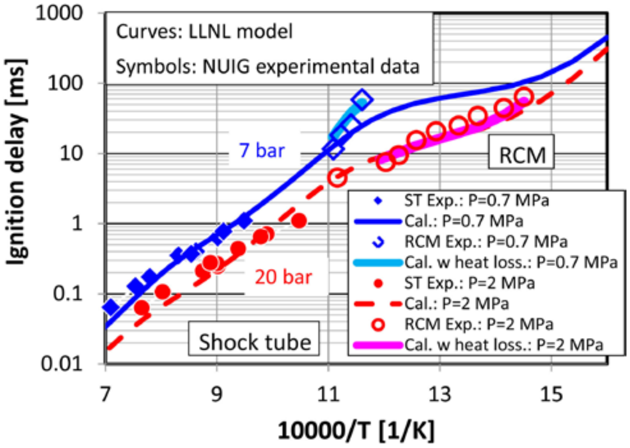


FIGURE 2. Comparisons of ignition delay times from the LLNL chemical kinetic model (lines) and experimental measurements (symbols) [1] in a shock tube for methyl linoleate, an actual methyl ester in soybean-derived biodiesel. The fuel/O_2 equivalence ratio (ϕ) is 1.25 and the reflected-shock pressures are 3.5 and 7 atm.

In further work on these large methyl ester mechanisms, we have also been updating and improving our estimates of the rate constants and species thermodynamic properties. This is an ambitious task to update the estimates of thousands of thermodynamic properties. These improvements will provide us with more accurate simulations of the ignition and oxidation of methyl esters under engine conditions. We expect an updated mechanism to be available in FY 2013.

Our next achievement is for the development of chemical kinetic models for larger alcohols. These alcohols are important candidates for transportation fuels because of their higher energy density compared to smaller alcohols like ethanol. In FY 2011, we developed a chemical kinetic model for iso-pentanol, a biofuel that can be derived from microorganisms. It has also been shown to be an excellent fuel for homogeneous charge compression ignition engines because of its inherent intermediate temperature heat release [2]. In FY 2012, we improved our iso-pentanol mechanism and developed a new mechanism for n-pentanol. Figure 3 shows results from the iso-pentanol mechanism compared with experimental data from a shock tube and a rapid compression machine [3] at pressure and temperature conditions relevant to internal combustion engines. The ability of the model to simulate the experimentally measured ignition times is excellent. Using our newly-developed mechanism for n-pentanol, we compared simulated and experimentally measured ignition delay times in a shock tube and a rapid compression machine (Figure 4). N-pentanol exhibits more low temperature chemistry than iso-pentanol as seen by the decrease in slope in the n-pentanol curves as the temperature decreases below about 900 K. The chemical kinetic model reproduces this experimental behavior which is an important characteristic of low-temperature combustion in engines.

Dimethylcarbonate is a biofuel that can be made from sugarcane, blended with diesel fuel, and used to displace conventional diesel in compression ignition engines. Because of its high oxygen content, blending it with diesel fuel significantly reduces soot emissions. In FY 2012, we developed a preliminary mechanism for dimethylcarbonate. We compared the results using our preliminary mechanism to unpublished dimethylcarbonate experiments in a jet stirred reactor from Dr. Philippe Dagaut's group in CNRS, Orleans, France. The mechanism simulated reasonably well the intermediate species experimentally measured at 10 atm over a range of reactor temperatures and equivalence ratios. We also compared results using the mechanism to unpublished ignition delays measured in a shock tube and rapid compression machine (RCM) at 30 atm at the National University of Ireland, Galway (NUIG). The mechanism simulated the experimental data well at high temperatures in the shock tube, but predicted ignition delay times were too slow at low to intermediate temperatures in the RCM. Reactions occurring at low temperature need to be added to properly simulate the ignition behavior in the RCM. We plan to add these reactions in FY 2013.



NUIG - National University of Ireland, Galway

FIGURE 3. Comparisons of ignition delay times for the LLNL chemical kinetic model (curves) and experimental measurements (symbols) [3] for iso-pentanol, an advanced biofuel. The solid symbols correspond to shock-tube ignition and the open symbols to RCM ignition. The simulations for shock tube ignition are thin curves and assume constant volume combustion. The simulations for RCM ignition are thick solid lines and include the effect of reaction in the RCM during compression and heat loss after compression. The results are for stoichiometric fuel/air mixtures and pressures of 7 and 20 bar.

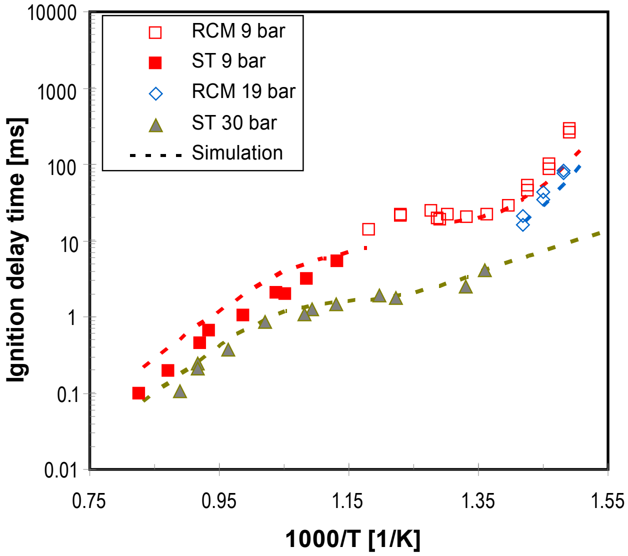


FIGURE 4. Comparisons of ignition delay times for n-pentanol from the LLNL chemical kinetic model (curves) and experimental measurements (symbols) [5]. The results are for stoichiometric fuel/air mixtures and pressures of 9, 19, and 30 bar. The solid symbols correspond to shock-tube (ST) experiments and the open symbols to RCM experiments. The dotted curves correspond to the simulations, including facility effects for each experimental device.

It is important to reduce large chemical kinetic models, so that they can be used in multidimensional CFD codes for engine simulations. In FY 2011, we collaborated with University of Connecticut to reduce our chemical kinetic mechanism for methyl decanoate, methyl 9-decenoate and n-heptane so that can be used as a surrogate for biodiesel [4]. In FY 2012, we used our detailed model and the reduced model to simulate cuphea methyl ester. We explored a number of surrogate mixtures comprised of the above components to obtain the optimal composition to match the compositional characteristics of cuphea methyl ester and its ignition properties. In collaboration with Argonne National Laboratory, a biodiesel reacting spray was computed with a multidimensional CFD code using the reduced mechanism and preliminary results were obtained.

In FY 2012, we participated in the FACE working group through the AVFL-18, a CRC project to develop diesel surrogate fuels. In this work with other industrial and national laboratory collaborators, we jointly developed a procedure to match the compositional, distillation, density, and ignition properties of a FACE diesel fuel and a certification diesel fuel with two corresponding surrogate fuels.

CONCLUSIONS

- We have validated our large methyl ester models using recently available experimental data on ignition properties from shock tubes.
- We have updated our iso-pentanol model using newly available ignition data from shock tubes and rapid compression machines.
- We have developed a new chemical kinetic model for n-pentanol, an alcohol with more energy density than ethanol or butanol.
- We developed a preliminary three-component reduced chemical kinetic model for cuphea methyl ester biodiesel.

ACKNOWLEDGEMENTS

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REFERENCES

1. M.F. Campbell, D.F. Davidson, R.K. Hanson and C.K. Westbrook, "Ignition delay times of methyl oleate and methyl linoleate behind reflected shock waves," *Proc. Combust. Inst.* 34 (1) (2013) 419-425.

2. Y. Yang, J. Dec, N. Dronniou and B. Simmons, "Characteristics of Isopentanol as a Fuel for HCCI Engines," *SAE Int. J. Fuels Lubr.* 3 (2) (2010) 725-741.

3. T. Tsujimura, W.J. Pitz, F. Gillespie, H.J. Curran, B.W. Weber, Y. Zhang and C.-J. Sung, "Development of isopentanol reaction mechanism reproducing auto-ignition character at high and low temperatures," *Energy & Fuels* 26 (8) (2012) 4871-4886.

4. Z. Luo, M. Plomer, T. Lu, S. Som, D.E. Longman, S.M. Sarathy and W. J. Pitz, "A Reduced Mechanism for Biodiesel Surrogates for Compression Ignition Engine Applications," *Fuel* (2011) Submitted.

5. K.A. Heufer, S.M. Sarathy, H.J. Curran, A.C. Davis, C.K. Westbrook and W.J. Pitz, "Detailed Kinetic Modeling Study of n-Pentanol Oxidation," *Energy & Fuels* 26 (11) (2012) 6678-6685.

FY 2012 PUBLICATIONS

1. T. Tsujimura, W.J. Pitz, F.R. Gillespie, H.J. Curran, B.W. Weber, Y. Zhang, C.-J. Sung, "Development of isopentanol reaction mechanism reproducing auto-ignition character at high and low temperatures", Energy & Fuels, 26 (8) (2012) 4871-4886.

2. Zhaoyu Luo, Max Plomer, Tianfeng Lu, Sibendu Som, Douglas E. Longman, S.M. Sarathy, William J. Pitz, "A Reduced Mechanism for Biodiesel Surrogates for Compression Ignition Engine Applications", Fuel, 99 (2012) 143-153.

3. S.M. Sarathy, S. Vranckx, K. Yasunaga, M. Mehl, P. Oßwald, C.K. Westbrook, W.J. Pitz, K. Kohse-Höinghaus, R.X. Fernandes, H.J Curran, "A comprehensive chemical kinetic combustion model for the four butanol isomers", Combustion and Flame, 159 (6) (2012) 2028–2055.

4. Heufer, K.A., Sarathy, S.M., Curran, H.J., Davis, A.C., Westbrook, C.K. and Pitz, W.J., "A Detailed Kinetic Modeling Study of n-Pentanol Oxidation," Energy and Fuels 26 (11) (2012) 6678-6685.

5. Mueller, C.J., Cannella, W.J., Bruno, T.J., Bunting, B., Dettman, H.D., Franz, J.A., Huber, M.L., Natarajan, M., Pitz, W.J., Ratcliff, M.A. and Wright, K., "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," Energy & Fuels 26 (6) (2012) 3284–3303.

6. Yang, B., Westbrook, C.K., Cool, T.A., Hansen, N., and Kohse-Hoinghaus, K., "The Effect of Carbon-Carbon Double Bonds on the Combustion Chemistry of Small Fatty Acid Esters", Z. Phys. Chem. 225, 1293-1314 (2011).

7. Veloo, P.S., Dagaut, P., Togbe, C., Dayma, G., Sarathy, S.M., Westbrook, C.K., and Egolfopoulos, F.N., "Jet-stirred reactor and flame studies of propanal oxidation", Proc. Combust. Inst. 34, (1) (2013) 599-606.

8. Westbrook, C.K., Pitz, W.J., Sarathy, S.M., and Mehl, M., "Detailed chemical kinetic modeling of the effects of C=C double bonds on the ignition of biodiesel fuels", Proc. Combust. Inst. 34, (2) (2013) 3049-3056.

9. Farooq, A., Ren, W., Lam, K.Y., Davidson, D.F., Hanson, R.K., and Westbrook, C.K., “Shock tube studies of methyl butanoate pyrolysis with relevance to biodiesel”, Combust. Flame 159, 3235-3241 (2012).

10. Campbell, M.F., Davidson, D.F., Hanson, R.K. and Westbrook, C.K., “Ignition Delay Times of Methyl Oleate and Methyl Linoleate Behind Reflected Shock Waves,” Proceedings of the Combustion Institute, (1) (2013) 419-425.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Westbrook, C.K., “Recent Advances in Autoignition Kinetics of Automotive Fuels”, (invited plenary lecture) COMODIA 2012, Fukuoka, Japan, July 23–26, 2012.

2. Charles K. Westbrook: 2008 - 2012 President of the Combustion Institute.

3. S.M. Sarathy: Postdoctoral Fellowship from Natural Sciences and Engineering Research Council of Canada, 4/2010 to 4/2012.

III.4 Improving Advanced Fuel Utilization through Detailed Chemical Kinetic Combustion Modeling

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Objectives

- Enhance understanding of advanced fuel combustion for application to clean and efficient engine technologies.
- Gain fundamental and practical insight into advanced fuel combustion through numerical simulations and experiments.
- Develop and apply numerical tools to analyze advanced fuel combustion regimes through multidimensional fluid mechanics with chemical kinetics.
- Improve the predictive capability of advanced fuel chemical kinetic mechanisms through analysis of high efficiency combustion regimes.

Fiscal Year (FY) 2012 Objectives

- Utilize the sensitivity and uncertainty analysis framework developed for improving predictive capability of chemical kinetic mechanisms for fuels and fuel surrogate combustion.
- Apply newly available high fidelity tools for multidimensional combustion simulation to investigate high efficiency and low emissions advanced fuel engines.
- Characterize advanced fuel combustion regimes with judicious application of experiments and simulation.

Accomplishments

- We have developed a methodology that combines experimental engine data, multizone detailed chemical kinetic engine simulations, sensitivity and uncertainty analysis software, and supercomputing resources to improve the predictive capability of advanced fuel chemical kinetic mechanisms for engine combustion regimes.
- We have applied Converge™—a parallel engine combustion computational fluid mechanics software package utilizing LLNL's multizone combustion model—to investigate engine operation with alternative fuels. We have demonstrated operation with direct injection of partially distilled ethanol; specifically, cold start using spark ignition and steady state homogenous charge compression ignition (HCCI) combustion. We have validated our model with the experimental ethanol-fueled direct-injected engine at the Combustion Research Facility at Sandia National Laboratory, Livermore.
- We have demonstrated operation of an experimental HCCI engine using an exhaust heat exchanger fueled with ethanol-water mixtures. The exhaust heat exchanger was sufficient to preheat the intake mixture, no external heat was required. The use of fuel mixtures ranging from pure ethanol to 70% ethanol/30% water was successfully demonstrated.

Future Directions

- Develop and distribute a robust software tool for refining advanced fuel chemical kinetic mechanisms based on engine experimental data.
- Investigate the effects of fuel characteristics on the multidimensional combustion processes in advanced engines.
- Quantify the uncertainty of our engine modeling tools to provide an accurate measure of their ability to predict engine behavior as a function of operating condition.

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INTRODUCTION

LLNL contributes to the efficient and clean utilization of advanced fuels through development of high-fidelity analysis tools. The work focuses on development, testing and tuning of chemical kinetic models for fuel components and fuel surrogates of interest to industry and engine researchers; and modeling to test the applicability of chemical kinetic mechanisms at engine conditions. We also develop and test concepts that contribute to improved utilization efficiency of advanced fuels.

APPROACH

The growing interest in advanced fuels has brought with it a broad need for new fuel characterization under advanced combustion regimes. We contribute to this task by collaborating with industry, other national laboratories, and universities in identifying modeling needs for advanced fuels. Typically we team up with other institutions (foreign and domestic) that conduct experimental work, and we perform detailed analysis leading to the development, testing and tuning of new chemical kinetic mechanisms. The approach has proven very successful and our combustion models are widely used around the world.

RESULTS

We have developed a methodology for improving the predictiveness of chemical kinetic mechanisms based on engine experiments, multidimensional simulations, and sensitivity analysis. Detailed chemical kinetic mechanisms for advanced engine fuels involve large hydrocarbon molecules, and the kinetics of these large combustion mechanisms can involve thousands of chemical species and tens-of-thousands of elementary reactions. Each reaction has a number of parameters defining the rate of progress of that reaction. Reaction rate parameters are determined based on experiments, first principles calculations, or by using rates from analogous reactions.

We have developed engine combustion models combining chemical kinetics and computational fluid dynamics (CFD) that are predictive of HCCI engine operation for naturally aspirated conditions [1,2]. However, turbocharging is an important design feature being employed to increase efficiency in next generation engines. Turbocharging results in high pressures during ignition in an internal combustion engine. Chemical kinetic models have had difficulty capturing certain features of the combustion process at elevated pressures; specifically, the low-temperature heat release (partial combustion reactions that are observed at temperatures between 700 K and 900 K). Engine experiments at Sandia National Laboratories showed that low temperature heat release increases with elevated pressures and significantly more than predicted by current chemical kinetic mechanisms [3].

The laboratory experiments typically used to measure chemical kinetic rate coefficients (shock tubes, rapid compression machines, jet-stirred reactors) operate at pressures significantly lower than turbocharged engine combustion conditions. These laboratory methods allow for very specific identification of individual reaction rates using well-controlled conditions.

Conventional diesel and spark-ignited engine operation present an environment where the chemical kinetics is intimately coupled with several complex physical phenomena, which includes: turbulent flow, temperature stratification, fuel-air inhomogeneity, vaporization, and electrical discharge. However, HCCI engines present an environment where the chemical kinetics of the combustion process can be isolated from turbulent flow and other processes. CFD-multi-zone simulations of naturally aspirated HCCI engines have been shown to be predictive of the rate of combustion and the exhaust composition for naturally aspirated engine operation [4].

Using HCCI engine experiments and multi-zone chemical kinetics simulations to adjust reaction rates, we have developed a methodology to make the mechanisms more predictive at engine conditions. This method begins by determining, which parameters of the chemical mechanism have the largest influence on low temperature heat release using sensitivity analysis. The most sensitive parameters are then optimized by comparing high quality HCCI engine data obtained from a variety of operating conditions to corresponding CFD-multi-zone simulations. The optimization minimizes a “figure of merit” that quantifies agreement between simulation and experiment. LLNL’s supercomputing facilities and sensitivity and uncertainty analysis codes enabled this effort. We use LLNL’s Problem Solving environment for Uncertainty Analysis and Design Exploration code [5] to manage hundreds of thousands of individual simulations of an engine operating condition subjected to perturbed chemical kinetic parameters.

Figure 1 shows a plot of the heat release from an engine simulation with detailed chemical kinetics. The magnitude of the low temperature heat release is monitored as the chemical kinetics parameters are perturbed during the sensitivity analysis. The Morris one-at-a-time (MOAT) sensitivity analysis method is used. This is a global technique in which a base case is run, then, in each following simulation, one parameter is perturbed and remains in this perturbed state for all subsequent simulations. In this way the parameter space

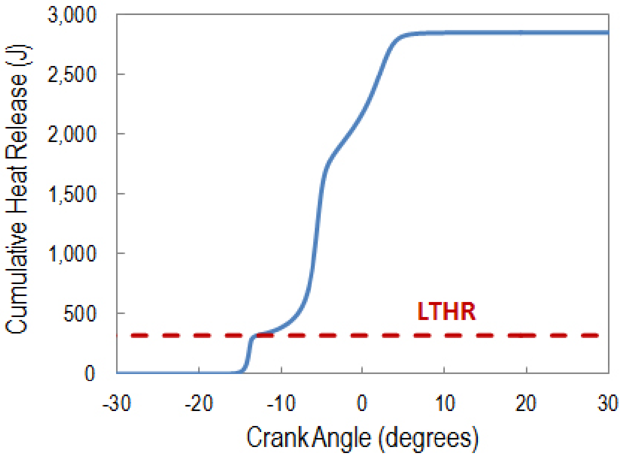
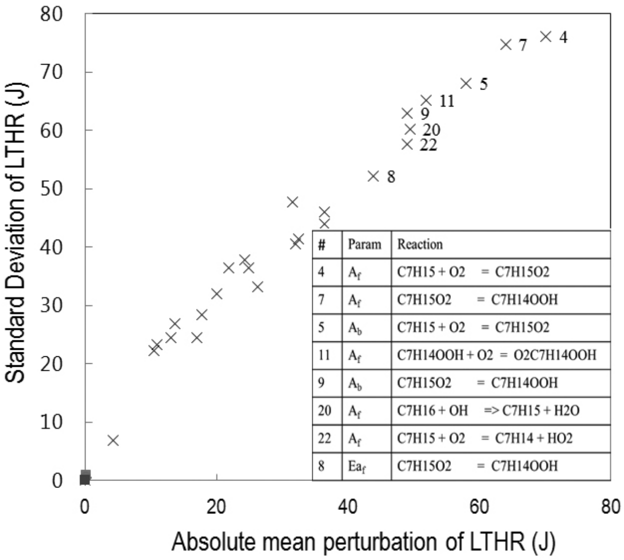


FIGURE 1. Cumulative heat release from an HCCI engine simulation with detailed chemical kinetics. The magnitude of the low-temperature heat release is indicated by the dashed line.

is explored by changing each of the parameters one-at-a-time per simulation. This results in N+ 1 simulations, where N is the number of parameters. This procedure is repeated numerous times until the results converge.

Figure 2 presents the results of the MOAT analysis of the low-temperature heat release (LTHR). The y-axis corresponds to the standard deviation of the LTHR with respect to each parameter and the x-axis corresponds to the mean value of the LTHR with respect to each parameter. A large mean value indicates that the parameter is influential, whereas a low value indicates the parameter does not influence the LTHR. A large standard deviation implies that the parameter has a nonlinear influence on the LTHR or interacts with other parameters whereas a small standard deviation implies the parameter has a linear effect on the LTHR and is independent of the value of other parameters. From Figure 2 we can see that LTHR is most sensitive to the parameters related to oxygen addition and isomerization. Due to the high standard deviation we can infer that these reactions are heavily influenced by other reactions. This analysis allows us to optimize those parameters that affect the LTHR most and fix those that affect the LTHR least. This screening process reduces the number of simulations and allows for effective use of computational resources available.

We continue to investigate the effect of alternative fuels on in-cylinder combustion processes through multi-dimensional simulations and experiments. “Wet ethanol” has been of great interest recently. Ethanol production from biological sources typically results in a water-ethanol mixture that is on the order of 15% ethanol and 85% water. This water-ethanol mixture is distilled and processed so that nearly pure ethanol is delivered for direct utilization or blending with gasoline. Distillation requires significant energy, reducing the well-to-wheels



#	Param	Reaction
4	A_f	C7H15 + O2 = C7H15O2
7	A_f	C7H15O2 = C7H14OOH
5	A_b	C7H15 + O2 = C7H15O2
11	A_f	C7H14OOH + O2 = O2C7H14OOH
9	A_b	C7H15O2 = C7H14OOH
20	A_f	C7H16 + OH => C7H15 + H2O
22	A_f	C7H15 + O2 = C7H14 + HO2
8	Ea_f	C7H15O2 = C7H14OOH

FIGURE 2. MOAT sensitivity analysis of the LTHR. The y-axis corresponds to the standard deviation of the LTHR with respect to each parameter and the x-axis corresponds to the mean value of the LTHR with respect to each parameter.

efficiency of bioethanol [6]. The concept of “wet ethanol” is to partially distill the mixture; distilling only to the level necessary to effectively use the wet-ethanol as a fuel. The most significant energy cost in ethanol purification is in removing the last 10 to 20% of the water from the ethanol. Thus, using an 80% ethanol/20% water blend could significantly reduce the energy costs relative to pure ethanol.

We have successfully demonstrated the use of wet ethanol in an experimental HCCI engine with an exhaust gas heat exchanger to heat the intake charge—vaporizing the fuel-water mixture and allowing more advanced ignition. Operation with fuel-water blends ranging from 100% to 70% ethanol (with the balance being water) was tested. The intake pressure of the engine was varied from ambient to 2.0 bar absolute and the fuel/air equivalence ratio, ϕ, ranged from 0.25 to 0.55. Figure 3 presents the gross indicated mean effective pressure (IMEP)—a proxy for the power produced by the engine—versus volume percent ethanol in the fuel at two intake pressures. This plot shows that it is possible for the engine to produce a range of gross IMEPs even with a high percentage of water in the fuel, all while producing low amounts of oxides of nitrogen.

CONCLUSIONS

LLNL has made significant progress in improving predictive capabilities enabling efficient and environmentally friendly utilization of advanced fuels in internal combustion engines.

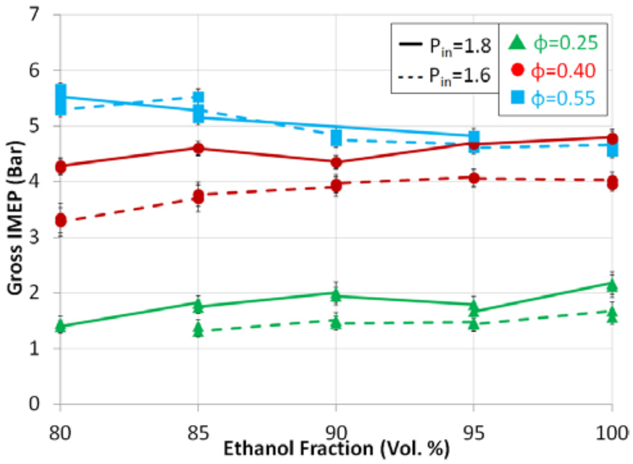


FIGURE 3. Gross IMEP versus volume fraction of ethanol in the ethanol/water fuel mixtures at two intake pressures and three fuel/air equivalence ratios (ϕ). Engine operation at a range of gross IMEPs is possible even with a high percentage of water in the fuel.

- We have developed a methodology to use engine experimental data, CFD multi-zone simulations, uncertainty and sensitivity analysis software, and supercomputing resources to tune chemical kinetics mechanisms to be more predictive at engine conditions.
- We have conducted experiments and simulations to investigate the effects of water in ethanol on engine combustion processes. We have successfully demonstrated HCCI engine operation with up to 30% water in ethanol utilizing exhaust heat to preheat the intake charge.

Future work will build on these successes and we anticipate significant further improvements in simulation of advanced fuel combustion processes.

REFERENCES

1. Aceves, S.M., Flowers, D.L., Westbrook, C.K., Smith, J.R., Pitz, W.J., Dibble, R.W., Christensen, M., Johansson, B., "A Multi-Zone Model for Prediction of HCCI Combustion and Emissions," SAE Paper 2000-01-0327.

2. Babajimopoulos, A., Assanis, D.N., Flowers, D.L., Aceves, S.M. and Hessel, R.P., "A fully coupled computational fluid dynamics and multi-zone model with detailed chemical kinetics for the simulation of premixed charge compression ignition engines," International Journal Engine Research, Volume 6, Issue 5, pages 497-512, 2005.

3. Naik, C.V., Pitz, W.J., Westbrook, C.K., Sjöberg, M., Dec, J.E., Orme, J., Curran, H.J., Simmie J., "Detailed Chemical Kinetic Modeling of Surrogate Fuels for Gasoline and Application to an HCCI Engine," SAE Paper 2005-01-3741, 2005.

4. Hessel, R., Babajimopoulos, A., Foster, D., Aceves, S., Davisson, M, Espinosa-Loza, F.J., Flowers, D.L., Pitz, W., Dec, J., Sjoberg, M., " Modeling Iso-octane HCCI using CFD with Multi-Zone Detailed Chemistry; Comparison to Detailed Speciation Data over a Range of Lean Equivalence Ratios," SAE Paper 2008-01-0047.

5. https://computation.llnl.gov/casc/uncertainty_quantification/

6. Flowers, D.L., Aceves, S.M., Martinez-Frias, J., "Improving Ethanol Life Cycle Energy Efficiency by Direct Utilization of Wet Ethanol in HCCI Engines," SAE Paper 2007-01-1867.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Killingsworth, N.J., "Improving Advanced Fuel Utilization through Detailed Chemical Kinetic Combustion Modeling," DOE/OFCVT Fuels Technologies FY11 Annual Report, 2011.

2. Schneider, S., Saxena, S., Krieck, M., Vuilleumier, D., Maas, U., Dibble, R., "Investigation of wet ethanol combustion in an HCCI engine using an exhaust gas heat exchanger," Proceedings of Fall Technical Meeting of the Western States Section of the Combustion Institute, Riverside, CA, October 16–18, 2011.

3. Raju, M., Wang, M., Dai, M., Piggott, W., Flowers, D., "Acceleration of Detailed Chemical Kinetics Using Multi-zone Modeling for CFD in Internal Combustion Engine Simulations," SAE Technical Paper 2012-01-0135, 2012.

4. Bedoya, I., Cadavid, F., Saxena, S., Dibble, R., Aceves, S., Flowers, D., "A Sequential Chemical Kinetics-CFD-Chemical Kinetics Methodology to Predict HCCI Combustion and Main Emissions," SAE Technical Paper 2012-01-1119, 2012.

5. Hsieh S., Havstad, M., Flowers, D., Petitpas, G., Sanz Argent, J., Sensitivity Analysis of Large System of Chemical Kinetic Parameters for Engine Combustion Simulation, ASME Verification and Validation Symposium, May 2–4, 2012.

6. Whitesides, R.A., McNenly, M.J., Piggott, W.T., Hessel, R.P., Flowers, D.L., Aceves, S.M., "Advances in Multi-dimensional Modeling of Clean & Efficient Engine Concepts," AEC/HCCI Working Group Meeting, Southfield MI, June 2012.

7. Saxena, S., Schneider, S., Aceves, S., and Dibble, R., "Wet ethanol in HCCI engines with exhaust heat recovery to improve the energy balance of ethanol fuels," Applied Energy, Volume 98, pages 448–457, 2012.

III.5 Advanced Combustion and Fuels Research at NREL

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Objectives

- Enable post-2010 advanced combustion regime engines and emission control systems with increased efficiency while meeting future emission standards.
- Address technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems.
- Develop understanding of fuel chemical and physical properties that enable furtherance of the Advanced Combustion Engines subprogram for high efficiency engines with cost-effective emission controls.

Fiscal Year (FY) 2012 Objectives

- Develop experimental and simulation tools to characterize fuel ignition behavior in support of advanced combustion engine development.
- Develop understanding of how fuel properties impact the operational range of low-temperature combustion (LTC) by linking ignition characterization to engine studies.
- Support the development of research fuels, fuel surrogates, and reduced kinetic mechanisms to further enable advanced combustion engine development and increased use of non-petroleum-based fuels.
- Investigate fuel chemistry effects and optimized controls on the emissions and efficiency of gasoline direct injection engines.

Accomplishments

- Continued development of Ignition Quality Tester (IQT)-based experimental and simulation research platform to characterize fuel ignition properties, which:
  - Provided critical unique ignition data for low volatility fuels
  - Evaluated and validated reduced kinetic mechanisms
  - Bridged fundamental ignition experiments to engine testing
  - Provided an intermediate simulation development platform used by other DOE laboratories to evaluate optimized computational strategies
- Supported development and utilization of research Fuels for Advanced Combustion Engines (FACE) to determine relationships between fuel chemistry and engine combustion performance and emissions.
- Collaborated with other DOE and Canadian national laboratories, along with corporate industrial partners via the Coordinating Research Council (CRC), to:
  - Expand fuels research to develop surrogate fuels with kinetic models
  - Characterize advanced alternative and renewable fuel streams
- Utilized a spark-ignition direct-injection (SIDI) single-cylinder research engine facility to investigate fuel chemistry effects on advanced combustion and leverage links to NREL's biomass fuels research program.

Future Directions

- Continue expanding IQT-based experimental and simulation research to:
  - Develop broader understanding of fuel chemistry impacts on ignition
  - Develop and validate improved kinetic model reductions
  - Develop chemical kinetic models for fuel compounds, including biofuels
  - Establish links between IQT-based ignition characterization and engine-based combustion performance and emissions
- Collaborate with other DOE and Canadian national laboratories, along with corporate industrial partners via the CRC, to:
  - Expand fuels research to develop surrogate fuels with kinetic models

  - Characterize advanced alternative and renewable fuel streams to address paucity of data relevant to engine research community
- Employ SIDI single-cylinder research engine to study fuel chemistry impacts on advanced combustion, enabling NREL to study span of renewable fuels from fuel production and processing to engine performance and emissions.

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INTRODUCTION

Development of more energy-efficient and environmentally friendly transportation vehicles demand simultaneous increases in powertrain efficiency and reduction in vehicle emissions, which drive the need for significant advances in internal combustion engines. In turn, advances in engine combustion increasingly rely on thorough understanding of fuel physicochemical properties, especially ignition kinetics behavior. In addition, the need for petroleum displacement leads towards increased use of advanced alternative and renewable fuels, many of which behave much differently than traditional petroleum-based fuels. As a critical enabler for advanced combustion engines and to eliminate barriers for alternative fuels, significant research is necessary to understand the relationships between fuel chemistry and engine performance and emissions. The DOE Vehicle Technologies Program's Fuel & Lubricant Technologies subprogram supports research and development (R&D) to address these needs, including R&D conducted by NREL's Advanced Combustion and Fuels (AC&F) research activity.

APPROACH

The focus of NREL's AC&F research activity is the intersection of fuel physicochemical properties, ignition kinetics, combustion, and emissions. The overall research goal is to support the simultaneous development of advanced fuel chemistries and advanced combustion engines by providing bridging experiments and simulation between fundamental chemical kinetics and engine studies. This goal translates into AC&F's research activities, which include:

- Developing and characterizing research-grade reference fuels, surrogate fuels, and advanced alternative/renewable blending streams
- Developing experimental and simulation research platforms to enable efficient combustion and diversification of fuel options
- Developing and validating accurate, efficient fuel ignition and combustion kinetic models
- Using engine-based studies to correlate date for experimental and simulation efforts
- Studying combustion-related fuel properties

AC&F's team members closely collaborate with relevant industry stakeholders (primarily through the CRC), academic researchers, and DOE and Canadian national laboratories colleagues. AC&F participates in the DOE Advanced Engine Combustion Memorandum of Understanding, ensuring our work is in close alignment with and supports DOE Vehicle Technologies Program's Advanced Combustion Engines subprogram. AC&F engages the academic research community through these forums, in addition to directly funding fuel ignition kinetics research at Colorado School of Mines (CSM). The strong collaboration with CSM continued in FY 2012 with the renewed joint appointment for Prof. Greg Bogin at CSM and NREL.

RESULTS

Ignition Kinetics Research

During FY 2012, AC&F continued to develop methods to characterize fuel ignition properties to support kinetics-dominated advanced engine combustion strategies. This effort largely built upon prior research using the IQT, focusing on development of the IQT as an experimental research platform to quantify fuel autoignition behavior, allowing links to fuel physicochemical properties [1]. Fundamental ignition chemistry experiments are commonly performed with shock tubes, rapid compression facilities, and jet-stirred reactors, all of which generally employ premixed gas phase fuel/air mixtures. While extremely valuable in producing data for the development and validation of ignition kinetic models, not all of these devices operate in pressure, temperature, and characteristic ignition delay time regimes comparable to compression ignition engines, including LTC engine concepts. Additionally, while researchers continue with improvements, these devices are generally experimentally challenged with low volatility, multi-component fuels. NREL's development of the IQT into a research platform provides an alternative, complementary source of experimental kinetics data, which is designed to operate with low volatility fuel blends. Ignition kinetic studies with the IQT are complicated by the integration of physical effects (spray droplet breakup and evaporation) and chemical effects, but the IQT provides an intermediate research platform that is easier to characterize and control than full engine studies.

In past years, NREL initially expanded IQT operation beyond its intended operating point to measure ignition delay time and calculate derived cetane number per ASTM D6890 [2]. This technique was applied to the nine fuels comprising the FACE diesel research fuel set [3-4], providing predictive Arrhenius ignition delay parameters over a range of pressure, temperature, and oxygen fraction. Expanding from that effort, NREL contracted with Prof. Tony Dean and Dr. Greg Bogin at CSM to further develop the IQT platform further develop and validate kinetic ignition models for renewable fuel compounds, including alkanes and methyl esters. The collaboration with CSM resulted in significant progress in characterizing the IQT and understanding the unique critical experimental ignition data produced [5]. Through valuable collaboration with Prof. J.Y. Chen at University of California – Berkeley, CSM and NREL developed a KIVA-3V ~65,000 cell computational fluid dynamics model of the IQT injection and combustion process, coupling it with CHEMKIN to evaluate kinetic mechanisms, initially starting with n-heptane (Figure 1). The resulting experimental and computational development led to significant understanding of the IQT, making it capable of providing critical ignition kinetics data. NREL significantly expanded simulation capability for the IQT through use of NREL's dedicated supercomputing resources, Red Mesa and Red Rock [6].

In FY 2012, NREL significantly expanded experimental and simulation studies with the IQT to probe negative temperature coefficient region ignition for C_7 isomers [7-10]. These data complement limited available experimental results from other devices, and are of importance to low-temperature combustion strategies. As shown in Figure 2, NREL's IQT platform can generate a significant amount of experimental ignition data over a range of temperature (and pressure). In addition to producing low-temperature-relevant ignition data for C7 isomers, NREL recently produced LTC-relevant data for 2,2,4,4,6,8,8-heptamethylnonane (iso-cetane), as shown in Figure 3. Iso-cetane (cetane number =15) is a low volatility fuel that is very difficult to study in traditional devices, but it is a key component for diesel surrogate blends. Ignition data for iso-cetane are very limited, and have only recently been measured in a shock tube at high temperatures and high pressures by Oehlschlaeger et al. [11]. The large amount of complementary ignition data NREL has generated is of great interest to the combustion research community.

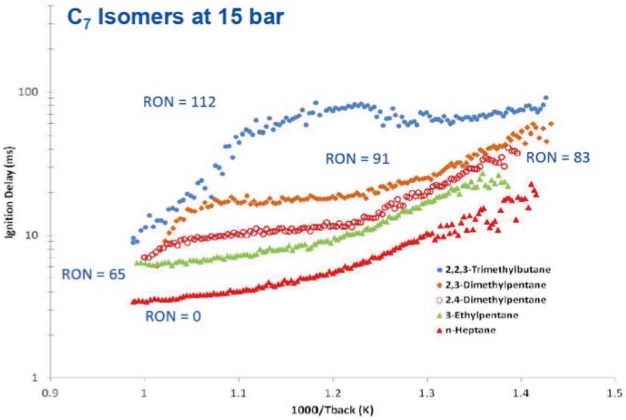


FIGURE 2. IQT-based experimental ignition delay data for C7 isomers.

Advanced Fuels for Advanced Combustion Engines

The AC&F research activity actively participated in CRC committees and projects, collaborating with industry stakeholders and DOE and Canadian national laboratory colleagues. Details of much of this work is covered another annual progress report chapter, covering

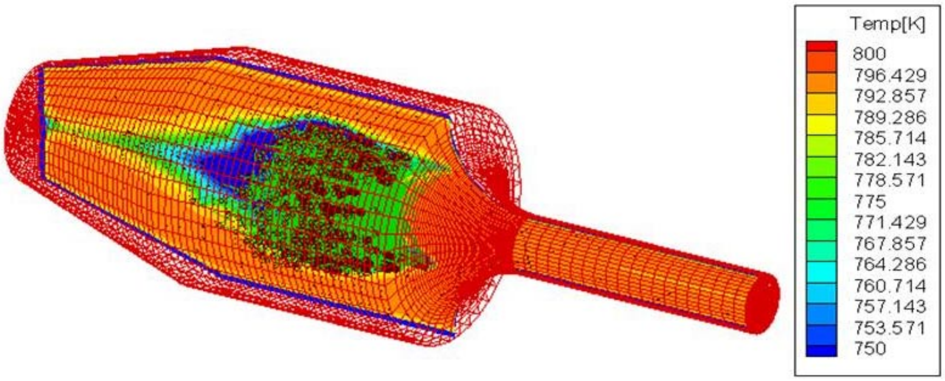


FIGURE 1. The KIVA-3V model (~65,000 cells) employs a Kelvin-Helmholtz Raleigh-Taylor spray breakup model and is linked with CHEMKIN to evaluate ignition kinetics in the IQT.

"Fuels for Advanced Combustion Engine (FACE) – Development of Research Fuels Matrix." AC&F's most significant contribution in this area in FY 2012 was to CRC's Advanced Vehicles, Fuels, and Lubricants (AVFL) AVFL-18 project to develop advanced diesel surrogates with full kinetic models [12], utilizing data and knowledge created in the FACE diesel research fuel set characterization effort. In FY 2012, NREL's AC&F team assisted the AVFL-18 team finalize selection of select candidate compounds, blend those compounds into candidate blends, and test the blends for ignition performance with the IQT [13].

Single-Cylinder Engine-Based Research Capability

In FY 2012 AC&F utilized the single-cylinder research engine facility at NREL's ReFUEL laboratory, which is based on a production General Motors 2.0-L SIDI turbocharged engine. In prior work, the engine was thoroughly mapped as a multi-cylinder engine prior to conversion, including a series of experimental studies with various ethanol and iso-butanol blends. These unique data included valuable information regarding particle number (PN) emissions sensitivity to engine operating parameters and biofuel content [14,15]. After conversion to a more flexible single-cylinder configuration with full independent engine control, additional fuels studies focused on PN emissions with ethanol and iso-butanol blends. These studies complement the findings from the multi-cylinder configuration, which are of particular interest as SIDI engines are challenged in some operating regimes with increased PN emissions. The work completed in FY 2012 demonstrated through a parametric study which controls may be effectively optimized to reduce PN reduction (Figures 4 and 5), and how biofuel content may both reduce PN or increase PN if controls are not compensated for biofuel content [16]. This work received considerable industry interest and demonstrates the flexibility of NREL's SIDI boosted single-cylinder research engine facility to conduct fuel chemistry effects studies on engine combustion, performance, and emissions. In addition, the facility enables DOE's Biomass and Vehicle Technologies Programs to leverage NREL's in-house capability to study the entire span from fuel processing (via NREL's National Bioenergy Center) to advanced combustion engine performance and emissions with alternative fuels.

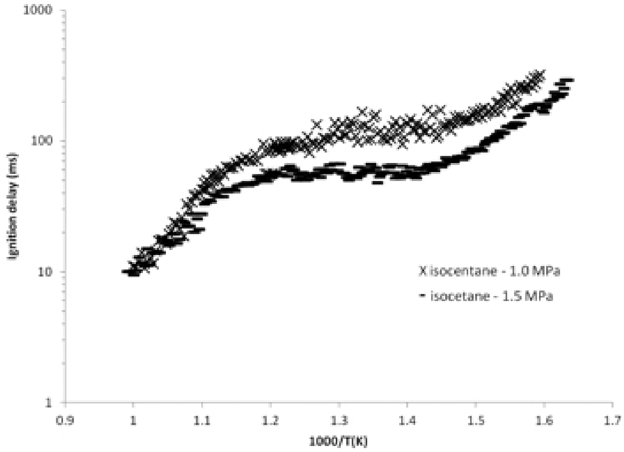


FIGURE 3. IQT-based experimental ignition delay data for iso-cetane.

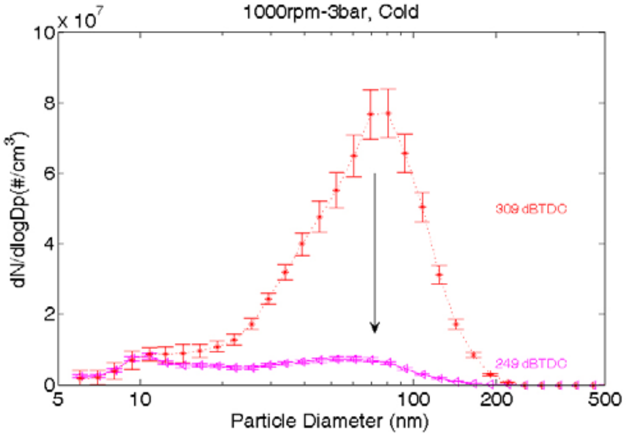
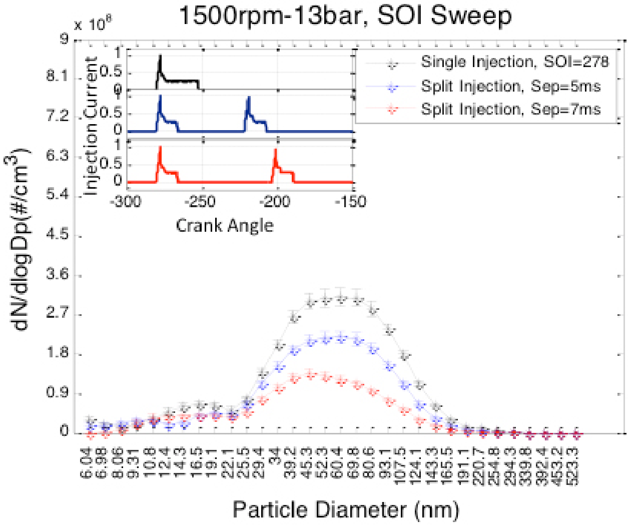


FIGURE 4. Demonstration of an 80% reduction in particle number emissions with delayed start-of-injection timing for cold operating conditions.



SOI - start of injection

FIGURE 5. Demonstration of reduced particle number emissions with a split injection strategy.

CONCLUSIONS

NREL's AC&F research activity made significant progress in supporting the simultaneous development of advanced fuel chemistries and enabling advanced combustion engines. The primary conclusions can be summarized as follows:

- AC&F's continued development of an IQT-based experimental and simulation research platform allowed ignition kinetics studies that provide unique, complementary data that are valuable in developing accurate, efficient chemical kinetics models.
- Collaborative efforts have produced well-characterized standardized research fuel sets that allow cross comparisons of results between different advanced combustion modes and engine design. These efforts enable the development of advanced surrogate fuels and characterization of advanced alternative and renewable fuels, which further benefit fuels and engine researchers.
- AC&F utilized engine-based research capability to both complement and expand studies of the intersection of fuel physicochemical properties, ignition kinetics, combustion, and emissions.

REFERENCES

1. B. Zigler, M. Ratcliff, X. He, and J. Luecke, "Advanced Combustion and Fuels Research at NREL", FY2011 Progress Report for Fuel & Lubricant Technologies, DOE-FT-2011AR, EERE/VTP, February 2012.

2. ASTM D6890-10a, "Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber", http://www.astm.org/Standards/D6890.htm, 2010.

3. M. Alnajjar, W. Cannella, H. Dettman, C. Fairbridge, J. Franz, T. Gallant, R. Gieleciak, D. Hager, C. Lay, S. Lewis, M. Ratcliff, S. Sluder, J. Storey, H. Yin, and B. Zigler, "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1, http://www.crcao.com/reports/recentstudies2010/FACE-1/FACE%201%20Chem%20and%20Phys%20Props%20of%20FACE%20Research%20Diesel%20Fuels.pdf, July, 2010.

4. T. Gallant, J.A. Franz, M.S. Alnajjar, J.M.E. Storey, S.A. Lewis, S.C. Sluder, W.J.Cannella, C. Fairbridge, D. Hager, H. Dettman, J. Luecke, M.A. Ratcliff, and B.T. Zigler, "Fuels for Advanced Combustion Engines Research Diesel Fuels: Analysis of Physical and Chemical Properties", SAE International Journal of Fuels and Lubricants, Vol. 2, Issue 2, pgs. 262-272, 2009.

5. G. Bogin, A.M. Dean, M.A. Ratcliff, J. Luecke, and B.T. Zigler, "Expanding the Experimental Capabilities of the Ignition Quality Tester for Autoigniting Fuels", SAE International Journal of Fuels and Lubricants, Vol. 3, Issue 1, pgs. 353-367, 2010.

6. G.E. Bogin Jr., A. DeFilippo, J.Y. Chen, G. Chin, J. Luecke, M.A. Ratcliff, B.T. Zigler, A.M. Dean, "Experimental Investigation of n-Heptane Autoignition in the Ignition Quality Tester (IQT)", *Energy Fuels*, 2011, 25 (12), pp 5562–5572, doi:10.1021/ef201079g, NREL Report No. JA-5400-51922, October 2011.

7. G. Bogin, J. Luecke, E. Osecky, M. Ratcliff, X. He, and B. Zigler, "Characterizing the Autoignition of Hexadecane and C7 Isomers in the IQT", Advanced Engine Combustion MOU Meeting, Sandia National Laboratories, Livermore, CA, February 15, 2012.

8. M. Ratcliff, G. Bogin, E. Osecky, J. Luecke, and B. Zigler, "IQT Experimental and Modeling Studies of Autoignition", Advanced Engine Combustion MOU meeting, USCAR, Southfield, MI, June 20, 2012.

9. G.E. Bogin Jr., E. Osecky, M.A. Ratcliff, J. Luecke, X. He, B.T. Zigler, A.M. Dean, "An Ignition Quality Tester (IQT) Investigation of the Negative Temperature Coefficient Region of Alkane Autoignition", submitted to *Energy Fuels*, 2012.

10. G. Bogin, E. Osceky, M.A. Ratcliff, J.Y. Chen, J. Luecke, B.T. Zigler, and A.M. Dean, "The Role of the Ignition Quality Tester as a Validation Tool for Ignition Kinetics of Low Volatility Fuels", American Chemical Society: Rocky Mountain Regional Meeting 2012, October 19, 2012.

11. M.A. Oehlschlaeger, J. Steinberg, C. K. Westbrook, and W.J. Pitz, "The Autoignition of Iso-Cetane at High to Moderate Temperatures and Elevated Pressures: Shock Tube Experiments and Kinetic Modeling", *Combustion and Flame*, 156, 2165-2172 (2009).

12. W.J. Pitz, "Recent Progress in the Development of Diesel Surrogate Fuels", CRC Report No. AVFL-18a, http://www.crcao.org/reports/recentstudies2009/AVFL-18a/AVFL-18a%20Pitz%20Literature%20review%20v5.pdf, December, 2009.

13. C.J. Mueller, W.J. Cannella, T.J. Bruno, B. Bunting, H.D. Dettman, J.A. Franz, M.L. Huber, M. Natarajan, W.J. Pitz, M.A. Ratcliff, and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics", *Energy Fuels*, 2012, 26 (6), pp 3284–3303, doi: 10.1021/ef300303e, http://www.crcao.org/reports/recentstudies2012/AVFL-18/AVFL-18 Final Report %5BE&F Journal Article%5D.pdf.

14. X. He, J.C. Ireland, B.T. Zigler, M.A. Ratcliff, K.E. Knoll, T.L. Alleman, and J.T. Tester, "The Impacts of Mid-level Biofuel Content in Gasoline on SIDI Engine-out and Tailpipe Particulate Matter Emissions", SAE Technical Paper No. 2010-01-2125, 2010 Powertrains Fuels and Lubricants Meeting, San Diego, CA, Oct 25–27, 2010.

15. X. He, J.C. Ireland, B.T. Zigler, M.A. Ratcliff, K.E. Knoll, T.L. Alleman, J.H. Luecke, and J.T. Tester, "The Impacts of Mid-level Alcohol Content in Gasoline on SIDI Engine-out and Tailpipe Emissions", ASME ICEF2010-35106, ASME 2010 Internal Combustion Engine Division Fall Technical Conference, Sept. 12–15, 2010.

16. X. He, M.A. Ratcliff, and B.T. Zigler, "Effects of Gasoline Direct Injection Engine Operating Parameters on Particle Number Emissions, *Energy Fuels*, 2012, 26 (4), pp 2014–2027, doi: 10.1021/ef201917p, March 2012.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. G.E. Bogin Jr., A. DeFilippo, J.Y. Chen, G. Chin, J. Luecke, M.A. Ratcliff, B.T. Zigler, A.M. Dean, "Experimental Investigation of n-Heptane Autoignition in the Ignition Quality Tester (IQT)", *Energy Fuels*, 2011, 25 (12), pp 5562–5572, doi:10.1021/ef201079g, NREL Report No. JA-5400-51922, October 2011.

2. B.T. Zigler, "Fuels for Advanced Combustion Engines", 2012 DOE Vehicle Technologies Program Annual Merit Review, Washington, DC, May 14–18, 2012.

3. G. Bogin, J. Luecke, E. Osecky, M. Ratcliff, X. He, and B. Zigler, "Characterizing the Autoignition of Hexadecane and C7 Isomers in the IQT", Advanced Engine Combustion MOU Meeting, Sandia National Laboratories, Livermore, CA, February 15, 2012.

4. C.J. Mueller, W.J. Cannella, T.J. Bruno, B. Bunting, H.D. Dettman, J.A. Franz, M.L. Huber, M. Natarajan, W.J. Pitz, M.A. Ratcliff, and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics", *Energy Fuels*, 2012, 26 (6), pp 3284–3303, doi: 10.1021/ef300303e, http://www.crcao.org/reports/recentstudies2012/AVFL-18/AVFL-18 Final Report %5BE&F Journal Article%5D.pdf.

5. M. Ratcliff, G. Bogin, E. Osecky, J. Luecke, and B. Zigler, "IQT Experimental and Modeling Studies of Autoignition", Advanced Engine Combustion MOU meeting, USCAR, Southfield, MI, June 20, 2012.

6. X. He, M.A. Ratcliff, and B.T. Zigler, "Effects of Gasoline Direct Injection Engine Operating Parameters on Particle Number Emissions, *Energy Fuels*, 2012, 26 (4), pp 2014–2027, doi: 10.1021/ef201917p, March 2012.

7. G.E. Bogin Jr., E. Osecky, M.A. Ratcliff, J. Luecke, X. He, B.T. Zigler, A.M. Dean, "An Ignition Quality Tester (IQT) Investigation of the Negative Temperature Coefficient Region of Alkane Autoignition", submitted to *Energy Fuels*, 2012.

8. G. Bogin, E. Osceky, M.A. Ratcliff, J.Y. Chen, J. Luecke, B.T. Zigler, and A.M. Dean, "The Role of the Ignition Quality Tester as a Validation Tool for Ignition Kinetics of Low Volatility Fuels", American Chemical Society: Rocky Mountain Regional Meeting 2012, October 19, 2012.

III.6 Fuels for Advanced Combustion Engines (FACE) – Development of Research Fuels Matrix

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Objectives

- Bring together a collection of stakeholders.
- Design a standard set of research gasoline and diesel fuels to enable cross comparisons of results between different research and development (R&D) organizations working on similar and different advanced combustion modes and engine designs.
- Engage a fuels blender to manufacture and sell the fuels.
- Conduct extensive characterization of the fuels and make results publicly available.
- Champion use of the fuels by government laboratories, university researchers, and industry R&D groups.

Fiscal Year (FY) 2012 Objectives

Continue leveraging technical expertise and capabilities from various DOE laboratories to benefit common goals with Coordinating Research Council (CRC) FACE Working Group.

Accomplishments

- Maintained and augmented a cross-industry working team cross-industry working team of subject matter experts through collaboration with the CRC, including stakeholder members from energy/petroleum industry, automotive/engine manufacturers, universities, and national laboratories.
- Leveraged CRC partnership with research collaboration between DOE and Canadian national laboratories, including:
  - Oak Ridge National Laboratory
  - Pacific Northwest National Laboratory (PNNL)
  - National Renewable Energy Laboratory
  - Lawrence Livermore National Laboratory (LLNL)
  - Sandia National Laboratories (SNL)
  - CanmetENERGY, Natural Resources Canada
- Developed nine FACE diesel fuels, which are currently available for purchase from Chevron-Phillips Chemical Company (CPChem). Reformulated three of the fuels to permit international sale and simultaneously increased the fidelity to commercial fuel compositions.
- Completed and published exhaustive advanced characterization of nine FACE diesel fuels, including application of novel techniques to fuel property characterization.
- Demonstrated initial engine performance in premixed charge compression ignition (PCCI) and homogeneous charge compression ignition (HCCI) operation with FACE diesel fuel matrix.
- Conducted CRC-sponsored research study on HCCI operation in a light-duty diesel engine with FACE diesel fuels (CRC Advanced Vehicles Fuels and Lubricants [AVFL]-16 project).
- Continued development of FACE gasoline matrix, with nine of the FACE gasoline fuels now available for purchase from CPChem.
- Expanded effort to include evaluation of advanced alternative and renewable fuels (CRC AVFL-19 project, formerly CRC FACE Advanced Alternatives and Renewable Fuels Team). In one fuel quite unexpected levels of ring compounds were reported and verified.
- Applied output of FACE diesel fuels advanced characterization effort to facilitate development of a diesel surrogate (CRC AVFL-18 project). This program aims to permit fast modeling of novel combustion chambers and provide useful indications of combustion evolution and emissions.

- Correlated available diesel, PCCI, and HCCI engine data using FACE diesel fuels with key fuel properties.

Future Directions

- Complete development and characterization of FACE gasoline fuel matrix.
- Apply techniques developed in FACE diesel advanced characterization effort to address paucity of data for advanced alternative and renewable fuels.
- Continue development of multi-component diesel surrogate with full kinetic model, complementing FACE diesel fuel matrix.

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INTRODUCTION

There are many embodiments of advanced combustion processes for engines burning both gasoline-like and diesel-like fuels. These include HCCI, PCCI, and numerous related processes known by their own acronyms. In gasoline engines, advanced combustion techniques such as those outlined above offer increased thermal efficiency without sacrifice of the traditionally low emissions offered by spark-ignited engines. In diesel engines, advanced combustion offers lower emissions of particulate matter (PM) and oxides of nitrogen (NOx) without the sacrifice of traditionally high thermal efficiency offered by compression-ignition engines. All of these processes generally focus on causing combustion to occur at a low enough temperature so that the formation of NOx is thermodynamically unfavorable and with enough air-fuel mixing to ensure low PM formation. In this way, the engine-out emissions of both pollutants are lowered simultaneously, without a trade-off relationship as had historically been the norm.

Advanced combustion techniques have been the focus of intense research at virtually every engine and vehicle manufacturer around the world for several years. As a result, there exists a breadth of specific techniques and hardware configurations, each aimed at determining the best path towards commercial viability. Some engines are known to use differing forms of advanced combustion as the speed and load demand on the engine change. The field is progressing rapidly, but at this point there is not one technology or hardware configuration that is universally more advantageous than others. Hence, it isn't possible to determine one "best" technology that can be used to study the importance of fuel properties on efficiency, emissions, and performance of advanced engines. However, if many research and development programs could utilize a common matrix of research fuels, the impact of fuel properties could be judged broadly across many specific applications of advanced combustion technology. The FACE program was conceived to bring together the stakeholders in industry together with researchers at universities and the national laboratories to begin the process of producing designed research fuels that can be used to fill this gap.

APPROACH

ORNL and NREL began to lay the groundwork for this project by assessing industrial interest and seeking the best forum in which to conduct it. A goal from the outset was to engage the energy companies as well as the automotive sector in the process of designing the research fuels. Consequently, NREL and ORNL sought to form a working group under the auspices of the CRC as a forum to support the necessary interactions among the stakeholders. CRC was identified as a logical forum for this effort because it presented opportunities to bring the required stakeholders (energy companies, automobile manufacturers, engine manufacturers, universities, and national laboratories) together in an environment conducive to information sharing among the participants. Several CRC members shared an interest in forming such a group. The CRC FACE Working Group was chartered in 2005 and a mission statement drafted and approved by CRC.

The mission of the FACE Working Group is to recommend sets of test fuels so that researchers evaluating advanced combustion systems may compare results from different laboratories using the same set (or sets) of fuels. Examples of advanced combustion systems are low-temperature combustion, HCCI, and high efficiency clean combustion (HECC).

The activities of the working group are focused and constrained by a well-defined and approved scope of work that is available on CRC's website [1].

The FACE working group is currently chaired by Bill Cannella of Chevron Energy Technology Company and co-chaired by Robert Wagner of ORNL and Brad Zigler of NREL. In excess of $500,000 per year in in-kind research are managed through FACE and AVFL projects proposed by FACE members who participate actively in those AVFL projects. The FACE Working Group roster includes 33 people representing 23 different organizations across industry, government, and academia. Working Group members from many different organizations have participated actively in the process of designing proposed fuel matrices for both gasoline-like and diesel-like fuels. Subcommittees were formed to specifically focus on both gasoline-like fuels and diesel-like fuels.

RESULTS

Diesel Fuel Matrix

The diesel subcommittee initially sought to determine the most important fuel properties that should be included in the fuel matrix. Recognition that keeping the number of fuels in the matrix to a manageable level demanded that many interesting and perhaps important fuel properties or characteristics be left to future studies. A measure of ignitability, a measure of fuel chemistry, and a measure of fuel volatility were selected as the most important variables for study if the fuel set were constrained to less than 10 fuels. Cetane number, aromatic content by volume, and the 90% recovery point of the fuel distillation were selected as the representative measures of the variables of interest (see Figure 1). The team recognized that these might not be the only or the best representative measures, but agreed that these would be the measures that a blender would be most successful in using to actually produce the fuels. Ranges of variation for the fuel properties to be studied were established. In order to keep the number of fuels manageable, only two levels for each variable were specified. The fuels were formulated by CPChem and have been made available for purchase by interested researchers. ORNL has facilitated distribution of the fuels from drums maintained by ORNL for those researchers who only require small volumes of the fuels. Research efforts have been conducted at ORNL, West Virginia University (under contract from CRC), Pennsylvania State University, Sandia National Laboratories, National Research Council-Canada, NREL, and other locations using the fuels.

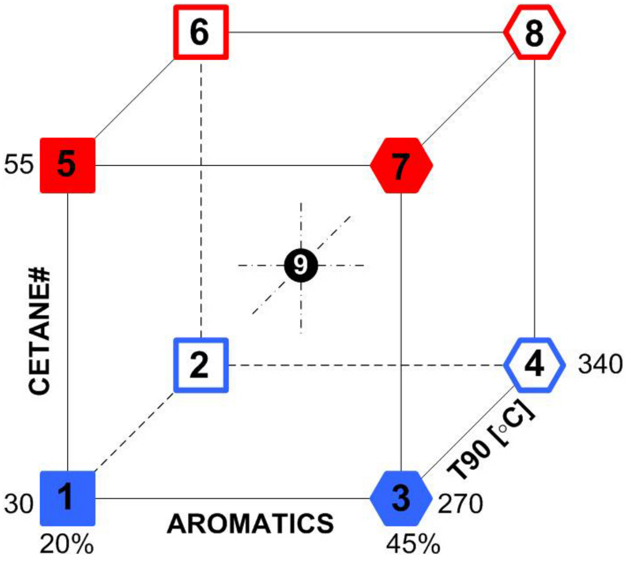


FIGURE 1. FACE Diesel Research Fuel Matrix

A CRC FACE Characterization Team was formed to perform an exhaustive characterization of the nine FACE diesel fuels. This team included ORNL, Chevron, PNNL, NREL, and CanmetENERGY, Natural Resources Canada. The team focused on both the chemical and physical properties of the first production run of the FACE fuel set, as well as implementation of emerging state-of-the-art tools for fuel analysis. One motivation was to come up with a tractable parameter set, based on chemical composition, to relate to observed combustion behavior or physical properties. Advanced analysis techniques applied included:

- 1-dimensional gas chromatography-mass spectrometry (GC-MS)
- 2-dimensional (2-D) GC-MS
- 2-D gas chromatography-flame ionization detection
- 2-D GC-field ionization mass spectrometry plus paraffins, isoparaffins, olefins, naphthenes, and aromatics
- Ignition Quality Tester derivation of Arrhenius ignition parameters
- ^{1}H and ^{13}C nuclear magnetic resonance

Well-characterized fuel chemistry improves the possibility of developing robust predictive models for combustion behavior in both conventional and advanced combustion modes, whereby the predictive models could be applied to more complex fuel streams from non-traditional sources. This characterization also allowed the group to reformulate some of the fuels that were not compliant with European Union (EU) regulations so that they might be sold and used in those countries. By using the advanced characterizations the team was actually able to improve the fidelity to the commercial chemistry of diesel fuel while bringing the new blends into compliance with EU requirements. The FACE team introduced the diesel research fuel set and preliminary characterization to the engine research community [2], and published the exhaustive characterization details in a CRC report [3]. Figures 2 and 3 illustrate examples of advanced characterization performed for these fuels, which provide a significant correlation a resource for researchers studying advanced engine combustion.

Development of the FACE diesel matrix prompted its immediate use in studies of advanced combustion. ORNL employed the full set in fuel effects studies on HECC [4], and on HCCI [5]. Additionally, NREL and CRC began a joint study employing the FACE set to enable light-duty diesel advanced combustion regimes, as the AVFL-16 project [6]. The unique knowledge gained in the advanced characterization study of the FACE diesel fuels also enabled CRC to begin the development of advanced diesel fuel surrogates which will eventually have full kinetic models (Advanced Vehicles Fuels and Lubricants, AVFL-18) [7-9]. ORNL subsequently correlated results from various researchers using the FACE diesel fuels to date [10]. The CRC FACE Working Group has continued to maintain availability of the FACE diesel research fuels, including support for blending of additional batches [11].

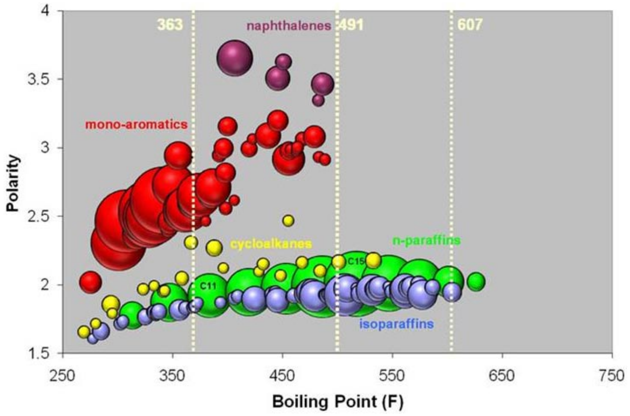


FIGURE 2. Two-Dimensional GC-MS Analysis of the Centerpoint FACE Diesel Fuel (FD-9A)

Gasoline Fuel Matrix

The gasoline subcommittee identified four key parameters as being important to capture in a matrix of test fuels for advanced combustion engines. The initial design matrix targeted four key fuel properties:

- Research Octane Number (70-95)
- Sensitivity (0-12)
- N-paraffins content by volume (5%-25%)
- Aromatics content by volume (0%-50%)

The approach in the gasoline subcommittee was to ask the blender to use a blending model and small quantity hand blends to determine which fuel targets could be met. Then an assessment and statistical analysis was used to determine which fuels would be blended and available for distribution. CPChem worked with their blending model to determine which fuel targets can be met and where constraints need to be relaxed. In short, the initial design placed too many constraints for any reasonable number of fuels to be produced. For example, the range of sensitivity of 0 to 12 is extremely difficult to meet under any case. Additionally, with normal paraffins,

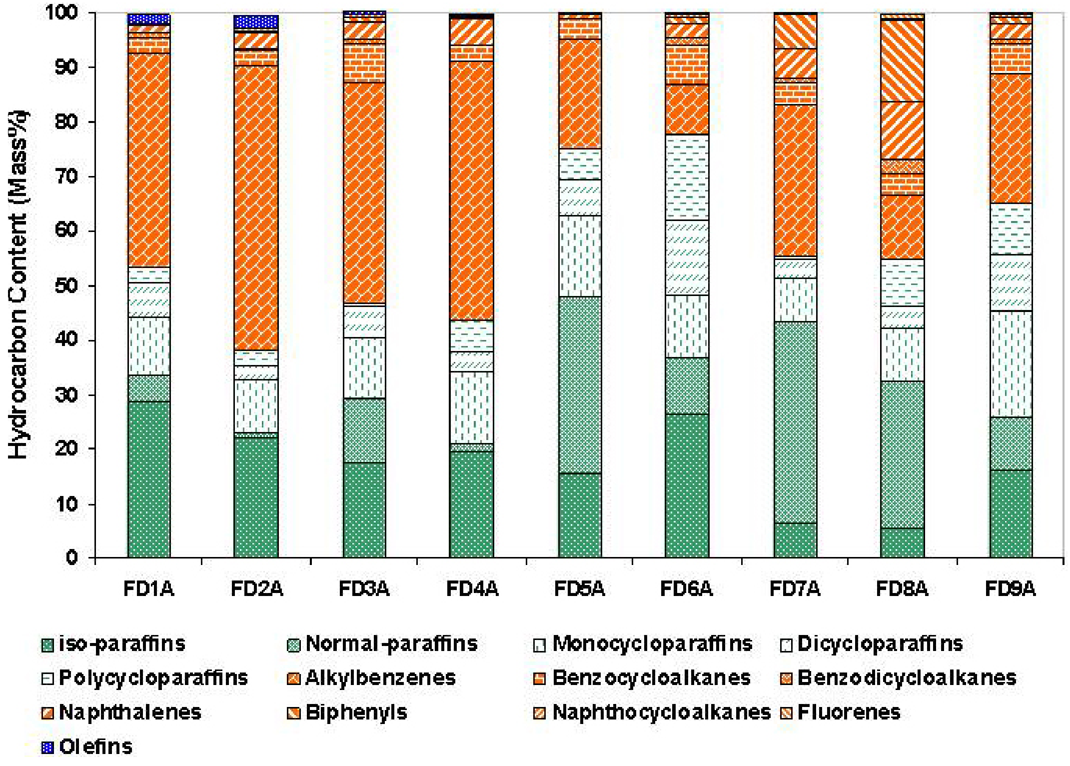


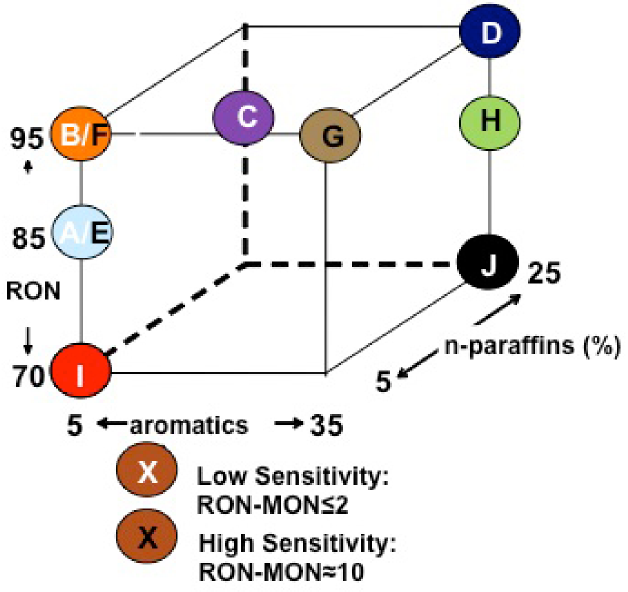
FIGURE 3. GC-Field Ionization Mass Spectrometry and Paraffins, Isoparaffins, Olefins, Naphthenes, and Aromatics Analysis of FACE Diesel Fuels

aromatics, and olefins constrained, the only remaining classes of chemical compounds to vary are cycloparaffins and isoparaffins. This makes it exceedingly difficult to reach the other target properties and can only even partially be met using large quantities of pure compounds (up to 85% by volume).

The gasoline subcommittee consulted with statistical experts at Battelle to steer how the design should be modified to target key fuel properties without placing too many constraints that make the fuels impossible to blend. Fifty-eight different fuel designs were modeled resulting in 37 candidate fuel blends. The 37 candidate blends were down-selected to 20 blendable recipes. Physical properties of the 20 hand blends were analyzed and statistically studied by Battelle. Based on that input, a final matrix of 10 fuels was identified, illustrated in Figure 4. The CRC FACE Working Group has continued working with CPChem to finalize and approve FACE gasoline matrix blends for production. Nine of the blends are currently available for purchase from CPChem [12]. Battelle also complemented the FACE gasoline set with modeling prediction of the effects of ethanol blending [13].

Advanced Alternatives and Renewable Fuels

The CRC FACE Working Group also began to expand work beyond the FACE petroleum-based diesel and gasoline research fuel sets. Increasing interest in advanced alternatives and renewable fuels led the team to consider the eventual need for standardized research fuel sets utilizing these blending streams. After consideration, the team decided to first address the paucity of fuel chemistry data for many of these blending streams. The lessons learned and techniques developed in the FACE diesel advanced characterization effort would provide valuable data regarding these fuels. The team, therefore, decided to first concentrate on this effort while not precluding the eventual development of advanced alternative and renewable fuels-based FACE research fuels.



MON - Motor Octane Number

FIGURE 4. FACE Gasoline Research Fuel Matrix

The Advanced Alternatives and Renewable Fuels sub-team was formed by the CRC FACE Working Group. The sub-team effort was later reorganized into the CRC AVFL-19 project. Initial focus is on identifying and characterizing streams of interest for diesel-type fuels, giving careful consideration to avoid declaring advanced alternative and renewable fuel "winners" but rather provide critical fuel chemistry data to enable further research. The AVFL-19 project has collected and is completing analysis of advanced alternative and renewable fuels in the diesel range.

CONCLUSIONS

The collaborative efforts of the DOE national laboratories and Canadian national laboratories, synergistically working with industry partners through the CRC FACE Working Group have enabled development of standard sets of research gasoline and diesel fuels to enable cross comparisons of results between different R&D organizations working on similar and different advanced combustion modes and engine designs. In FY 2012, the FACE-related research effort has:

- Fostered continued use of the FACE diesel research fuels in advanced engine combustion research, including completion of the AVFL-16 study.
- Correlated existing diesel, PCCI, and HCCI engine data using FACE diesel fuels with key fuel properties.
- Supported continued development of the FACE gasoline matrix, including offering seven blends for purchase.
- Supported the AVFL-19 project to identify advanced alternative and renewable fuel streams about which critical fuel chemistry data are lacking and characterize them, applying techniques developed in the FACE diesel characterization effort.
- Developed advanced diesel surrogates via the AVFL-18 project.

REFERENCES

1. "Fuels for Advanced Combustion Engines (FACE) Working Group Mission Statement", http://www.crcao.com/publications/advancedVehiclesFuelsLubricants/FACE/index.html.

2. T. Gallant, J.A. Franz, M.S. Alnajjar, J.M.E. Storey, S.A. Lewis, S.C. Sluder, W.J. Cannella, C. Fairbridge, D. Hager, H. Dettman, J. Luecke, M.A. Ratcliff, and B.T. Zigler, "Fuels for Advanced Combustion Engines Research Diesel Fuels: Analysis of Physical and Chemical Properties", SAE Technical Paper 2009-01-2769, SAE 2009 Powertrains Fuels and Lubricants Meeting, San Antonio, TX, November 2–4, 2009.

3. M. Alnajjar, W. Cannella, H. Dettman, C. Fairbridge, J. Franz, T. Gallant, R. Gieleciak, D. Hager, C. Lay, S. Lewis, M. Ratcliff, S. Sluder, J. Storey, H. Yin, and B. Zigler, "Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels", CRC Report No. FACE-1, http://www.crcao.com/reports/recentstudies2010/FACE-1/FACE%201%20Chem%20and%20Phys%20Props%20of%20FACE%20Research%20Diesel%20Fuels.pdf, July, 2010.

4. K. Cho, M. Han, R. Wagner, C.S. Sluder, and G.K. Lilik, "Experimental Investigation of the Effects of Fuel Characteristics on High Efficiency Clean Combustion (HECC) in a Light-Duty Diesel Engine", SAE Technical Paper 2009-01-2669, SAE 2009 Powertrains Fuels and Lubricants Meeting, San Antonio, TX, November 2–4, 2009.

5. B.G. Bunting, S. Eaton, and R. Crawford, "Performance Evaluation and Optimization of Diesel Fuel Properties and Chemistry in an HCCI Engine", SAE Technical Paper 2009-01-2645, SAE 2009 Powertrains Fuels and Lubricants Meeting, San Antonio, TX, November 2–4, 2009.

6. D. Carder, R. Ryskamp, J. Nuszkowski, H. Li, N. Clark, G. Thompson, M. Gautam, and S. Wayne, "Fuels to Enable Light-Duty Diesel Advanced Combustion Regimes", CRC Report No. AVFL-16, Coordinating Research Council, August 2012, http://www.crcao.org/reports/recentstudies2012/AVFL-16/CRC AVFL-16 Final Report_Aug2012.pdf.

7. W.J. Pitz, "Recent Progress in the Development of Diesel Surrogate Fuels", CRC Report No. AVFL-18a, http://www.crcao.org/reports/recentstudies2009/AVFL-18a/AVFL-18a%20Pitz%20Literature%20review%20v5.pdf, December 2009.

8. W.J. Pitz and C.J. Mueller, "Recent Progress in the Development of Diesel Surrogate Fuels," *Progress in Energy and Combustion Science* 37 (3) (2011) 330-350.

9. C.J. Mueller, W.J. Cannella, T.J. Bruno, B. Bunting, H.D. Dettman, J.A. Franz, M.L. Huber, M. Natarajan, W.J. Pitz, M.A. Ratcliff, and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics", *Energy Fuels*, 2012, 26 (6), pp 3284–3303, DOI: 10.1021/ef300303e, http://www.crcao.org/reports/recentstudies2012/AVFL-18/AVFL-18 Final Report %5BE&F Journal Article%5D.pdf.

10. J. Kim, C. Sluder, and R. Wagner, "Combustion Studies with FACE Diesel Fuels: A Literature Review," SAE Technical Paper 2012-01-1688, 2012, doi:10.4271/2012-01-1688.

11. J.T. Bays, D.L. King, and M.J. O'Hagan, "Carbon-Type Analysis and Comparison of Original and Reblended FACE Diesel Fuels (FACE 2, FACE 4, and FACE 7)", Pacific Northwest National Laboratory Report, PNNL-21955, October 2012.

12. http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/FACE/FACE Fuel Properties 2012.02.08.pdf.

13. http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/FACE/FACE-Gasoline Fuel Properties with Ethanol - Sept 10 2010 v3.pdf.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. B.T. Zigler and C.S. Sluder, "Fuels for Advanced Combustion Engines (FACE) – Development of Research Fuels Matrix", FY2011 Progress Report for Fuel & Lubricant Technologies, DOE-FT-2011AR, EERE/VTP, February 2012.

2. W.J. Cannella, "CRC Fuels for Advanced Combustion Engines (FACE)", AEC/HCCI Working Group Meeting, February 14, 2012.

3. B.T. Zigler, "Fuels for Advanced Combustion Engines", 2012 DOE Vehicle Technologies Program Annual Merit Review, Washington, DC, May 14–18, 2012.

4. C.J. Mueller, W.J. Cannella, T.J. Bruno, B. Bunting, H.D. Dettman, J.A. Franz, M.L. Huber, M. Natarajan, W.J. Pitz, M.A. Ratcliff, and K. Wright, "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics", *Energy Fuels*, 2012, 26 (6), pp 3284–3303, DOI: 10.1021/ef300303e, http://www.crcao.org/reports/recentstudies2012/AVFL-18/AVFL-18 Final Report %5BE&F Journal Article%5D.pdf.

5. D. Carder, R. Ryskamp, J. Nuszkowski, H. Li, N. Clark, G. Thompson, M. Gautam, and S. Wayne, "Fuels to Enable Light-Duty Diesel Advanced Combustion Regimes", CRC Report No. AVFL-16, Coordinating Research Council, August 2012, http://www.crcao.org/reports/recentstudies2012/AVFL-16/CRC AVFL-16 Final Report_Aug2012.pdf.

6. J. Kim, C. Sluder, and R. Wagner, "Combustion Studies with FACE Diesel Fuels: A Literature Review," SAE Technical Paper 2012-01-1688, 2012, doi:10.4271/2012-01-1688.

7. J.T. Bays, D.L. King, and M.J. O'Hagan, "Carbon-Type Analysis and Comparison of Original and Reblended FACE Diesel Fuels (FACE 2, FACE 4, and FACE 7)", Pacific Northwest National Laboratory Report, PNNL-21955, October 2012.

III.7 Alternative Fuels DISI Engine Research

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DOE Technology Development Manager:
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Objectives

Provide the science-base needed to understand:

- How emerging alternative fuels, with an initial focus on ethanol, will impact the new highly-efficient direct-injection, spark ignition (DISI) light-duty engines being developed by industry.
- How engine design and operation can be optimized to make the most efficient use of future fuels.

Fiscal Year (FY) 2012 Objectives

- Examine combined effects of injection timing and fuel type on oxides of nitrogen/particulate matter (NO_x/PM) trade-offs and useful load ranges for fuel-stratified combustion.
- Perform high-speed imaging to identify causes for the onset of misfire and partial-burn cycles for high exhaust gas recirculation (EGR)/low NO_x operation.
- Conduct spray and flame modeling to understand fundamental differences between gasoline and ethanol fuels when used for stratified-charge SI combustion.

Accomplishments

- Demonstrated the ability of injection-timing retard with 85% ethanol in gasoline (E85) to enable ultra-low emissions of NO and PM.
- Performed multiple high-speed optical diagnostics of stratified gasoline and E85 combustion, and identified one stochastic in-cylinder phenomenon that correlates with cyclic variability of both flame development and indicated mean effective pressure (IMEP).
- Performed a spectroscopic characterization of flame luminosity of the various stages of highly-stratified E85 combustion.
- Combined a spray model and a flame-speed model in CHEMKIN. Used models to quantify fuel effects, like vaporization cooling, on mixture formation and combustion in various regions of fuel jets.

Future Directions

- Examine the effects of fuel blend in the E0 to E100 range on exhaust NO_x and PM for stratified operation, and evaluate potential implications for flex-fuel vehicles.
- Examine effects of engine speed and intake air temperature on stratified operation with selected gasoline/ethanol blends.
- Apply planar laser induced fluorescence to measure in-cylinder fuel distribution for better understanding of both low-emissions operation and sources of cyclic variability.
- Perform particle image velocimetry measurements of intake and compression flows, and examine correlation between flow field and variability of combustion.

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INTRODUCTION

In the light of limited petroleum reserves and accelerating global climate change, both renewable fuels and improved engine efficiency are important areas of research. This project focuses on DISI engine operation with a spray-guided, stratified-charge combustion system. This lean-burn technology has potential to achieve diesel engine fuel efficiency by utilizing overall dilute combustion and minimal intake throttling, but there are several technical challenges that need to be addressed: first, while maintaining high combustion stability, low engine-out NO_x and PM emissions must be achieved to avoid expensive aftertreatment technology. Second, operating the engine in overall lean but stratified mode requires precise and robust control of the fuel/air mixing to ensure that an ignitable and flammable mixture exists around the spark-plug gap at the time of ignition. This is particularly challenging to accomplish for flex-fuel engines as the fuel properties change depending on the exact mix of gasoline and E85 being present in the fuel tank.

Compared to gasoline, E85 has a lower heating value, higher latent heat, and high O_2 content. Thus, it requires considerably more fuel mass injected (thereby changing stratification), cools the charge more, and has different reaction chemistry. This project aims to provide the fundamental understanding needed by industry to effectively develop engines that use alternative fuels like E85. This development includes minimizing any negative influence of the different fuel properties, while also examining venues for increased engine efficiency, performance, and reduced emissions.

APPROACH

The Alternative Fuels DISI Engine Lab at Sandia houses an engine that is set up for both performance testing and in-cylinder optical diagnostics. First, performance testing with an all-metal engine configuration is conducted over wide ranges of operating conditions and alternative-fuel blends. Second, in-cylinder processes are examined with high-speed optical diagnostics, including advanced laser-based techniques. Also, low-speed diagnostics like spectroscopic characterization of the combustion luminosity are applied. Parallel to the experiments, modeling provides insights into the fundamentals that govern the spray-driven combustion event. The combination of performance testing, exhaust-emissions measurements, optical diagnostics, and modeling allows building the science-base required by industry to develop these stratified-charge engines to their full potential.

RESULTS

Figure 1 shows both a cross section of the combustion chamber (top), and a camera view from below via the piston bowl window (bottom). For the FY 2012 results, the engine was fueled with single injections using an 8-hole injector. The injector was oriented such that two of the fuel sprays straddled the spark plug gap.

Figure 2 shows key results from an emissions and stability study [1] of gasoline and E85, utilizing unthrottled high-efficiency stratified combustion. Figure 2a shows that with start of injection (SOI) = -31 degrees crank angle (°CA, which is a typical SOI for stratified operation), both gasoline and E85 have NO and soot emissions with comparable magnitudes. The U.S. 2007/2010 NO_x and PM emissions standards are not met with SOI = -31°CA. However, with E85, it is possible to find operating points that achieve the legislated engine-out emission objectives. The simultaneous low NO and soot emissions shown in Figure 2a are achieved using a late SOI = -6°CA while reducing the load to $IMEP_{net}$ = 260 kPa. The benefits and challenges with injection-timing retard are discussed in detail in Ref. [2]. Figure 2b shows the NO/stability trade-off for these conditions. For E85 with SOI = -6°CA, sufficient NO reduction is achieved with only a modest reduction of intake $[O_2]$ at the expense of combustion stability. Comparing Figures 2a and 2b shows that not only does E85 with SOI = -6°CA achieve low NO and soot, it also achieves a superior NO/stability trade-off.

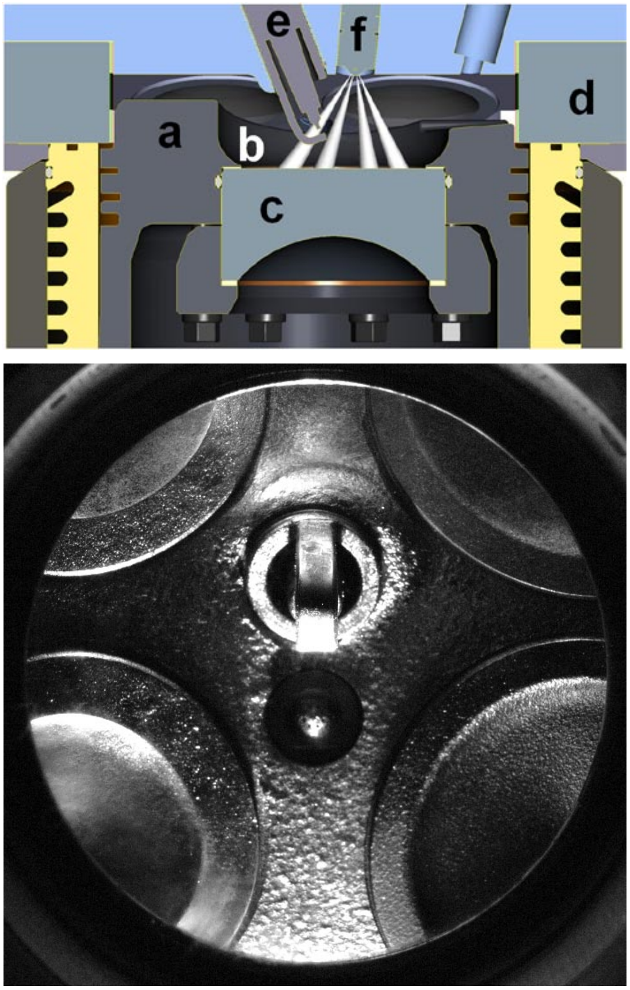
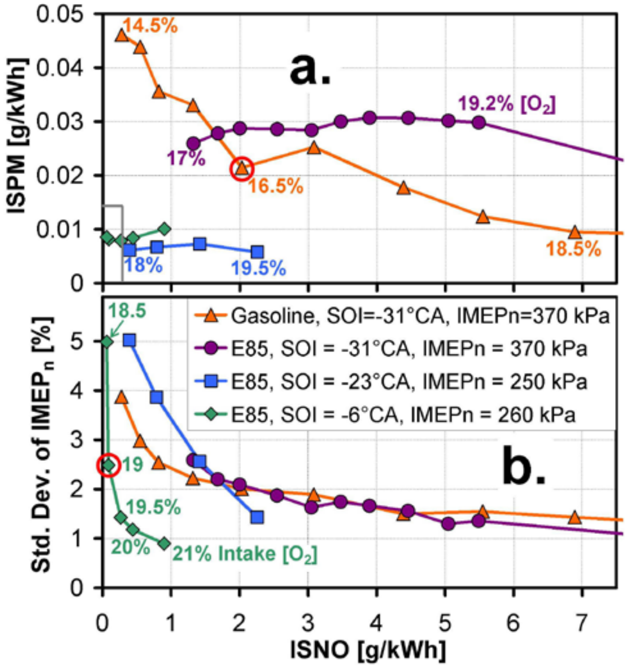


FIGURE 1. Top: computer-aided design rendering of cross-section of combustion chamber at top-dead center with a - piston, b - piston bowl, c - piston-bowl window, d - pent-roof window, e - spark plug, and f - fuel injector. Bottom: view from below via piston-bowl window with piston at -10°CA position.

Figure 3 shows results from high-speed imaging of broadband luminosity collected via the wide-angle view provided by the piston-bowl window. One gasoline case and one E85 case are presented, and the corresponding data points in Figure 2 are marked by red circles. Light-emitting diode (LED) illumination for Mie-scattering of liquid fuel was applied for each of the two left-most frames, as annotated by "LED" in the upper right hand corner these frames.

For the data presented in this report, the spark timing (ST) was adjusted for each operating point to minimize cyclic variations of IMEP. This leads to remarkably different STs relative to the injection event. For gasoline in Figure 3a, ST occurs near the end of injection (EOI),



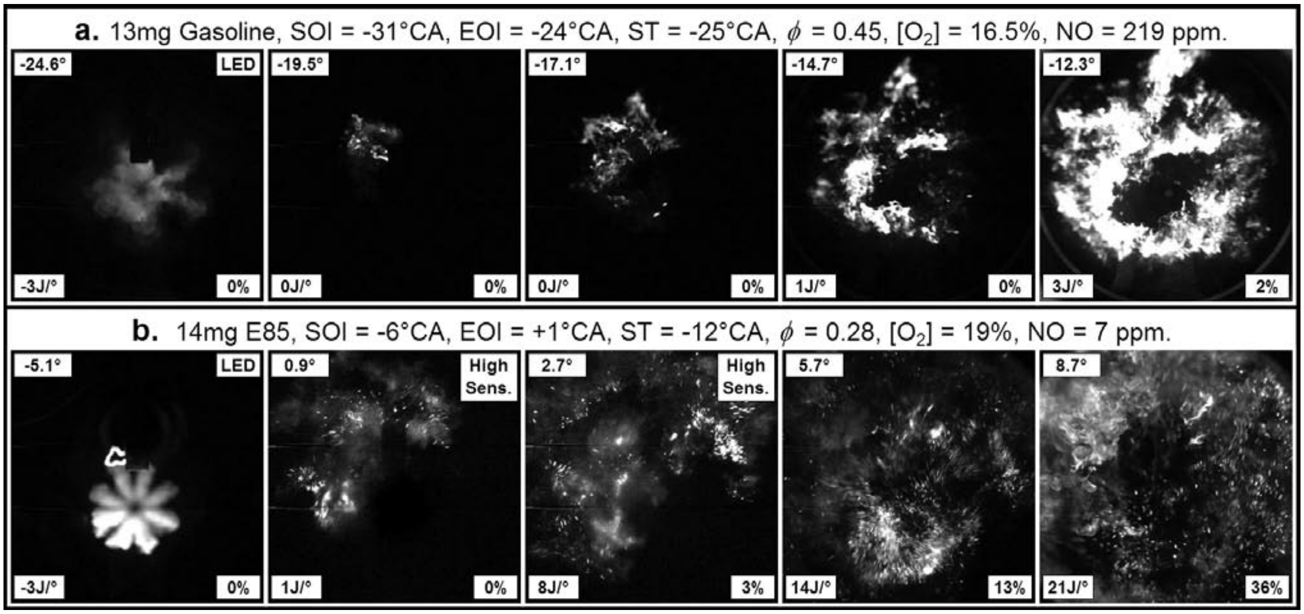
ISPM - indicated specific particulate matter

FIGURE 2. a) NO/PM and b) NO/combustion-instability trade-offs obtained by sweeping intake [O$_2$] for various conditions at 1,000 rpm. The two circled data points correspond to the two images sequences in Figure 3.

consistent with literature for gasoline [3]. In contrast, for E85 in Figure 3b, ST is well before SOI. These different combinations of SOIs and STs lead to very different flame developments. For gasoline in Figure 3a, moderately corrugated flamelets develop from the spark gap and spread to medium radii in the piston bowl, forming a toroidal combustion region during the early part of the combustion process. In contrast, for E85 in Figure 3b, the spark plasma first develops and is convected towards the left of the spark gap by the in-cylinder swirl flow. Once fuel injection starts, the head of the spray in the 11 o'clock direction quickly penetrates towards the spark plasma. The interaction of the spark plasma and the fuel jet disperses rich and weakly luminous flames over a wide area prior to onset of the main combustion event. As the heat release enters its main phase, the combustion luminosity increases simultaneously over large areas and the combustion appears very turbulent.

Figure 2b shows that the low NO emissions for E85 operation with SOI = -6°CA and [O$_2$] = 19% come with the penalty of elevated cyclic variability. Image analysis reveals that cycles with faint early luminosity have increased risk of developing into a low-IMEP cycle. Figure 4a exemplifies the early combustion luminosity for two typical and two weak cycles. The typical cycles are shown in the two left-most columns and have features that are generally similar to that of the other typical cycle presented in Figure 3b. In contrast, the weak cycles in the two right-hand columns in Figure 4a both show spark plasmas that instead extend towards the injector. This leads to weak early flame luminosity, which corresponds to delayed onset of the heat release, as Figure 4b shows.

Engine tests show that the emissions benefits of injection-timing retard are more difficult to realize for gasoline. Gasoline's requirement for ST near EOI contributes to its inability to accept a late SOI [2].


a. 13mg Gasoline, SOI = -31°CA, EOI = -24°CA, ST = -25°CA, ϕ = 0.45, [O$_2$] = 16.5%, NO = 219 ppm.

b. 14mg E85, SOI = -6°CA, EOI = +1°CA, ST = -12°CA, ϕ = 0.28, [O$_2$] = 19%, NO = 7 ppm.

FIGURE 3. Combined natural-luminosity and Mie-scattering imaging for representative cycles for gasoline (a.) and E85 (b.). Crank angle in upper left, apparent heat release rate (AHRR) in lower left, cumulative AHRR in lower right, and LED illumination or high sensitivity settings in upper right.

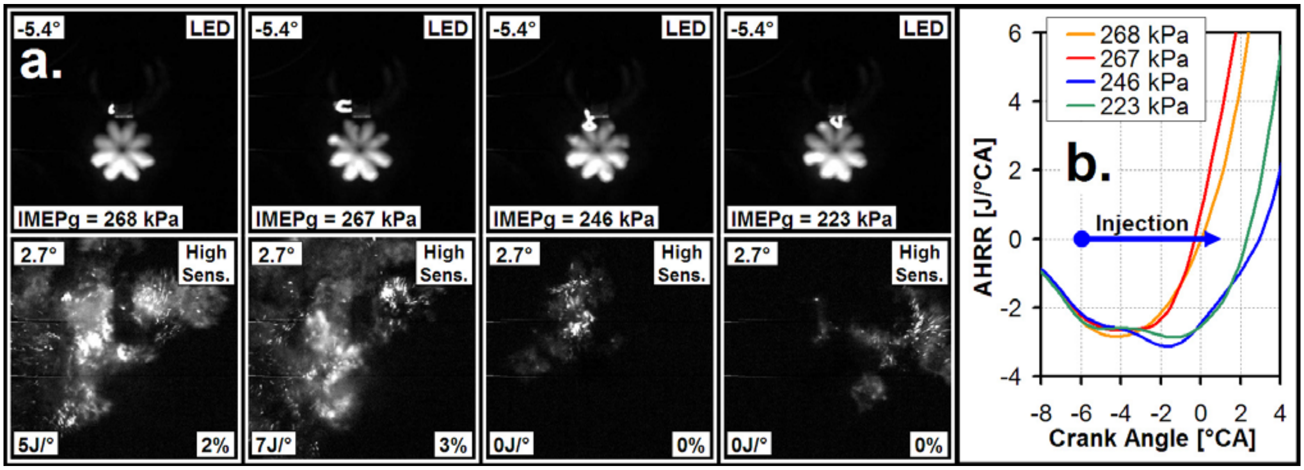


FIGURE 4. a) Imaging for two typical and two weak cycles, using E85 with SOI = -6°CA and ST = -12°CA. b) Corresponding AHRR during the early part of combustion.

Calculations of the fuel/air mixing process and flame-speed modeling provide understanding of fundamental differences between gasoline and E85 under these conditions. In the following discussion, ethanol is used as a surrogate for E85, and iso-octane as a surrogate for gasoline. Because of the large latent heat of vaporization of ethanol, much more ambient gas needs to be entrained into the fuel spray to fully vaporize the liquid. Because of this, the liquid penetration length is much longer for E85. More importantly, the local ϕ where the liquid just has vaporized (*e.g.* the liquid length in the fuel jet) is much less rich for ethanol compared to iso-octane. The circles at each of the starting points of the two curves in Figure 5 represent the conditions in fluid parcels that have just entrained sufficient ambient gas to fully vaporize all liquid fuel. The conditions are very rich for iso-octane with a ϕ near 15. In strong contrast, for ethanol the richest gas-phase fluid parcels have a ϕ near 5. Each curved line in Figure 5 shows the temperature/ϕ -trajectory of a gas-phase fluid parcel that mixes with the ambient gas as it travels downstream in the fuel jet. The two curves meet at ϕ = 0 and 810 K, which corresponds to the estimated bulk gas conditions at -6° CA. The very large difference in local ϕ near any liquid may be one of the reasons why gasoline and E85 require very different ST. In addition, the high oxygen content of E85 may be an important factor for the ignition process by effectively bringing the reactants closer to stoichiometry [4].

To examine why engine-out soot level are low for operation with late injection of E85, despite the highly stratified combustion (Figure 3b), CHEMKIN was used to compute the laminar flame speed (S_L) for ethanol. Selected results are plotted in Figure 6 and show that a peak S_L of 48 cm/s is found near ϕ =1.1. However, S_L drops very quickly for richer (and therefore cooler) mixtures. It can be assumed that mixtures with S_L below 10 cm/s will not sustain combustion. The dashed line represents this hypothetical quench limit. It can be seen that it intersects the S_L curve that is based on vaporization cooling at ϕ = 2.3, but the theoretical constant-temperature curve at ϕ = 4.5. This illustrates that the strong vaporization cooling of ethanol has the potential to limit combustion activity in the richest regions, possibly contributing to low soot formation for E85, in addition to the direct chemical effect of its high oxygen content.

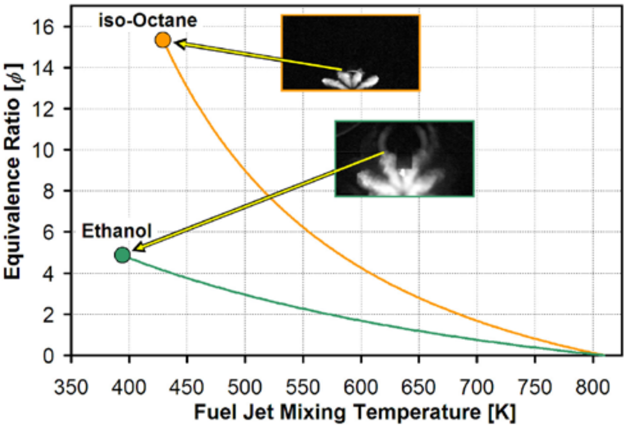


FIGURE 5. Comparison of ϕ/temperature trajectories in the fuel jet downstream of the liquid length for ethanol and iso-octane. Starting circles mark conditions at quasi-steady liquid tip. Ambient temperature = 810 K, pressure = 25 bar. Insets show examples of liquid penetration.

CONCLUSIONS

- When using E85 in a spray-guided combustion system, retarding the injection to near top-dead center enables ultra-low emissions of NO and PM.

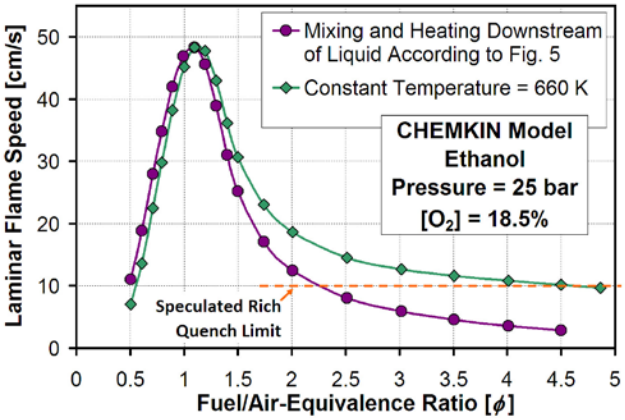


FIGURE 6. Computed laminar flame speed for ethanol under the assumption of constant temperature or with realistic mixing temperatures according to Figure 5.

Attaining such low emissions with gasoline was not possible for these tests that used single-injection strategies.

- For late fuel injection, the spark timing required for lowest IMEP variations is drastically different for the two fuels, with gasoline requiring a spark at the end of the injection event (igniting the tail of the fuel jet), and E85 requiring a spark well ahead of the fuel jet (igniting the head).
- High-speed imaging shows that the combustion process is distinctly different for gasoline and E85, partly due to the very different combinations of SOI and ST required for efficient and stable combustion for each fuel.
- A spectroscopic characterization of the flame luminosity shows that the early E85 flames are predominately fuel rich for operation with near-top-dead center fuel injection.
- Spray modeling shows that E85 requires much more gas entrainment to fully vaporize the fuel, and this strongly reduces ϕ of the richest gas-phase fluid compared to gasoline. This could be an important factor in explaining why E85 allows ignition of the head of the fuel jet.
- Flame-speed modeling reveals highly suppressed flame speeds for rich ethanol mixtures due to the strong vaporization cooling. This should limit combustion activity in these rich zones, contributing to the observed low soot emissions.
- Based on the observed correlation between spark-plasma stretch direction, early flame area, and IMEP, it was shown that cyclic variability of the flow field prior to fuel injection is one factor that contributes to the occurrence of partial-burn cycles.

REFERENCES

1. M. Sjöberg and D.L. Reuss, "High-Speed Imaging of Spray-guided DISI Engine Combustion with near-TDC Injection of E85 for Ultra-low NO and Soot", in press for the Proceeding of the Combustion Institute (2012), http://dx.doi.org/10.1016/j.proci.2012.05.033.

2. M. Sjöberg and D.L. Reuss, "NO_x-Reduction by Injection-Timing Retard in a Stratified-Charge DISI Engine using Gasoline and E85", SAE Paper 2012-01-1643, doi:10.4271/2012-01-1643.

3. M.C. Drake, T.D. Fansler, and K. H. Peterson, "Stratified Ignition Processes in Spray-Guided SIDI Engines", Proceedings of the 9th International Symposium on Combustion Diagnostics, Baden-Baden, 2010.

4. C. Mueller, "The Quantification of Mixture Stoichiometry When Fuel Molecules Contain Oxidizer Elements or Oxidizer Molecules Contain Fuel Elements", SAE Technical Paper 2005-01-3705, 2005, doi:10.4271/2005-01-3705.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. M. Sjöberg and J.E. Dec, "Smoothing HCCI Heat Release with Vaporization-Cooling-Induced Thermal Stratification using Ethanol, published in SAE Int. J. Fuels Lubr. 5(1):7-27, 2012.

2. M. Sjöberg and D.L. Reuss,"High-Speed Imaging of Spray-guided DISI Engine Combustion with near-TDC Injection of E85 for Ultra-low NO and Soot", presented at AEC Working Group Meeting, Sandia, Livermore, CA, Feb 2012.

3. A. Krisman, E.R. Hawkes, S. Kook, M. Sjöberg, and J.E. Dec "On the potential of ethanol fuel stratification to extend the high load limit in stratified-charge compression-ignition engines", published in Journal of Fuel 99: 45–54.

4. M. Sjöberg, "Advanced Lean-Burn DI Spark Ignition Fuels Research", presented at the 2012 Annual Merit Review and Peer Evaluation Meeting, Arlington, VI, May 2012.

5. M. Sjöberg and D.L. Reuss, "Spray-guided DISI Engine Combustion using E85", presented at AEC Working Group Meeting, USCAR, Southfield, MI, June 2012.

6. M. Sjöberg and D.L. Reuss, "High-Speed Imaging of Spray-guided DISI Engine Combustion with near-TDC Injection of E85 for Ultra-low NO and Soot", presented at 34th International Symposium on Combustion, Warsaw, Poland, July 2012, in press for the Proceeding of the Combustion Institute (2012).

7. M. Sjöberg and D.L. Reuss, "NO_x-Reduction by Injection-Timing Retard in a Stratified-Charge DISI Engine using Gasoline and E85", SAE Paper 2012-01-1643 presented at SAE 2012 Powertrains, F&L Meeting, Malmö, Sweden, Sept 2012.

III.8 CRADA with Reaction Design

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Objectives

- Provide experimental engine data with combustion and emissions analysis for selected fuels to support development of the Reaction Design (RD) Model Fuels Consortium (MFC) modeling tools and reaction mechanisms.
- Use MFC modeling tools and mechanisms in ORNL research and provide feedback and suggestions regarding use, accuracy, and improvements.

Fiscal Year (FY) 2012 Objectives

- Conduct engine experiments with pure compounds and blends of surrogate species with emissions and combustion analysis.
- Apply RD modeling tools to ORNL engine data to provide experience and feedback of their application.

Accomplishments

- Performed a blending study to measure the fuel properties of 86 fuel blends in the gasoline boiling range.
- Operated a series of seven fuel blends under diesel conditions, performed statistical analysis, and reported results to RD. The fuel blends were made from pure hydrocarbons as surrogate species for kinetic modeling.

Future Directions

This Cooperative Research and Development Agreement (CRADA) is coming to a natural and successful conclusion that coincides with the conclusion of the MFC. There are plans to continue an informal collaboration with RD as alignment with other projects permits. The informal collaboration will be based on ORNL sharing experimental data collected with other project, especially as it pertains to engine knock in spark ignition engines with varying fuel composition. In return, RD will provide modeling results as they are able and may provide access to the RD modeling tools.

* * *

INTRODUCTION

The automotive and engine industries are in a period of very rapid change being driven by new emission standards, new types of exhaust aftertreatment, new combustion strategies, and the introduction of new fuels. The rapid pace of these changes has put more demand on modeling of engine combustion and performance in order to shorten product design and introduction cycles. New combustion strategies include homogeneous charge compression ignition (HCCI) and premixed charge compression ignition (PCCI) which are being developed for lower emissions and improved efficiency. New fuels include those derived from bio-materials such as ethanol and biodiesel, as well as those derived from new crude oil sources such as gas-to-liquids, coal-to-liquids, oil sands, and oil shale. Kinetic modeling of the combustion process for these new combustion regimes and new fuels is necessary in order to allow modeling and performance assessment for engine design purposes.

APPROACH

The RD MFC has two work-in-kind members, of which ORNL is one and participates under a CRADA. IFP Energies nouvelles provided spray/combustion bomb data and diesel PCCI data and ORNL provided gasoline and diesel HCCI and diesel engine data. The consortium is concluding at the end of 2012, the seventh year of membership. Work-in-kind members provide experimental data, participate in analysis and publications, and have access to the consortium tools for internal work. Modeling tools are available to all members of the consortium and will be made available by RD to other companies and researchers after a waiting period.

RESULTS

In 2012, data was supplied on blending characteristics of ethanol, gasoline surrogates, n-butanol, tetrahydrofuran (THF), and ethyltetrahydrofurfuryl ether (ETE) to support improvements in the surrogate blend optimizer. The three latter fuel blending components can be manufactured using bacterial fermentation of sugars and are of current interest as drop-in biofuels. The ethanol data was developed for two different DOE projects related to the octane of intermediate ethanol blends and substituting renewable hydrocarbons for ethanol in terminal blending [1,2]. This data encompassed Research Octane Number, Motor Octane Number, distillation, and Reid Vapor Pressure measurements on 86 blends spanning 0 to 85% ethanol in two gasoline formulations and blends of n-heptane, i-octane, i-octene, and toluene. Additionally, RD requested that we evaluate a series of n-butane, THF, and ETE in pure hydrocarbon blends. The n-butanol and ETE are intended for gasoline range fuels and were evaluated as 20% blends in various mixtures of iso-octane, n-heptane, methyl cyclohexane, and 1-hexene. The THF is intended as a diesel component and was evaluated as 20% blends in mixtures of n-hexadecane, 1-methyl naphthalene, decalin, and heptamethylnonane. Overall, 27 blends were evaluated, spanning a Research Octane Number range of 80 to 101 and a cetane range of 13 to 66.

Accurate modeling of internal combustion engines requires both accurate chemical representation of a fuel for combustion and also accurate physical representation of the fuel for accurate spray, evaporation, and mixing of the fuel. Surrogates are often set up with one surrogate fuel representing both chemical and physical properties, but this results in large mechanisms for diesel fuels, where fuel molecules can be large (up to about C22). RD's computational fluid dynamics (CFD) program with kinetic solvers, FORTE', has an option to split a mechanism to a chemical and physical part by designing a mechanism to accurately represent chemistry in a homogeneous combustion system and then to assign the resulting surrogate compounds to have the physical properties of larger molecules to match physical properties. In order to demonstrate the importance of fuel reactivity and volatility, a CFD modeling study was undertaken to match diesel engine results with the Fuels for Advanced Combustion Engines (FACE) fuels, where cetane was controlled by using blends of n-heptane and benzene and T50 was matched by using n-neptane, n-dodecane, or n-hexadecane for physical properties [3]. In this work, the surrogate fuels and kinetic modeling were able to reproduce the range and direction of fuel effects, although further model tuning was indicated to reproduce exact values. Figure 1 indicates the match of cylinder pressure for experimental data (grey) and CFD modeling (colored lines).

Combustion phasing was shown to be sensitive to both cetane number and fuel volatility, with lower cetane and lower volatility (higher 50% evaporated, T50) resulting in later combustion. These trends are shown in Figure 2 for the crank angle of 10% heat release, the crank angle position where 10% of the fuel has been burned.

As another application of MFC surrogate tools and kinetic modeling, a set of seven fuels was designed, similar to the FACE diesel fuels, but designed to provide three levels and as wide a range possible of cetane, volatility, and threshold sooting index (TSI). These surrogate fuel blends are described in Table 1. The compositions for the surrogates are percent by volume and the compound naming convention is the same as used by RD in the surrogate data base.

These surrogates were blended and run in a single-cylinder Hatz diesel engine and this data is also being used to support a modeling study that will be completed

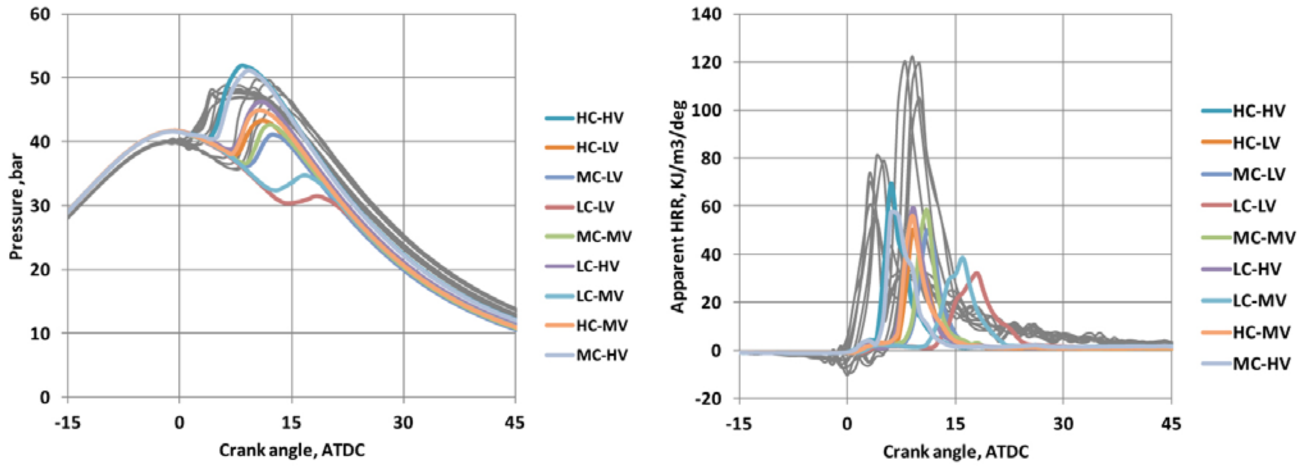

FIGURE 1. Match of CFD modeling to experimental data for cylinder pressure and heat release rate. HC, MC, and LC = high, medium, and low cetane and HV, MV, and LV = high, medium, and low volatility.

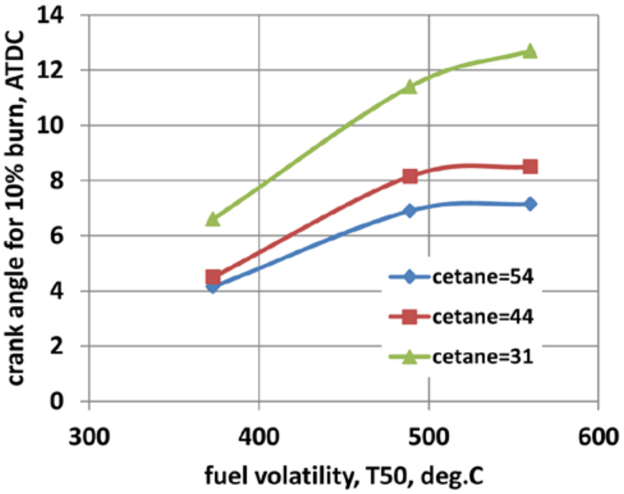

FIGURE 2. Trends of combustion phasing for results in Figure 1 as related to cetane and volatility.

TABLE 1. Surrogate fuel blends designed to study cetane, sooting index, and volatility effects. Compositions are volume fractions.

BLEND	1	2	3	4	5	6	7
CETANE	L	M	H	M	M	M	M
TSI	M	M	M	L	H	M	M
T50 K	M	M	M	M	M	L	H
CETANE	40	48	60	50	50	48	50
TSI	35	34	35	10	60	35	35
T50 K	475	473	478	478	517	447	517
A2CH3	0.25	0.19	0.19	0.02	0.43	0.11	0.22
C6H5CH3	0.00	0.18	0.10	0.03	0.00	0.25	0.04
DECALIN	0.05	0.03	0.04	0.00	0.02	0.30	0.00
MCH	0.08	0.00	0.00	0.33	0.00	0.00	0.18
HMN	0.00	0.00	0.00	0.14	0.00	0.00	0.04
IC8H18	0.23	0.00	0.00	0.00	0.00	0.00	0.05
NC12H26	0.27	0.19	0.65	0.05	0.12	0.00	0.00
NC16H34	0.07	0.20	0.02	0.31	0.40	0.34	0.46
NC7H16	0.05	0.21	0.00	0.12	0.03	0.00	0.01

by year end. Results indicate that the engine responded to the fuels in an expected manner. For example, combustion phasing (5%, 10%, 50%, and 90% burn points) is plotted against four experimental variables in Figure 3. Combustion advances with both cetane and sooting index and retards with T50.

Emissions also respond in a logical manner with cetane increasing oxides of nitrogen (NO_x) and soot and decreasing HC and CO, sooting index increasing NO_x and soot, and T50 increasing NO_x. These trends can be a result of both the properties quoted and also a result of the chemistries that were used to obtain these properties. The experimental trends and results quoted are mainly of value in the context of CFD and kinetic modeling, to see if they can be reproduced using the MFC kinetic mechanisms. This modeling work is under way. The goal of this modeling is to represent the entire dataset, using a single mechanism and CFD model, of sufficient complexity to reproduce the data, but of small enough size to allow modeling runs to be completed in less than 24 hours using advanced chemistry solvers, such as those incorporated in FORTE'.

CONCLUSIONS

The RD MFC is completing its seventh and probably final year of full operation, although there will be a subscription service offered for future additions to and improvements of the MFC master mechanisms. ORNL participated in the MFC through a CRADA project with RD (for the benefit of the MFC) for all but the first year of the consortium. ORNL was considered a work-in-kind member of the consortium and supplied experimental fuels and engine data, which was used to develop or

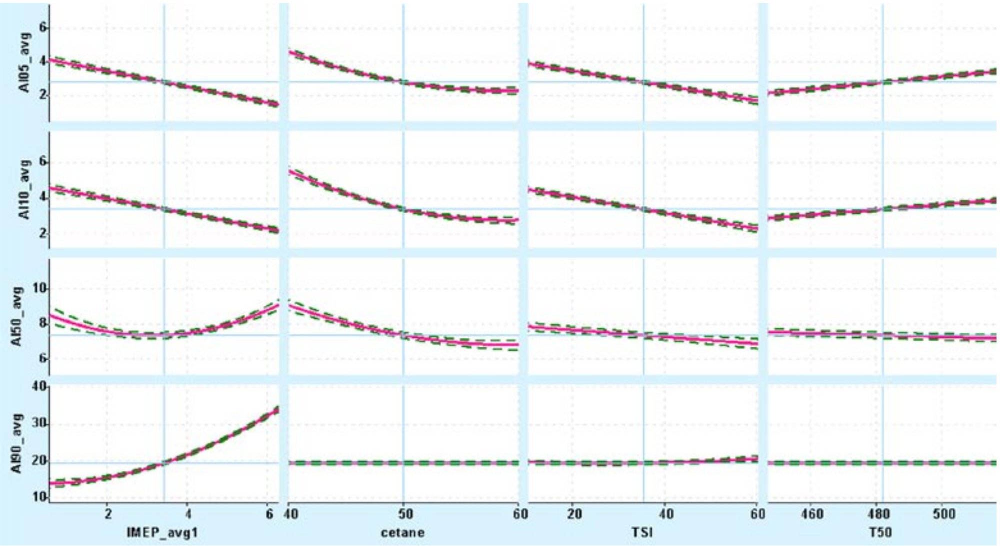

FIGURE 3. Combustion phasing of surrogate fuels as affected by engine load (indicated mean effective pressure, IMEP), cetane, sooting index, and T50.

test kinetic mechanisms, blending tools, and reaction models. Our data was considered to be in the public domain and was widely published, both with RD and for other purposes. This is why this CRADA report could be assembled from public sources. More details of the experiments and analysis of the results are contained in the list of publications and presentatons.

During the course of the MFC, work progressed in a logical manner and resulted in continual improvements in verified master mechanisms, tools for designing surrogate mixtures, tools for mimicking various engine and kinetic measurement equipment, improving chemical solvers to improve calculation speed, integrating these tools and mechanisms into a special version of Chemkin (Chemkin MFC), and a large data base of sources and analysis kinetic measurements from literature. Additionally, many of these tools were made compatible with FORTE' over the same time frame. CFD allows the entire strength of the MFC tools to be applied and the mechanism reduction tools combined with fast solving techniques allows complex chemistry to be incorporated into CFD for accurate representation of fuels.

REFERENCES

1. Kukwon Cho, Bruce G. Bunting, and Brian H. West, High Level Blend Octane Study, poster presentation at 2011 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2011.

2. Bruce G. Bunting, The Use of Renewable Hydrocarbons as a Partial Substitution for ethanol in Gasoline terminal Blending, poster presentation at 2012 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2012.

3. Bruce G. Bunting, Michael Bunce, Karthik Puduppakkam, and Chitralkumar Niak, Kinetic Modeling of Fuel Effects Over a Wide Range of Chemistry, Properties, and Sources, International Conference on Sustainable Automobile Technologies 2012, Melbourne, AU, March 21–23, 2012.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Bruce Bunting, Michael Bunce, Karthik Puduppakkam, and Chitralkumar Niak, Kinetic Modeling of Fuel Effects Over a Wide Range of Chemistry, Properties, and Sources, International Conference on Sustainable Automobile Technologies 2012, Melbourne, AU, March 21–23, 2012.

2. Bruce Bunting, The Use of Renewable Hydrocarbons as a Partial Substitution for ethanol in Gasoline terminal Blending, poster presentation at 2012 DOE DEER Conference, Directions in Engine Efficiency and Emissions research, 2012.

3. Bruce Bunting and Michael Bunce, ORNL Fuels Research on Behalf of Reaction Design Model Fuels Consortium, presentation at Reaction Design MFC Annual Meeting, San Diego, CA, Nov 14–15, 2011.

4. Michael Bunce, Bruce Bunting, Robert Crawford, and Jun Wang, Experimental and Statistical Comparison of Engine Response as a Function of Fuel Chemistry and Properties in CI and HCCI Engines, SAE Paper 2012-01-0857, 2012.

III.9 Non-Petroleum Fuel Effects in Advanced Combustion Regimes

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Objectives

- Investigate the opportunities and challenges of gasoline boiling range non-petroleum-based fuels on advanced combustion regimes and emerging engine technologies.
- Develop advanced combustion technologies that make use of the opportunities provided by unique fuel properties to reduce petroleum consumption in future engines and vehicles through a combination of increased efficiency and direct substitution.

Fiscal Year (FY) 2012 Objectives

- Characterize the potential of biofuels to enable and expand the operating range of reactivity controlled compression ignition (RCCI) combustion in a multi-cylinder engine (Q2 Joule Milestone).
- Experimentally determine the impact of lower ethanol content and low octane number hydrocarbon blending streams on high ethanol fuel blends (i.e., “E85” as defined by the 2011 revision of ASTM D5798).

Accomplishments

- Characterized the potential of biofuels to enable and expand the operating range of RCCI combustion in a multi-cylinder engine.
- Published and presented study related to the Q2 RCCI Joule Milestone.
- Upgraded the engine dynamometer for the multi-cylinder RCCI experiments allowing for motoring the engine which will aid in future advanced combustion experiments.
- Upgraded the air handling system on the ORNL single-cylinder engine with hydraulic valve actuation (HVA) to enable external exhaust gas recirculation (EGR) and boosted operation.
- Demonstrated that there is a significant opportunity to optimize an engine for high ethanol fuels compliant with the 2011 revision of ASTM D5798.

Future Directions

- Investigate the fuel effects on multiple advanced combustion strategies on the same light-duty multi-cylinder engine for direct comparison of the combustion strategies.
- 2013 DOE Vehicle Technologies Milestone:
  - Demonstrate an increase in RCCI operating range allowing 60% coverage of non-idling portions of the city and highway light-duty federal drive cycles (Q2).
- Investigate fuel-specific impacts of the chemistry occurring when fuel is injected into the negative valve overlap (NVO), as is relevant to homogeneous charge compression ignition (HCCI) and spark-assisted HCCI (SA-HCCI) using the ORNL 6-stroke engine cycle.
- Map the efficiency, emissions, and operable load range of gasoline, an ethanol fuel blend, and an iso-butanol fuel blend using conventional spark ignited (SI) combustion, SI combustion with high levels of EGR, lean burn HCCI, and SA-HCCI.

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INTRODUCTION

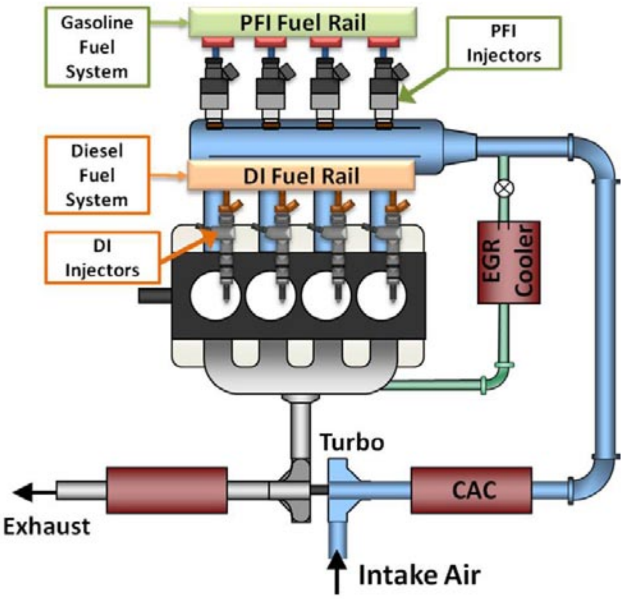
Consumption of non-petroleum-based fuel is steadily increasing, displacing conventional petroleum-derived gasoline and diesel fuel in accordance with the Energy Independence and Security Act of 2007. Concurrently, advanced combustion strategies are being developed for both gasoline and diesel engine platforms as a means to increase fuel efficiency and/or reduce engine emissions to meet future regulations. Non-petroleum fuels, such as ethanol, butanol and biodiesel, are largely compatible with conventional engine platforms optimized for petroleum-based gasoline and diesel fuels. However, there is a need to investigate whether these fuels offer potential advantages in conventional operating modes, and to determine their impact on advanced combustion strategies where there is less direct control over the start of combustion

The purpose of this research is to investigate fuel effects on advanced combustion strategies with a focus on alternative fuels capable of displacing large volumes of petroleum. The advanced combustion strategies being investigated (ethanol-optimized SI, SA-HCCI, and RCCI) have the potential for production-intent development and have expanded operating load ranges compared with the previous generation of advanced combustion strategies, namely HCCI and premixed charge compression ignition (PCCI). We are specifically attempting to identify fuel compositions that may offer combustion control or load range expansion advantages, pose compatibility challenges, and to help ensure that future engines will provide robust performance over the wide range of fuels expected worldwide either in efficiency, emissions, or the operating envelope that is achievable in advanced combustion modes.

APPROACH

Investigations of fuel effects on advanced combustion regimes are being performed using two different engine platforms: a single-cylinder SI engine platform and a compression ignition multi-cylinder engine (MCE) platform. The single-cylinder engine is a highly modified 2.0-L General Motors Ecotec engine with direct fuel injection. The engine has been highly modified to enhance versatility for research purposes. Modifications include conversion to single-cylinder operation, a fully flexible hydraulically actuated valve train, and an increased compression ratio. A laboratory air handling system capable of delivering boost and external EGR was added to this platform to offer expanded capability in FY 2012. This engine is an enabling tool for numerous advanced combustion regimes, and in previous years the focus was on expanding the load range and determining fuel-specific behavior of the SA-HCCI combustion strategy. In FY 2012 an investigation was performed to determine the impact of the 2011 ASTM D5798 specification revision on the ability to optimize an engine for “E85.” Additionally, a second study was initiated to investigate the fuel-specific chemistry that occurs when fuel is injected into the hot recompressed gas in the NVO event by using the ORNL 6-stroke engine cycle combined with extensive analytical tools. Fuel specific chemistry in the NVO is relevant to both the HCCI and SA-HCCI modes of combustion.

The MCE platform is a 4-cylinder General Motors 1.9-L diesel engine modified to include a port fuel injection system using conventional gasoline injectors and pistons that were designed for RCCI operation. A schematic of the MCE platform is shown in Figure 1. A flexible microprocessor based control system allowed for control over both fueling systems and complete authority over engine operating parameters. In addition to certification diesel and gasoline fuels, biodiesel blends of 5% and 20% biodiesel (B5 and B20 respectively) and ethanol blends of 20% and 40% (E20 and E40 respectively) were prepared via splash blending on-site. FY 2012 investigations were focused on mapping the RCCI load range from 1,000 to 3,000 rpm with the biodiesel and ethanol fuel blends, and quantifying the engine efficiency and emissions relative to conventional diesel combustion.



PFI – port fuel injection; DI – direct injection; CAC - charge air cooler

FIGURE 1. Schematic of the ORNL Multi-Cylinder RCCI Engine

RESULTS

Impact of 2011 ASTM Revision on “E85” Fuel Quality

Ethanol is an attractive fuel from an end-use perspective because it has a high chemical octane number and a high latent heat of vaporization. When an engine is optimized to take advantage of these fuel properties, both efficiency and power can be increased through higher compression ratio, direct fuel injection, higher levels of boost, and a reduced need for enrichment to mitigate knock or protect the engine and aftertreatment system from overheating. The ASTM D5798 specification for high level ethanol blends, commonly called “E85,” underwent a major revision in 2011. The minimum ethanol content was revised downward from 68 vol% to 51 vol%, and the use of low octane hydrocarbon blending streams introduces the possibility of a lower octane *“E85”* fuel. This study experimentally examines whether engines can still be aggressively optimized for the resultant fuel from the revised ASTM D5798 specification.

The performance of six ethanol fuel blends, ranging from 51-85% ethanol, were compared to premium-grade gasoline in the single-cylinder HVA engine at a compression ratio of 12.9:1 at knock-prone engine conditions. Premium-grade gasoline (Research Octane Number [RON] = 96.1), straight run gasoline (RON = 63.6), and n-heptane (RON = 0) were used as the hydrocarbon blending streams for the ethanol-containing fuels in an effort to establish a broad range of knock resistance for high ethanol fuels.

Results show that nearly all ethanol-containing fuels are more resistant to engine knock than premium grade gasoline (the only exception being the ethanol blend with 49% n-heptane). To illustrate this, Figure 2 shows the cylinder pressure trace and heat release rate for the ethanol fuels and for the premium gasoline. More advanced combustion phasing allows higher utilization of the expansion stroke, leading to higher efficiency, as can be seen in Figure 3. While experimental results show that the octane number of the hydrocarbon blend stock does impact engine performance, there remains a significant opportunity for engine optimization when considering even the lowest octane fuels that are in compliance with the current revision of ASTM D5798 compared to premium-grade gasoline.

RCCI

ORNL's RCCI combustion methodology was used on a multi-cylinder light-duty diesel engine to demonstrate the potential of biofuels to expand RCCI's speed/load operating range. The investigation was performed over a range of engines speeds spanning 1,500 rpm to 3,000 rpm with a focus on maximum engine load under RCCI operation using ethanol blends for the port-injected fuel and biodiesel blends for the direct-injected fuel. Figures 4 and 5 show the emissions and efficiency performance and combustion behavior respectively for RCCI cases with diesel and biodiesel blends.

Improvements in maximum engine load with were as high as 20% with E20 and B20 as compared to the baseline certification gasoline (UTG) and diesel fuel. The load expansion improvements realized with ethanol blends were found to be a result of the increased octane

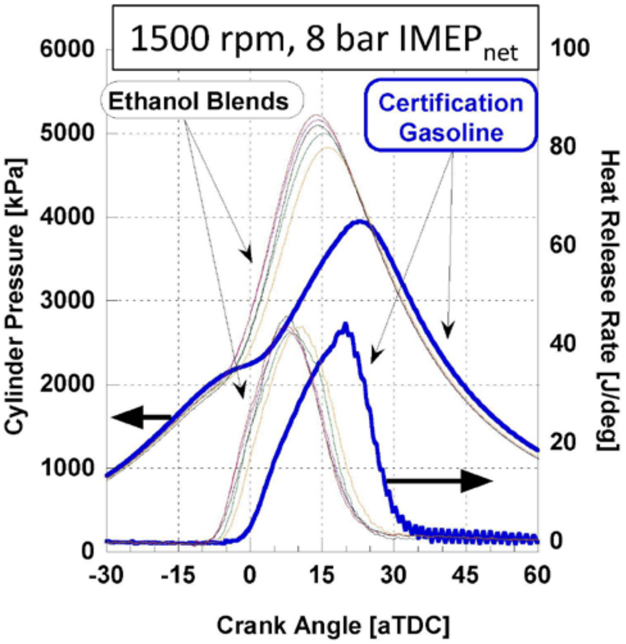


FIGURE 2. Cylinder pressure and heat release rate for ethanol fuel blends and premium grade certification gasoline at 1,500 rpm and 8 bar indicated mean effective pressure (IMEP$_{net}$).

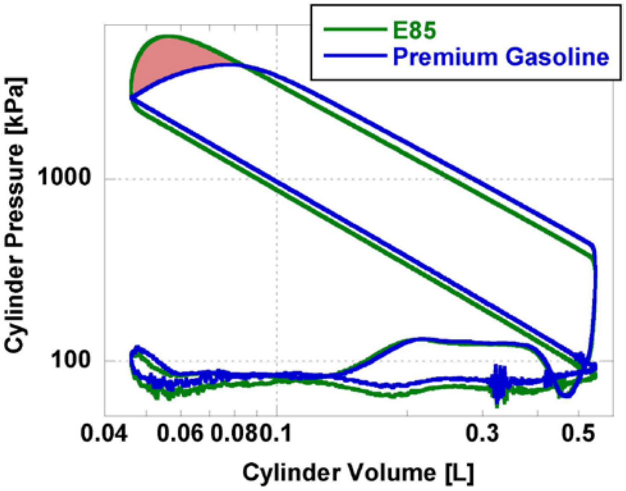
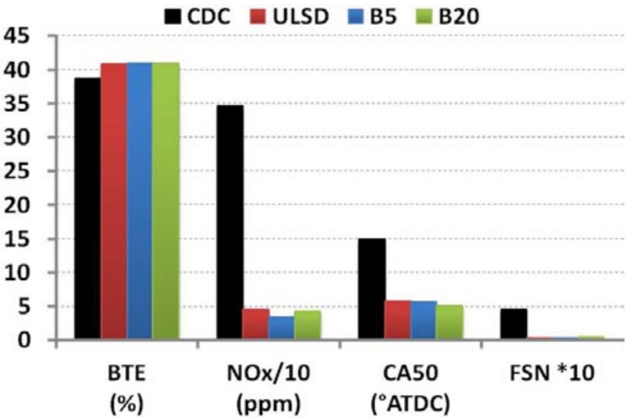
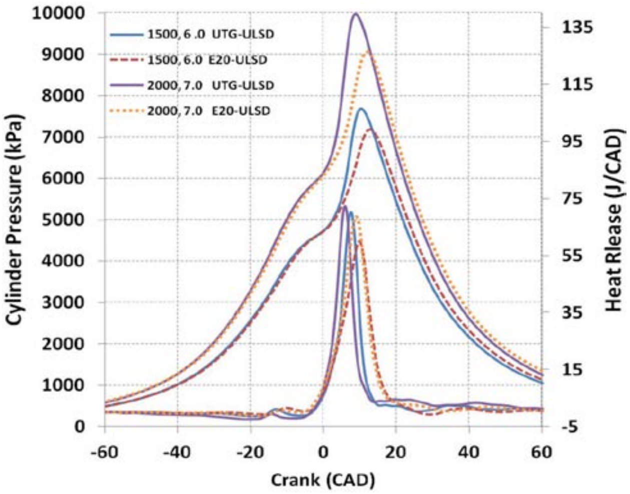


FIGURE 3. PV diagram comparing E85 and premium grade gasoline at 2,000 rpm and 10 bar IMEP$_{net}$.



CDC – conventional diesel combustion; ULSD – ultra-low sulfur diesel; BTE – brake thermal efficiency; CA50 – crank angle 50; FSN – filter smoke number; ATDC – after top-dead center

FIGURE 4. Efficiency and combustion performance comparison at 2,500 rpm 8.0 bar brake mean effective pressure (BMEP) with RCCI and conventional diesel combustion (black).



CAD - crank angle degree; UTG - unleaded test gasoline

FIGURE 5. Cylinder pressure and heat release traces for RCCI operation with ethanol blends compared to UTG-ULSD and UTG-biodiesel blends at 2,000 rpm 7.0 bar BMEP.

number of ethanol and increased charge cooling effect which significantly retard combustion phasing allowing the cylinder pressure rise rate to be lowered without adversely affecting CO and hydrocarbon emissions. Biodiesel blends were found to advance combustion phasing without significantly increasing pressure rise rate allowing higher ratios of ethanol blends to be run stably without exceeding the self-imposed pressure rise rate limit of 10 bar/crank angle degree. The RCCI load expansion potential using biofuels was demonstrated for both high and low cetane number diesel fuel. The synergy between using ethanol and biodiesel blends was found to be important for fully realizing the full load expansion potential with RCCI. The higher RCCI efficiency was demonstrated under conditions applicable to the federal drive cycle, whereas the peak efficiency of the base diesel engine is at very high load and outside conditions observed over the federal drive cycle.

Though this work has shown the potential for biofuels to be used in increasing the load range of RCCI, more complete studies of the fuel effects from ethanol and biodiesel blends on multi-cylinder RCCI operation are planned.

SA-HCCI

A study to investigate the fuel-specific chemistry that occurs when fuel is injected into the NVO was initiated in FY 2012. Fuel injection into the NVO is a highly effective means of controlling combustion for both HCCI and SA-HCCI, so this experiment is relevant to both of these combustion modes. The investigation is using the ORNL 6-stroke engine cycle, which is possible on the single-cylinder HVA engine because there is no mechanical linkage between the crankshaft and the valve train. By using the 6-stroke cycle, the contents of the NVO can be exhausted for detailed chemical speciation with a mass spectrometer to measure the hydrogen concentration in the exhaust, and a Fourier transform infrared analyzer to quantify the short-chain hydrocarbon species in the exhaust. A custom exhaust divider has been installed on the engine to isolate the NVO exhaust from the combustion exhaust, as is shown in Figure 6. This study will be completed and reported in FY 2013.

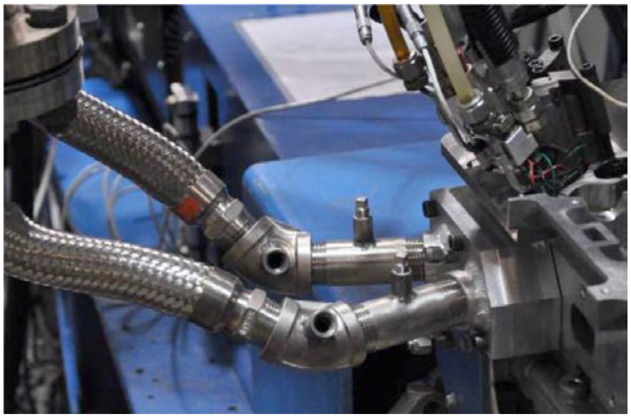


FIGURE 6. Exhaust system of the ORNL single-cylinder HVA engine with the exhaust separator installed to investigate fuel-specific chemistry during the NVO event.

CONCLUSIONS

A significant amount of progress is being made to understand the impact of non-petroleum-based fuels on a number of different advanced combustion strategies.

For advanced SI engines, it was concluded that there is still a significant opportunity for engine optimization even with the revisions to the “E85” specification revisions (ASTM D5798). Engine optimization for high ethanol content fuels is well understood, and can be accomplished through high compression ratio, direct injection, downsizing and down-speeding, and high peak cylinder pressure. The lower ethanol content (51%) permitted by the ASTM D5798 revision is actually preferable because the energy density penalty is less significant while octane number remains high. This allows engine optimization for ethanol for efficiency increases, incurs less of a volumetric fuel economy penalty.

The use of ethanol and biodiesel is also advantageous for RCCI combustion. Their unique properties can increase the engine load range and can simultaneously increase engine efficiency and lower NO_X and PM emissions. This activity has shown the importance of taking a comprehensive engine systems approach, looking at the interdependency of advanced combustion and fuel effects from renewable fuels, to help meet Vehicle Technologies goals and milestones.

FY 2012 PUBLICATIONS/PRESENTATIONS

Invited Presentations

1. Curran, S.J., Wagner, R.M., and Gao, Z., "Background on RCCI and B20 RCCI Results With Both Gasoline and Ethanol Blends ", Presentation, 2012 National Biodiesel Board Biodiesel Technical Workshop, (October 30–31, 2012, Kansas City, MO.

2. Szybist, J.P., "A Comparison of Two Methods for High Load Expansion of HCCI: Boosted lean HCCI vs. Naturally Aspirated Stoichiometric Spark-Assisted HCCI" IEA 34th Combustion Agreement TLM/ExCo Meeting, (October 8, 2012, Jeju Island, South Korea).

3. Curran, S.J., Wagner, R.M., Hanson, R.M., and Szybist, J.P., "Reactivity Controlled Compression Ignition Combustion in a Multi-Cylinder Light-Duty Diesel Engine", SAE Powertrain Fuels and Lubricants Meeting, (September, 2012, Malmo Sweden).

4. Curran, S.J., "The role of renewable fuels in enabling high efficiency internal combustion engines", Sustainable Technology through Advanced Interdisciplinary Research (STAIR) Seminar Series at the University of Tennessee, (September 11, 2012, Knoxville, TN).

Refereed Publications and Presentations

1. Curran, S.J., Hanson, R.M., and Wagner, R.M., "Reactivity controlled compression ignition (RCCI) combustion on a multi-cylinder light-duty diesel engine," International Journal of Engine Research, 2012, vol. 13(3), pp 216-225.

2. Hanson, R.M., Curran, S.J., Reitz, R., and Wagner, R.M., "Piston optimization for RCCI in Light-Duty Multi-Cylinder Engine," SAE Technical Paper, 2012, 2012-01-0380.

3. Curran, S.J., Hanson, R.M., and Wagner, R.M., "Effect of E85 on RCCI Performance and Emissions on a Multi-Cylinder Light-Duty Diesel Engine," SAE Technical Paper, 2012, 2012-01-0376.

4. Curran, S.J., Szybist, J.P., and Wagner, R.M., "Reactivity Controlled Compression Ignition Performance with Renewable Fuels," Proceedings of the ASME 2012 Internal Combustion Engine Division Fall Technical Conference, ICEF2012-92192, September 23–26, 2012.

5. Curran S.J., Hanson, R.M., Barone, T.L., Storey, J.M., Wagner, R.M., "Range-extension and multi-cylinder performance of RCCI Combustion," Presentation at the Advanced Engine Combustion (AEC) Working Group Meeting, Livermore, CA; February 2012.

6. Curran S.J., Szybist, J.P., Barone, T.L., Storey, J.M., Wagner, R.M, "Recent Advancements in Multi-Cylinder RCCI Combustion," Presentation at the Advanced Engine Combustion (AEC) Working Group Meeting, Southfield, MI; June 2012.

7. Curran S.J., Prikhodko, V.Y., Parks, J.E., and Wagner, R.M., "High Efficiency Clean Combustion in Multi-Cylinder Light-Duty Engines," Presentation at the 2012 DOE Hydrogen Program and Vehicle Technologies Merit Review, Washington, D.C.; May 2012.

8. Curran, S.J., Gao, Z., and Wagner, R.M., "Light-Duty Reactivity Controlled Compression Ignition Drive Cycle Fuel Economy and Emissions Estimates," Poster Presentation at the 2012 U.S. DOE Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Dearborn, MI; October 15–19, 2012.

9. Weall, A.J. and J.P. Szybist, "The Effects of Fuel Characteristics on Stoichiometric Spark-Assisted HCCI," Journal of Engineering for Gas Turbines and Power, 2012, vol.134(7).

10. Weall, A. J. and J.P. Szybist. "The Effects of Fuel Characteristics on Stoichiometric Spark-Assisted HCCI." Proceedings of the ASME 2011 Internal Combustion Engin Division Fall Technical Conference, ICEF2011-60122, October 2011.

11. Szybist, J.P., A.D. Youngquist, T.L. Barone, J.M. Storey, W.R. Moore, M. Foster and K. Confer, "Ethanol Blends and Engine Operating Strategy Effects on Light-Duty Spark-Ignition Engine Particle Emissions," Energy & Fuels, 2011, vol. 25(11), pp 4977-4985.

12. Szybist, J.P. and B.H. West, "The Impact of Low Octane Hydrocarbon Blending Streams on "E85" Engine Optimization," Presentation at the 2012 U.S. DOE Directions in Engine-Efficiency and Emissions Research (DEER) Conference, Dearborn, MI; October 15–19, 2012.

13. Szybist, J.P. and West, B.H., "The Impact of Low Octane Hydrocarbon Blending Streams on Ethanol Engine Optimization," SAE Technical Paper 13PFL-0246 (submitted), 2013.

14. Szybist, J.P., Curran, S.J, West, B.H., Bunting, B.G., Sluder, C.S., and Wagner, R.M., "Gasoline-like Fuel Effects on Advanced Combustion Regimes," Presentation at the 2012 DOE Hydrogen Program and Vehicle Technologies Merit Review, Washington, D.C.; May 2012.

15. Curran, S.J., Gao, Z., and Wagner, R.M., "Reactivity controlled compression ignition drive cycle emissions and fuel economy estimations using vehicle systems simulations," SAE Technical Paper, 13PFL-0698 (submitted), 2013.

16. Curran, S.J., Hanson, R.M., Wagner, R.M., and Reitz, R.D, "Efficiency and Emissions Mapping of Reactivity Controlled Compression Ignition in a Light-Duty Diesel Engine," SAE Technical Paper 13PFL-0700 (submitted), 2013.

17. Hanson, R.M., Curran, S.J., Wagner, R.M., and Reitz, R.D., "Effects of Biofuel Blends on Light-Duty Multi-Cylinder RCCI Operation," SAE Technical Paper 13PFL-1088 (submitted), 2013.

18. Szybist, J.P. and West, B.H., "The Impact of Low Octane Hydrocarbon Blending Streams on "E85" Engine Optimization," Presentation at the Advanced Engine Combustion (AEC) Working Group Meeting, Southfield, MI; June 2012.

III.10 Ionic Liquids as Novel Lubricants and/or Lubricant Additives

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Objectives

- Investigate the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion (IC) engine applications.
- Explore potential advantages/disadvantages of this new category of lubricants/additives with a combination of systematic experiments, materials characterization, and modeling.

Fiscal Year (FY) 2012 Objectives

- For ILs as neat lubricants, demonstrate friction benefits in elastohydrodynamic lubricants (EHLs) and mixed lubrication (ML) for ILs over hydrocarbon lubricating oils in bench testing.
- For ILs as oil additives, determine the IL's critical concentration in the base oil to meet International Lubricants Standardization and Approval Committee (ILSAC) GF-5 and investigate the effects of the IL content on the lubricant's friction and wear performance.
- Demonstrate the feasibility of IL-additized lubricants in small single-cylinder motored and fired engines.
- Conduct exhaust analysis for IL-additized lubricants in fired single-cylinder engine tests.

Accomplishments

- ~30% lower friction in EHD and mixed lubrication has been demonstrated for a low-viscosity IL [BMIM][NTf_2] when compared to Mobil 1^{TM} polyalphaolefin (PAO) 4 cSt base and Royal Purple^{TM} 0W10 racing oil that have similar viscosities as the IL.
- The oil-miscible IL [P_{66614}][DEHP] is potentially an ashless anti-scuffing/anti-wear (AW) oil additive. Its AW functionality has been demonstrated at concentrations as low as 1 wt%, which falls into the range of 0.78-1.03 wt% to meet the ILSAC GF-5.
- The tribo-film formed on the metal surface by the IL [P_{66614}][DEHP] possesses higher hardness and modulus as well as better corrosion resistance than those formed in oil lubrication.
- The oil-miscible IL [P_{66614}][DEHP] has demonstrated 100% volatility (ashless) when thermally oxidized. Its thermal stability is ~100°C higher than zinc dialkyldithiophosphate (ZDDP).
- Small single-cylinder motored and fired engine tests were conducted for IL-additized lubricants. Normal engine behavior was observed during testing and no measurable wear was detected on the piston ring or cylinder liner after disassembly.
- Engine exhaust analysis did not detect any IL decomposition products on the particulate matter filter, confirming its ashless feature.

Future Directions

- Investigate the interactions between the IL [P_{66614}][DEHP] and emission catalysts.
- Work with a lubricant additive company to formulate an engine oil using the IL [P_{66614}][DEHP] as an anti-wear additive.
- Conduct high-temperature, high-load full-size engine tests.

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INTRODUCTION

For the transportation sector, parasitic friction accounts for the consumption of ~500 million barrels of oil annually, which has significant implications for the U.S. economy as well as national security. The magnitude of such friction-induced losses depends on engine design, materials of construction, operating conditions, and most importantly, on lubrication. A new class of more effective lubricants could therefore lead to huge energy savings.

Based on an ORNL's U.S. patent on ILs lubrication [1], ORNL and GM signed a Cooperative Research and Development Agreement (CRADA) on May 28, 2009 to investigate the potential of using ILs as lubricants and/or lubricant additives specifically for IC engines. ILs are, as the name indicates, composed solely of cations and anions instead of neutral molecules. Their unique chemical and physical properties of ILs, such as inherent polarity, high thermal stability, non-flammability, low volatility, and low viscosity-pressure coefficient, offer a great potential for lubricant applications.

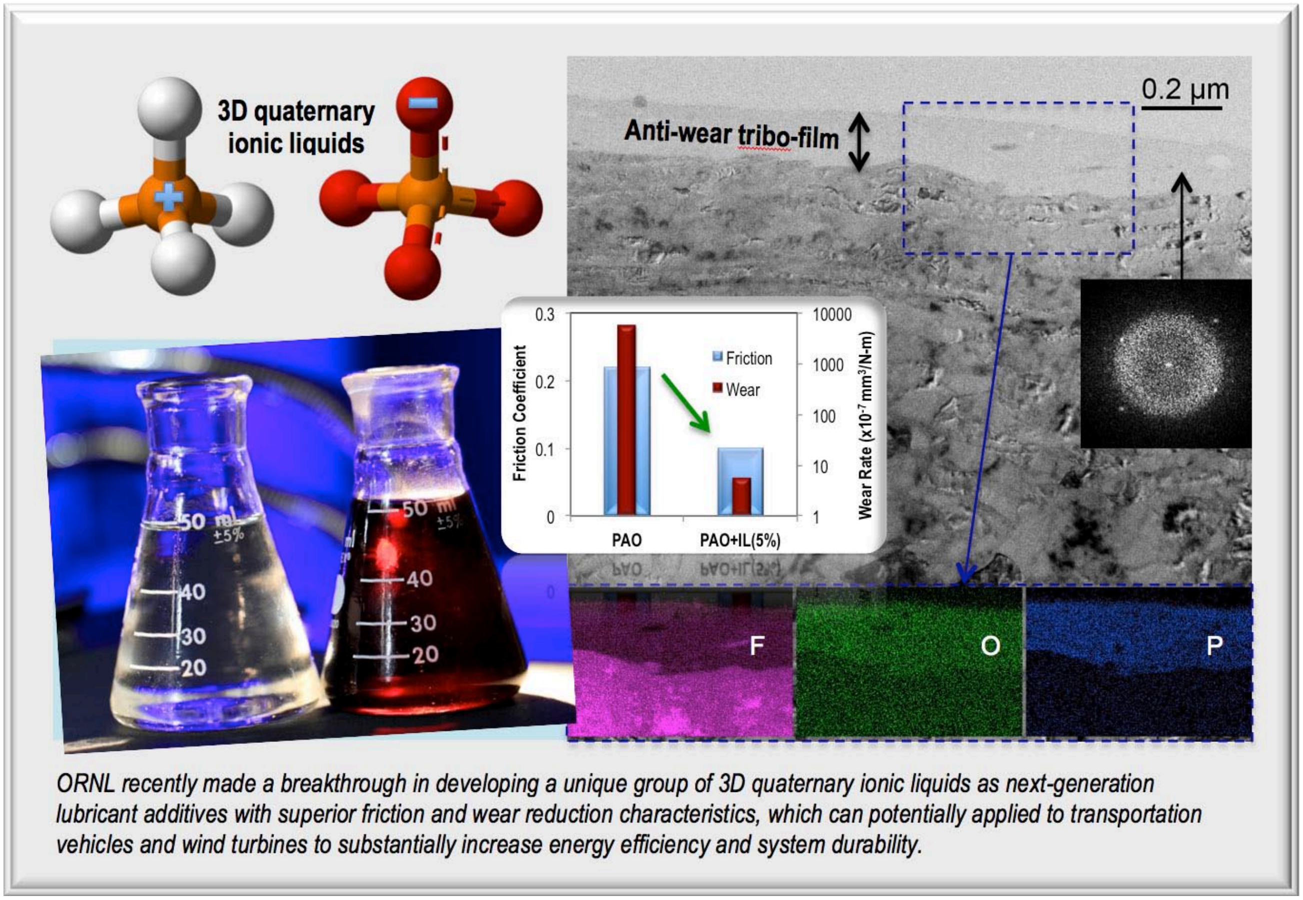
APPROACH

Two approaches have been taken in this joint effort to develop ILs for lubricant applications: (i) using ILs as neat lubricants or base stocks, which can fully take advantage of the ILs' unique chemical and physical properties and are particularly suitable for specialty bearing components in extreme environments involving high temperature and/or high pressure, and (ii) using ILs as lubricant additives, which are truly ashless with multi-function additives including anti-wear/extreme-pressure, friction modifiers, anti-corrosion agents, detergents, etc., and potentially allow the use of lower viscosity engine oils to improve fuel economy. This approach is more cost effective and easier to penetrate into current lubricant market.

This ORNL-GM CRADA project contains four phases of R&D: (1) design, synthesis, and characterization of candidate ionic liquids; (2) friction and wear bench tests and analysis; (3) instrumented single-cylinder engine tests; and (4) full-scale multi-cylinder engine tests.

RESULTS

The team made a breakthrough in using ILs as lubricant additives (see Figure 1) by developing a unique group of three-dimensional quaternary-structured ionic liquids, such as trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P_{66614}][DEHP]), that exhibit a combination of oil-miscibility, non-corrosivity, high thermal-stability, excellent metal wettability, and superior friction and wear reduction characteristics (Pubs. 1,2). Previous results were achieved for oils containing 3-5 wt% ILs. The concentration of [P_{66614}][DEHP] in an engine oil would be in the range of 0.78-1.03 wt% to meet the new ILSAC GF-5 specification. More recent test results at ORNL and GM suggest that 1 wt% of IL is sufficient to eliminate scuffing failure and performed



ORNL recently made a breakthrough in developing a unique group of 3D quaternary ionic liquids as next-generation lubricant additives with superior friction and wear reduction characteristics, which can potentially applied to transportation vehicles and wind turbines to substantially increase energy efficiency and system durability.

FIGURE 1. ORNL's breakthrough type development of oil-miscible ILs as lubricant anti-wear additives.

as well as 3 or 5 wt% in terms of friction and wear, as shown in Figure 2.

Nanoindentation was used to characterize the hardness and modulus of the tribo-films formed on cast iron liner surfaces lubricated by Mobil 1^{TM} 5W30 engine oil, PAO+3% IL [P_{66614}][DEHP], and 5W30+5% IL. Results are summarized in Figure 3. The reduced modulus Er is related to Young's modulus Es of the test specimen through the relationship $1/E_\gamma = 8.7 \times 10^{-4} + (1 - v_s^2)/E_s$.

The tribo-films formed by IL showed slightly higher hardness and modulus than the ZDDP-based tribo-film formed in the 5W30 engine oil. The tribo-film formed in 5W30+IL (containing both ZDDP and IL) is harder and stronger than the tribo-film formed by either ZDDP or IL18 alone. The tribo-film formed in the IL-additized lubricant shows signs of corrosion-resistance. Water droplets were placed on the wear scars of cast iron liner surfaces in the ambient environment. Less rust appeared on the surface lubricated by PAO+IL compared to those lubricated by PAO base or fully-formulated 10W30 engine oil. This may be a hint suggesting that the IL18-produced tribo-film may have better corrosion resistance than ZDDP-based tribo-film.

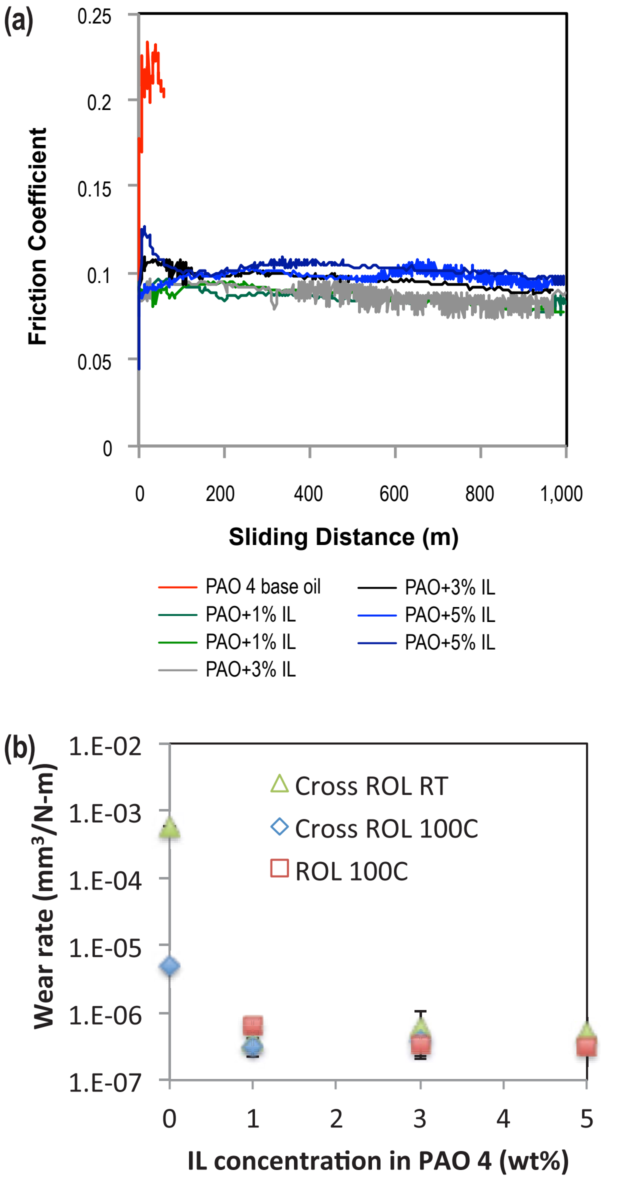


FIGURE 2. Bench test results showing 1 wt% IL [P_{66614}][DEHP] as effective as 3-5 wt% in scuffing elimination and wear protection. (a) friction traces and (b) wear rates.

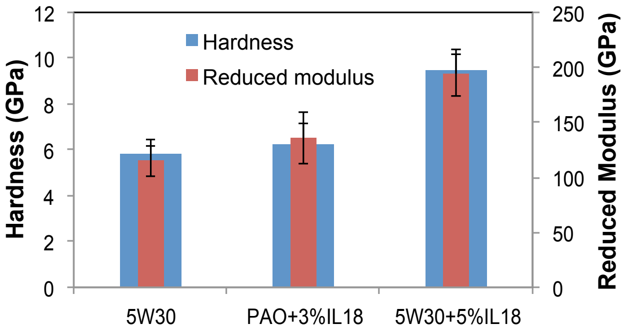


FIGURE 3. Comparison of the hardness and modulus of tribo-films formed in lubricants containing ZDDP and/or IL.

A low-viscosity IL 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIM][NTf_2]) was investigated as candidate base oil for engine lubrication. This IL has a relatively low viscosity of 4.7 cSt (similar to 0W10 racing engine oil) and a low viscosity-pressure (V-P) coefficient of 6.5 GPa^{-1} at 100°C, a high viscosity index of 159, and a high onset decomposition temperature of 472°C. The lubricating performance of [BMIM][NTf_2] was benchmarked against that of the PAO 4 cSt and 0W10 oils under both EHL/ML and boundary lubrication at the GM Tech Center. The EHL/ML friction coefficient of the IL was consistently lower than that of the oils by ~30% (Figure 4a). This is possibly due to the IL's lower V-P coefficient and a hypothetical layered-structure boundary film. Although a low V-P coefficient usually is a challenge to boundary lubrication, the IL exhibited higher scuffing resistance and less surface damage than did oils in the scuffing tests (Figure 4b). This is attributed to the formation of a protective tribo-film in IL lubrication, which was revealed by focused ion beam-aided cross-sectional transmission electron microscopy microstructural examination and energy-dispersive X-ray spectroscopy analysis (see details in Pub. 3).

Initial motored and fired single-cylinder engine tests have been conducted at the ORNL National Transportation Research Center. The test rigs are shown in Figure 5. The fired test was a screening version for 2 hours only to detect abnormal behavior if any and the

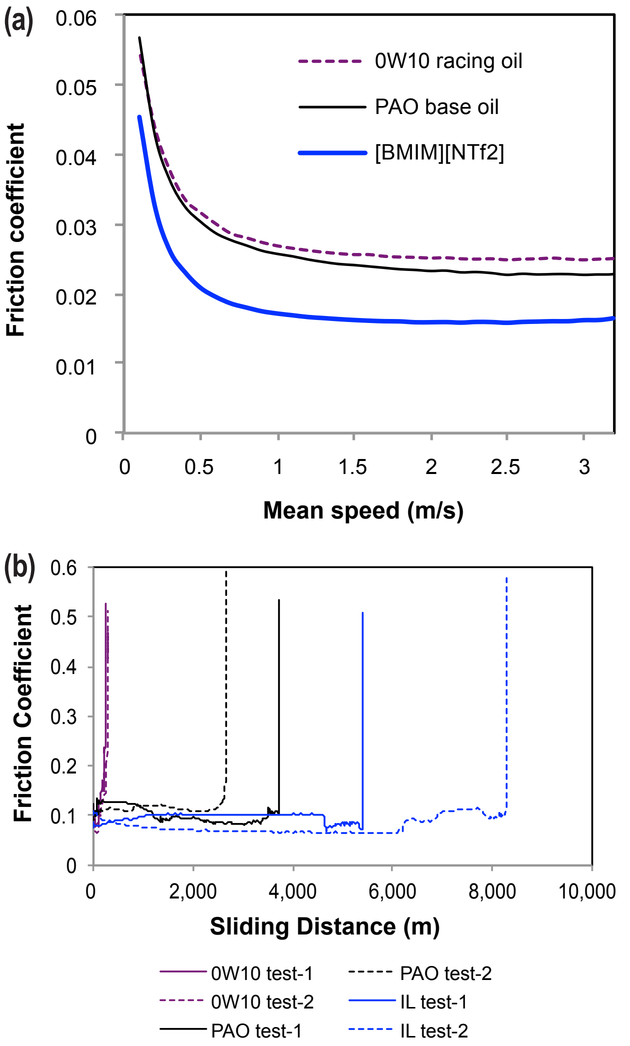


FIGURE 4. GM tribological test results of a low-viscosity IL [BMIM][NTf$_2$] compared with that of baseline oils. (a) Stribeck curves (EHL/ML) at 100°C and (b) friction traces of boundary lubrication scuffing tests.

motored test runs for 15 hours to intend to compare the friction and wear performance. The fired engine test of the PAO oil containing 3% [P$_{66614}$][DEHP] showed normal behavior in terms of combustion, indicated efficiency, and emissions without any hint of operation problems. This gave us the confidence for further engine testing using the IL as oil additive. The 15-hr motored test has been proven to be too short to generate enough wear to distinguish among lubricants.

The oil-miscible anti-wear [P$_{66614}$][DEHP] has been confirmed ashless by thermo and pyrolysis analyses. In oxygen, the IL was stable below 200°C (when ZDDP fully decomposed/oxidized) but completely decomposed at 300°C. All decomposition products were volatile phosphorous. The large number of carbonyl compounds suggests that the alkyl legs were oxidized. Engine exhaust analysis was then conducted for [P$_{66614}$][DEHP].

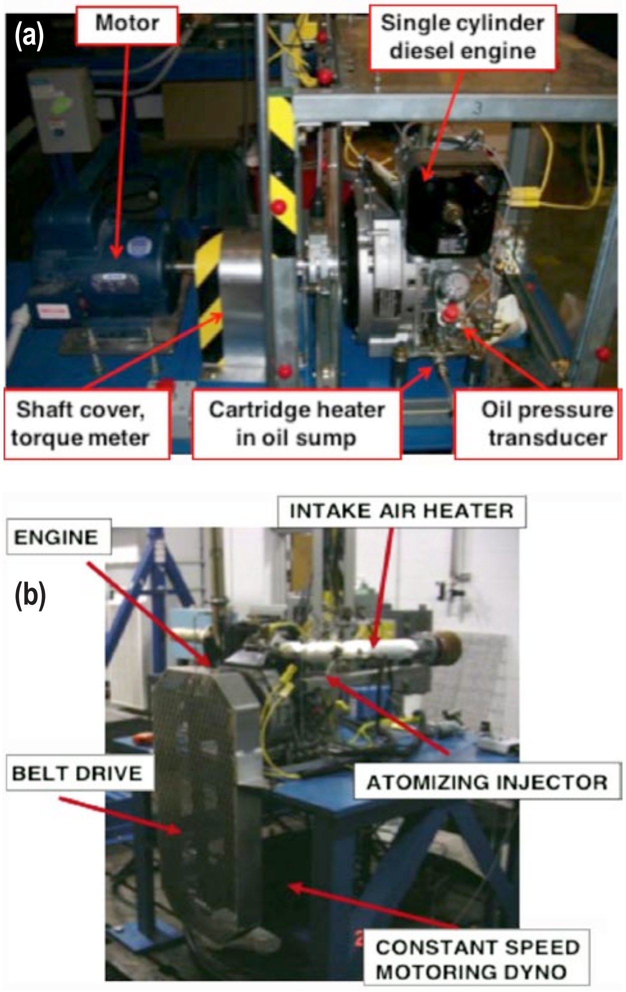


FIGURE 5. ORNL (a) motored and (b) fired single-cylinder engine test rigs.

Three fuels, base diesel, base diesel + ZDDP, and base diesel + IL, were evaluated in a fired single-cylinder research engine under three engine loads. A heated (190°C) stainless steel sample line was used to bring the sample to the filter oven, and a glass filter holder held the filter in the oven. Figure 6 shows the schematic and actual setup of the exhaust sampling system. Initial pyrolysis analysis did not detect IL decomposition products on the loaded filters – confirming the ashless nature of the IL.

The oil-miscible ILs developed in this CRADA have attracted significant interest from the lubricant and automotive industry. As a result, Lubrizol Corporation, the global No. 1 supplier of lubricant additives, is currently working with GM to produce the first-ever full engine oil formulation using the unique ORNL IL additives. GM has scheduled to full-size high-temperature, high-load engine tests for the new IL-additized engine oil.

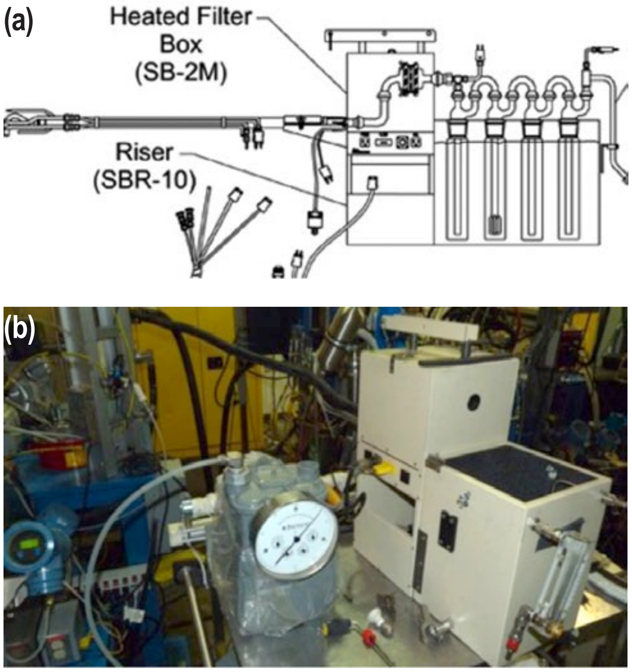


FIGURE 6. ORNL engine exhaust analysis setup. (a) Schematic of exhaust sampling system and (b) actual system hooked up to an engine.

CONCLUSIONS

Significant progress has been achieved in both approaches using ILs as neat lubricants or oil additives for engine lubrication. Significantly lower EHL/ML friction has been observed for a low-viscosity IL when compared to hydrocarbon oils with similar viscosities. The team has successfully developed oil-miscible ILs as lubricant additives and has demonstrated superior anti-scuffing/anti-wear functionality in systematic bench testing. This breakthrough has attracted significant interest from the lubricant and automotive industry. GM is currently working with Lubrizol to formulate and test the first-ever IL-additized engine lubricant.

REFERENCES

1. J. Qu, J.J. Truhan, S. Dai, H. Luo, P.J. Blau, “Lubricants or Lubricant Additives Composed of Ionic Liquids Containing Ammonium Cations,” U.S. Patent #7,754,664.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. J. Qu, D.G. Bansal, B. Yu, J. Howe, H. Luo, S. Dai, H. Li, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Anti-Wear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive,” *ACS Applied Materials & Interfaces* 4 (2) (2012) 997–1002.

2. B. Yu, D.G. Bansal, J. Qu, X. Sun, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Oil-Miscible and Non-Corrosive Phosphonium-Phosphate Ionic Liquids as Candidate Lubricant Additives,” *Wear* 289 (2012) 58–64.

3. G. Mordukhovich, J. Qu, J.Y. Howe, S.S. Bair, B. Yu, H. Luo, D.J. Smolenski, P.J. Blau, B.G. Bunting, S. Dai, “A Low-Viscosity Ionic Liquid Demonstrating Superior Lubricating Performance from Mixed to Boundary Lubrication,” *Wear* (in press) DOI: 10.1016/j.wear.2012.11.076.

4. D.G. Bansal, J. Qu, B. Yu, H. Luo, S. Dai, B. Bunting, P. Blau, G. Mordukhovich, D.J. Smolenskid, “Characterization and Tribological Evaluation of 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide as Neat Lubricant and Oil Additive,” *Proceedings of the ASME/STLE 2011 International Joint Tribology Conference (IJTC2011)*, Los Angeles, CA, Oct. 23–26, 2011.

5. J. Qu, B. Yu, D.G. Bansal, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Ionic Liquids as Novel Engine Lubricants or Lubricant Additives,” *2011 Directions in Engine-Efficiency and Emissions Research (DEER) Conference*, Detroit, MI, Oct. 3-6, 2011.

6. D.G. Bansal, S. Kuiry, B. Yu, H. Luo, D. Koosau, J. Qu, “Tribo-Corrosion Behavior of Selected Imidazolium-Based Ionic Liquids,” presented at *the Third International Symposium on Tribo-Corrosion*, Atlanta, GA, April 19-20 2012.

7. J. Qu, “Ionic Liquids as Novel Lubricants or Lubricant Additives,” presented at *the SAE 2012 High Efficiency IC Engines Symposium*, Detroit, MI, April 22–23, 2012. (invited)

8. J. Qu, B. Yu, D.G. Bansal, J. Howe, H. Luo, S. Dai, P.J. Blau, B.G. Bunting, G. Mordukhovich, D.J. Smolenski, “Oil-Miscible and Non-Corrosive Ionic Liquids as Candidate Lubricant Additives,” presented at *the STLE 67th Annual Meeting & Exhibition*, St. Louis, MO, May 6–10, 2012.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Invited candidature by the Scientific Secretariat for the 2013 ENI Award.

- to recognize the paper, J. Qu et al., “Anti-Wear Performance and Mechanism of an Oil-Miscible Ionic Liquid as a Lubricant Additive,” *ACS Applied Materials & Interfaces* 4 (2) (2012) 997–1002.

III.11 Fuel Properties to Enable Lifted-Flame Combustion

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Subcontractors:
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Objectives

- Identify fuel properties that can be used to enable controllable extended lift-off combustion (ELOC) with low nitrogen oxides (NOx).
- Enhance the state of knowledge on ELOC.
- Identify and test possible fuels that enable ELOC and also meet other fuel system requirements (e.g. lubricity, oxidative stability, cold flow).
- Enhance combustion models to capture the effect of key fuel properties on combustion in advanced combustion regimes.

Fiscal Year (FY) 2012 Objectives

- Develop a master list of possible oxygenate compounds and their properties.
- Select specific fuels to be used in spray characterization studies, and combustion model development.
- Initiate modeling projects to account for fuel properties related to ELOC (i.e. cetane, oxygen content).
- Initiate spray characterization studies to understand the effect of fuel properties on the achievability of ELOC.

Accomplishments

- Developed a master list of possible oxygenated compounds and properties.
- Evaluated fuel properties of mixtures of tri-propylene glycol methyl ether (TPGME) and n-hexadecane with 15% and 50% TPGME. Purified compounds and supplied fuel mixtures for spray characterization.
- Conducted smoke point lamp experiments to screen different oxygenated compounds for soot formation tendency.
- Used a grouped chemistry model to develop fuel surrogate models of varying cetane number (CN) for use in computational fluid dynamics simulations.
- Investigated combustion models with TPGME. Found issues with the low-temperature chemistry representation leading to issues with greater than 50% TPGME.
- Investigated modeling oxygenated fuels and obtained necessary fuel properties to adjust inputs to spray and combustion models.
- Initiated an experimental plan to characterize ELOC in a controlled combustion spray facility.

Future Directions

- Identify and confirm fuel properties needed to achieve ELOC and evaluate their spray characteristics and optical engine behavior.
- Validate and use fuel and combustion models to optimize selected fuel properties and identify combustion system design changes needed to facilitate non-sooting diesel combustion.
- Continue to improve and use models to guide fuel selection and boundary conditions for future engine testing.

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INTRODUCTION

The intent of this project is to identify how fuel properties can be used to achieve controllable ELOC with low NOx and particulate matter (PM) emissions. Specifically, this project is expected to enhance the state of knowledge, identify and test key fuel properties to enable ELOC and their compatibility with current fuel systems, and enhance combustion models to capture the effect of fuel properties on advanced combustion. Successful demonstration of ELOC may reduce the need for aftertreatment devices, which would reduce costs and improve thermal efficiency.

The project team consists of key technical personnel from Ford Motor Company (FMC), the University of Wisconsin-Madison (UW), and Sandia National Laboratories (SNL). The project is led by Dr. Eric Kurtz and supported by Dr. Jim Anderson (FMC), Dr. Lyle Pickett and Dr. Charles Mueller (SNL) and Professor Rolf Reitz (UW).

APPROACH

All three partners will have key roles in achieving the project objectives. Together, FMC and UW will develop and integrate three-dimensional combustion models to capture fuel property combustion effects. FMC will use modeling results to modify the single-cylinder combustion system and demonstrate fuel-enabled ELOC. FMC will also lead fuels activities to identify appropriate fuels and fuel properties for spray and engine evaluations. UW will investigate modeling the location of flame lift-off and the equivalence ratio within the fuel spray to capture lifted flame combustion. SNL will lead spray combustion experiments to quantify and identify key fuel properties, as well as single-cylinder optical engine experiments to improve fundamental understanding of flame lift-off, generate model validation data, and also demonstrate ELOC concurrent with FMC efforts.

RESULTS

Fuels Development and Property Testing and Single-Cylinder Engine

A master list of oxygenate compounds and properties was created for use in the fuel sooting and CN/derived cetane number (DCN) studies. Initially, two fuel blends of TPGME and a primary reference fuel mixture of n-hexadecane (NHD) and 2,2,4,4,6,8,8-heptamethylnonane (HMN) were selected for testing at the SNL spray lab. The intent was for both to have the same DCN but varied oxygen ratio to determine its influence on the ability to achieve leaner lifted flame combustion. Testing, however, showed the CN and DCN values for TPGME were significantly higher than what was expected and required further testing to determine cause. Both peroxide contamination and the method used to measure cetane number were found to contribute to the CN discrepancy. Since it is not well understood which method for DCN measurement best correlates with a diesel engine, it was assumed that TPGME and NHD had similar CNs based on Fuel Ignition Tester results. Mixtures of 15% and 50% TPGME in NHD were created, tested and sent to SNL for spray testing.

A smoke point lamp (ASTM D1322) was used to evaluate the sooting tendency of diesel-range oxygenates, hydrocarbons and blends; 1,2,4-trimethylbenzene (TMB) at 30% by volume was mixed with blends of NHD and different oxygenates. TMB provided sufficient soot for a stable smoke point reading within the smoke point method range. A constant TMB level was used to isolate the effect of oxygenate composition and oxygen content based on initial measurements which indicated aromatic content dominated the results. Results did not compare well with soot results from existing engine experiments.

Modeling

Surrogate models were developed to characterize spray and combustion properties of three different diesel fuels. Computations were performed at a constant engine speed of 1,500 rev/min using the KIVA-ERC-CHEMKIN code incorporated with a “MultiChem” mechanism having 90 species and 348 reactions. Model predictions compared well with measured data from a single-cylinder diesel engine operated under conventional and low-temperature combustion conditions.

The models, when applied over wider operating conditions, predicted the measured combustion phasing trends quite well but predicted slightly higher peak pressures. Additional effort was spent exploring the kinetic rate constants and the pressure dependency of the CO oxidation reaction. Results show the pressure dependent CO reactions were unable to reduce the predicted higher peak pressures, however, increasing the rate constant of the reaction between hydroxyl and hydroperoxy radicals improved peak pressure, CO concentrations, NOx and unburned hydrocarbon predictions.

A reduced combined TRF-TPGME mechanism with 50 species and 173 reactions was also explored for use in modeling spray combustion chamber data with the TPGME-NHD mixtures. Results of constant volume simulations appeared reasonable with TPGME mixtures below 70%, where misfire was found due to issues with the TPGME mechanism at low temperature.

Spray Work and Optical Engine

SNL has developed a set of experiments to characterize ELOC and provide a detailed understanding of spray evaporation, mixing, ignition, lift-off stabilization, and soot formation. The ambient temperature and pressure variation will identify the conditions where ELOC can be achieved. This testing is ongoing.

CONCLUSIONS

- Mixtures of TPGME and NHD will be used to evaluate the range of conditions under which ELOC is possible by varying fuel oxygen content at roughly constant CN.

- Smoke point measurements did not correlate with existing soot data from engine testing. Further investigation is needed to determine whether this technique is useful for screening fuels for ELOC.
- A fuel surrogate approach has been used successfully to model the effect of fuels of different CNs under various engine operating conditions.
- A chemical mechanism has been developed that is capable of simulating the combusting spray vessel experiments with TPGME and NHD mixtures.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Completed and submitted to DOE contractually-required quarterly reports, an updated project management plan (September 2012) and a Continuation Application for budget period 2 (October 2012).

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Invention Disclosure: 83238953 - 212-0297 Combustion system for leaner lifted flame combustion (LLFC) Strategy

IV.1 Impact of Fuel Metal Impurities on the Performance and Durability of DOC, DPF and SCR Systems

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- United Soybean Board, Chesterfield, MO

Research Partners:
- Todd Toops, Michael Lance – Oak Ridge National Laboratory
- Giovanni Cavataio – Ford Motor Company
- Rasto Brezny – Manufacturers of Emissions Control Association

Objectives

- Assess the impact of fuel metal impurities on the long-term durability of emission control systems found in modern diesel engines.
- Determine if the impact of Na, K or Ca on catalyst durability would warrant a tightening of the current ASTM International specifications for these metals in biodiesel.

Fiscal Year (FY) 2012 Objectives

Assess the impact of fuel metal impurities on the full-useful-life durability of an emission control system found in a light-duty application (Ford F250 pickup).

Accomplishments

- A method for accelerated aging of light-duty catalyst parts was developed which results in full-useful-life exposure to fuel metal impurities and thermal aging.
- Using this accelerated method four separate exhaust systems from a Ford F250 pickup were aged to the equivalent of 150,000 miles. Each of the four systems was aged with a different fuel; ultra-low sulfur diesel (ULSD) containing no metals, 20 vol% biodiesel in diesel (B20) containing Na, B20 containing K, and B20 containing Ca.
- Post mortem analysis of the aged systems (conducted by our collaborators at Ford and Oak Ridge National Laboratory) showed that the first inch of the selective catalytic reduction (SCR) catalysts aged with B20+Na and B20+K only achieved 70% oxides of nitrogen (NOx) conversion at 200ºC, compared to greater than 80% NOx conversion for the systems aged with ULSD and B20+Ca.
- Post mortem analysis of the aged systems showed that the first inch of the SCR catalysts aged with B20+Na and B20+K could only adsorb about 50% of the ammonia that the ULSD system could adsorb.
- While the first inch of the SCR catalysts aged with B20+Na and B20+K showed diminished performance, further down the length of the catalyst the performance was the same as the system aged with ULSD.
- Although the catalysts aged with B20+Na and B20+K showed signs of deactivation, both systems were still able to pass the 0.2 g/mile NOx emission standards when installed onto a Ford F250 pickup.

Future Directions

The next phase of testing will be to conduct similar accelerated aging experiments on a heavy-duty catalyst system with a much longer full-useful-life requirement of 435,000 miles.

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INTRODUCTION

Biodiesel may contain residual amounts of metal impurities (Na, K, Ca or Mg) from the fuel production process. Sodium and calcium may also be present in conventional diesel fuel and have been implicated in internal injector deposits. Regardless of the source, these metallic fuel contaminants are converted to oxides, sulfates, hydroxides or carbonates in the combustion process and form an inorganic ash that can be deposited onto the exhaust emission control devices found in modern diesel engines. Alkali metals are well known poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic substrates [1,2,3]. Furthermore, alkali metal hydroxides such as sodium and potassium are volatilized in the presence of steam and can therefore penetrate the catalyst washcoat or substrate. In this work we examine the long-term impacts of these residual metals on the performance and durability of diesel exhaust catalysts.

APPROACH

Alkali and alkaline earth metal impurities found in diesel fuels are potential poisons for diesel exhaust catalysts. Using an accelerated aging procedure, a set of production exhaust systems from a 2011 Ford F250 equipped with a 6.7-L diesel engine have been aged to an equivalent of 150,000 miles of thermal aging and metal exposure. These exhaust systems included a diesel oxidation catalyst (DOC), SCR and diesel particulate filter (DPF). Four separate exhaust systems were aged, each with a different fuel; ULSD containing no measureable metals, B20 containing sodium, B20 containing potassium and B20 containing calcium. Metals levels were selected to simulate the maximum allowable levels in 100% biodiesel (B100) according to the ASTM D6751 standard. Analysis of the aged catalysts included Federal Test Procedure emissions testing with the systems installed on a Ford F250 pickup, bench flow reactor testing of catalyst cores, and electron probe microanalysis (EPMA). The thermo-mechanical properties of the aged DPFs were also measured. Bench flow reactor experiments were conducted by our collaborators at Ford. EPMA and analysis of the DPF material properties was conducted by our collaborators at Oak Ridge National Laboratory.

RESULTS

EPMA imaging of aged catalyst parts, shown in Figure 1, found that both the Na and K penetrated into the washcoat of the DOC and SCR catalysts, while Ca remained on the surface of the washcoat. Bench flow reactor experiments were used to measure the standard NOx conversion, NH_3 storage and NH_3 oxidation for each of the aged SCR catalysts. Flow reactor results, shown in Figures 2 and 3, showed that the first inch of the SCR catalysts exposed to Na and K had reduced NOx conversion through a range of temperatures and also had reduced NH_3 storage capacity. The SCR catalyst exposed to Ca had similar NOx conversion and NH_3 storage performance compared to the catalyst aged with ULSD. Using a chassis dynamometer, vehicle emissions tests were conducted with each of the aged catalyst systems installed onto a Ford F250 pickup. Regardless of the evidence of catalyst deactivation seen in flow reactor experiments and EPMA imaging, the vehicle successfully passed the 0.2 gram/mile NOx emission standard with each of the four aged exhaust systems. Vehicle emission test results are shown in Figure 4. This indicates that total catalyst volume is adequate to accommodate the catalyst activity loss observed in the flow reactor experiments.

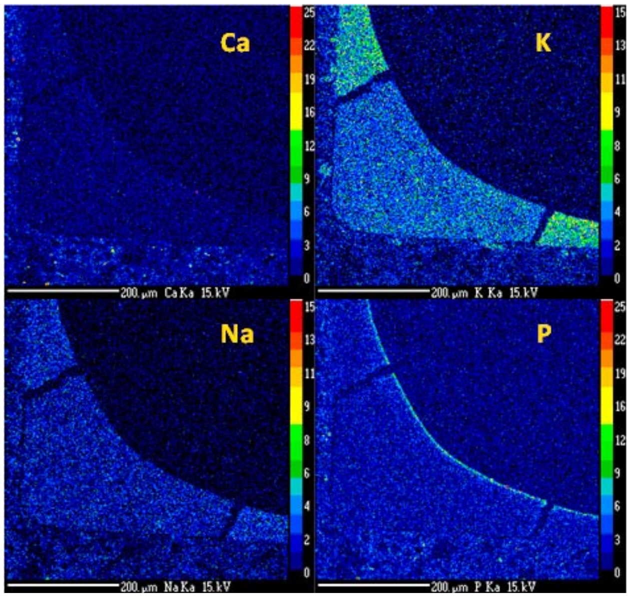

FIGURE 1. EPMA of the First Inch of the B20+K Aged SCR

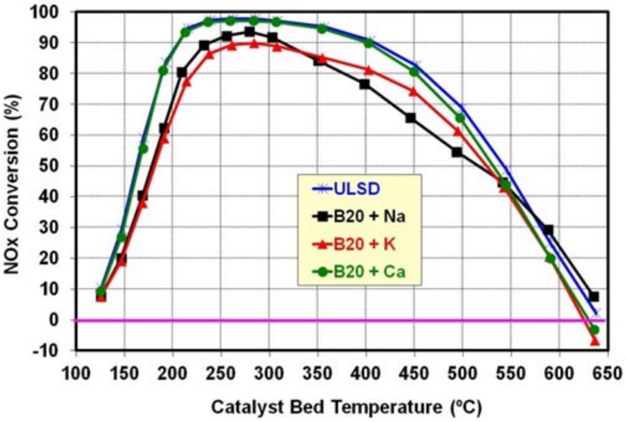

FIGURE 2. Standard SCR Reaction for the First Inch of the Aged SCR Catalysts

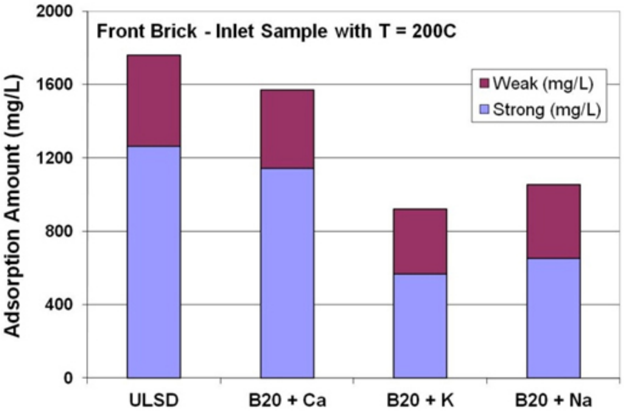

FIGURE 3. Ammonia Storage of the First Inch of the Aged SCR Catalysts

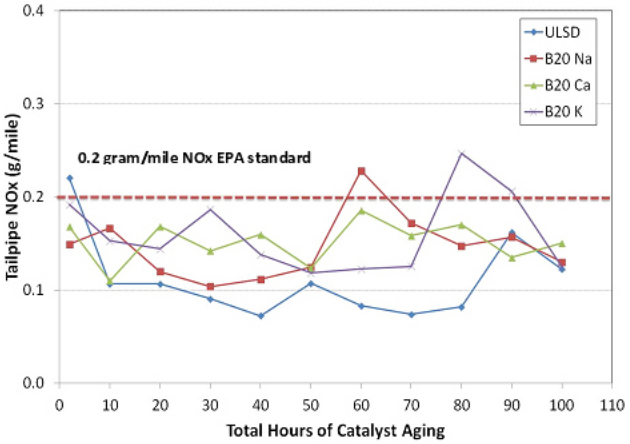

FIGURE 4. NOx Emissions Test Results

CONCLUSIONS

- Four separate exhaust systems, which included a DOC, SCR and DPF from a Ford F250 pickup were aged to the equivalent of 150,000 miles using an accelerated method. Each of the four systems was aged with a different fuel; ULSD containing no metals, B20 containing Na, B20 containing K, and B20 containing Ca.
- Post mortem analysis of the aged systems showed that the first inch of the SCR catalysts aged with B20+Na and B20+K only achieved 70% NOx conversion at 200ºC, compared to greater than 80% NOx conversion for the systems aged with ULSD and B20+Ca.
- Post mortem analysis of the aged systems showed that the first inch of the SCR catalysts aged with B20+Na and B20+K could only adsorb about 50% of the ammonia that the ULSD system could adsorb.
- While the first inch of the SCR catalysts aged with B20+Na and B20+K showed diminished performance, further down the length of the catalyst the performance was the same as the system aged with ULSD.
- Although the catalysts aged with B20+Na and B20+K showed signs of deactivation, both systems were still able to pass the 0.2 g/mile NOx emission standards when installed onto a Ford F250 pickup.

REFERENCES

1. Williams, A., Luecke, J., McCormick, R.L., Brezny, R., Geisselmann, A., Voss, K., Hallstrom, K., Leustek, M., Parsons, J., Abi-Akar, H. “Impact of Biodiesel Impurities on the Performance and Durability of DOC, DPF and SCR Technologies,” SAE Technical Paper 2011-01-1136 (2011).

2. Dou, D., Balland, J., “Impact of Alkali Metals on the Performance and Mechanical Properties of NOx Adsorber Catalysts,” SAE Technical Paper No. 2002-01-0734 (2002).

3. Cavataio, G., Jen, H., Dobson, D., Warner, J., Lambert, C., “Laboratory Study to Determine Impact of Na and K Exposure on the Durability of DOC and SCR Catalyst Formulations,” SAE Technical Paper No. 2009-01-2823 (2009).

FY 2012 PUBLICATIONS/PRESENTATIONS

Publications

1. Williams, A., Burton, J., McCormick, R.L., Toops, T., Wereszczak, A.A., Fox, E.E., Lance, M.J., Cavataio, G., Dobson, D., Warner, J., Brezny, R. “Impact of Fuel Metal Impurities on the Durability of a Light Duty Diesel Aftertreatment System” SAE Congress submitted.

Presentations

1. National Biodiesel Conference, February 2012 – Orlando, FL

2. DOE Annual Merit Review, May 2012 – Washington, D.C.

3. DEER Conference, October 2012 – Detroit, MI

4. Biodiesel Technical Workshop, October 2012 – Kansas City, MO

IV.2 Biofuels Quality Surveys in 2012

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Kevin Stork

Objectives

- Assess the quality of biofuels to determine if quality is changing, particularly in response to changes in specifications.
- Publish the results of quality surveys to provide unbiased data to standards bodies to develop, modify, and improve biofuels specifications.

Fiscal Year (FY) 2012 Objectives

- Survey the quality of neat biodiesel (B100) from terminals and producers in the United States.
- Develop and validate new analytical methodology to describe monoglycerides, a critical quality parameter of B100.

Accomplishments

- Collected B100 samples from 14 terminals and 53 producers across the United States.
- Developed new method based on liquid chromatography with mass spectrometric detection (LC/MS) method for monoglycerides.

Future Directions

- Publish journal article on results from B100 survey.
- Continue to work with ASTM International to improve the D6584 method for glyceride determination.
- In collaboration with the Coordinating Research Council (CRC), survey and report on mid-level ethanol blend (MLEB) quality from so-called blender pumps.

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INTRODUCTION

The focus of this research area is to document the changes in quality to current and emerging biofuels in the United States marketplace. ASTM International specifications are frequently adopted by state and local agencies to enforce fuel quality and promote commerce. The ASTM specification covering B100 quality is D6751. The specification has been recently updated to include a No.1-B grade of biodiesel in an effort to ward off problems with cold weather operability [1]. The No.1-B grade is optional and sometimes thought of as a wintertime grade.

The initial quality of B100 is determined by the producer. However, once the B100 enters the distribution system, it may be comingled with B100 from several producers, resulting in quality changes of the product. This effort examined the quality of B100 from the producers, similar to the work by the National Renewable Energy Laboratory (NREL) in 2007 [2], as well as the quality of B100 at the terminals, similar to NREL's 2006 quality survey [3].

APPROACH

A B100 survey from producers and terminals was completed in 2012. The producers were identified through one of two mechanisms. First, the National Biodiesel Board provided list of the top 50 biodiesel producers, by volume. Each of these 50 companies was contacted. The second method used to identify producers was through the BQ-9000 quality program [4], a voluntary industry quality assurance program. Samples were collected from 53 different producers or production facilities. In the event a producer operated more than one plant at different locations, a unique sample was collected from each location. Samples were requested from terminals throughout the U.S. and came from both coasts, as well as the Midwestern United States Samples were tested for critical properties in D6751 and are listed in Table 1.

One of the largest issues facing biodiesel blends today is the formation of precipitates above the cloud point (CP). The CP is an analytical test where crystals first form in fuels and is described by a test that cools fuels at a specific rate. Unfortunately, in rare instances, biodiesel blends have been found with precipitates, or crystals, above the CP [5]. The industry has worked to try to prevent this phenomenon through improvements, such as the No.1-B grade, to neat biodiesel, prior to blending. One of the most likely compounds thought to cause

TABLE 1. Properties Measured for B100 Quality Survey.

Property	Method^A	D6751 Limit	D6751 No.1-B grade requirements
Acid number, mgKOH/g	D664	0.50, max	Same
Cold soak filtration test, sec	D7501	360, max^B	200, max
Free glycerin, wt%	D6584	0.020, max	Same
Total glycerin, wt%	D6584	0.240, max	Same
Monoglycerides, wt%	D6584	Report^C	0.40, max
Diglycerides, wt%			Report
Triglycerides, wt%			
Saturated monoglycerides, wt%	Modified D6584	None	None
	In-house LC/MS		None
Cloud point, °C	D5773^D	Report	Report
Calcium and magnesium, ppm	D7111^E	5, max	Same
Sodium and potassium, ppm	D7111^E	5, max	Same
Oxidation stability, hrs	EN15751	3, min	Same
Fatty acid methyl ester (FAME) profile	In-house	None	None

A: Methods are ASTM unless otherwise noted.
B: B100 blended in diesel fuel for an end use of -12°C or lower shall meet a 200 sec limit.
C: Although glycerin species are not required to be reported in D6751, the D6584 method reports the values for these species.
D: D2500 is the referee cloud point method.
E: EN14538 is the referee method for metals.

precipitates above the CP is the presence of saturated monoglycerides (SMG).

While SMGs are routinely measured by the ASTM D6584 method for glycerides, they are not commonly reported. The D6584 method was modified to quantify and report SMGs. The likelihood of SMGs to be the root cause of the operability problems requires a high level of confidence in quantifying these compounds.

A novel method for quantifying monoglycerides (MAGs) was developed as part of this work. The new method was based on LC/MS detection. Further details of the LC/MS technique are available in the report and are omitted here due to space restrictions.

RESULTS

Error bars are determined from the ASTM method reproducibility. Sample ID is kept consistent throughout the reporting, with producer samples identified by circles and terminal samples identified by squares.

The FAME profile, along with the CP, was used to determine the likely feedstock of the samples collected. As with the most recently B6-B20 survey, the feedstocks were split between soy and mixed feedstocks. The term mixed feedstocks includes a mixture of two or more feedstocks, and may include soy, corn, canola, animal tallows, and palm. The CP analysis verified the likely feedstocks predicted through the FAME profile. Figure 1 shows the range of CP in this work.

The last NREL B100 survey was conducted prior to the adoption of cold soak filtration (CSFT) in D6751. Figure 2 shows the results for CSFT, with only one sample failing to meet the year-round 360 sec limit. The sample that failed the CSFT also failed other tests, notably metals and oxidation stability.

The average oxidation stability of these samples was 9.5 hrs, well above the 3-hr minimum required in

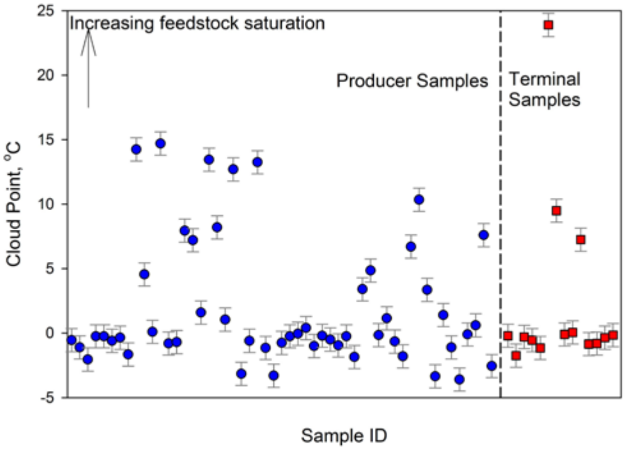

FIGURE 1. CP Results from B100 Survey

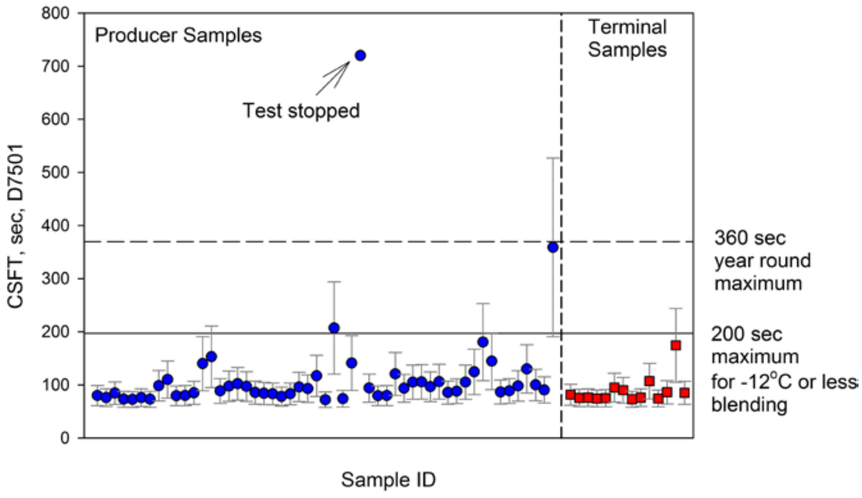

FIGURE 2. CSFT Results from B100 Survey

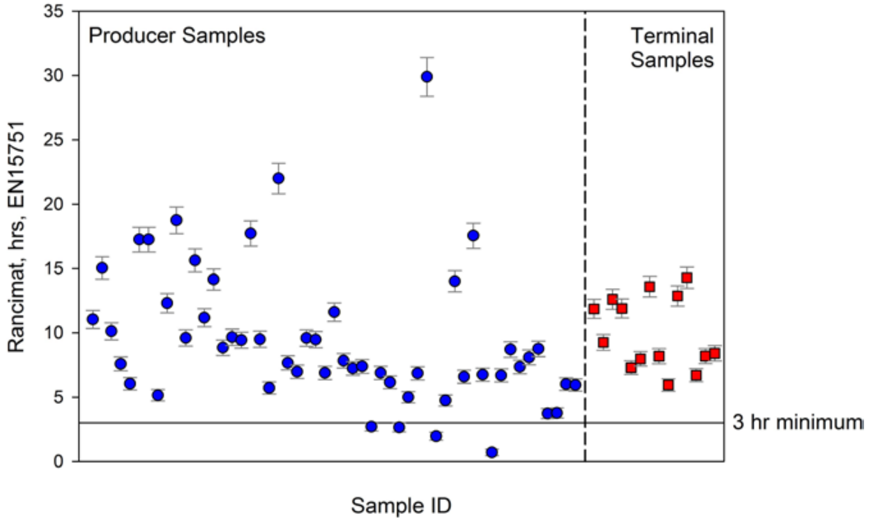

FIGURE 3. Oxidation Stability Results of B100 Samples

D6751 (Figure 3). Only two samples fell below the 3-hr minimum, a notable improvement over 2007, when nearly 30% of the failed the requirement.

The emerging importance of MAGs and SMGs, in particular, led to an in-depth investigation of these parameters. The average MAG content of these samples was 0.327 wt% and was normally distributed. The normal distribution was an expected result, as the MAG levels are a result of different production processes and technologies. While the MAG levels are normally distributed, the SMGs are not. The average SMG content was 0.069 wt%.

A new method for MAGs was developed using LC/MS. The method was validated using the current gas chromatographic methodology. The new LC/MS method showed excellent correlation to the GC method, with an

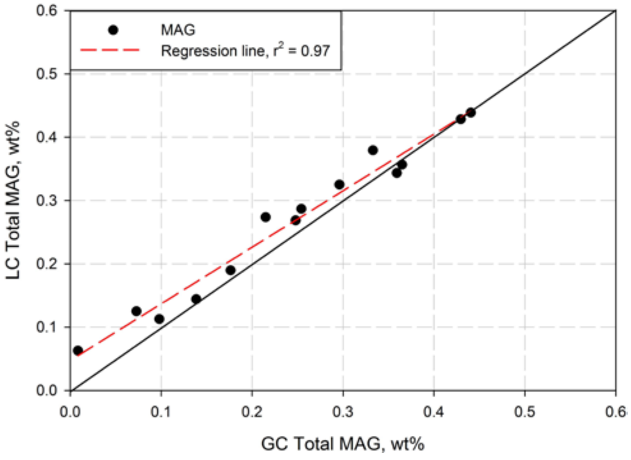

FIGURE 4. Correlation between MAGs Measured by Gas Chromatography and Liquid Chromatography

r^2 of 0.97. A small offset was observed at very low MAG levels and further investigation will determine the cause of this offset.

Beyond the properties highlighted above, the quality of the B100s collected in this effort was very high. Only one failure was recorded on flash point due to excess methanol content due to a poorly processed sample. No failures were recorded on free and total glycerin and acid value. Only one failure was found on metals.

CONCLUSIONS

Samples of B100 were tested for critical properties and found to typically meet the D6751 specification.

- All samples met free and total glycerin and acid value requirements.
- Two failures were observed on oxidation stability. One of these samples also failed the CSFT and metal content requirements.
- Only one sample failed multiple properties and was clearly the lowest quality sample in this survey.
- A new LC/MS method was developed and validated for MAGs, showing excellent correlation to the current GC method.

REFERENCES

1. ASTM International Standard D6751-12, "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels," Annual Book of ASTM Standards, ASTM International, West Conshohocken, PA, 2011.

2. Alleman, T.L.; McCormick, R.L.; "Results of the 2007 B100 Quality Survey;" NREL/TP-540-42787, March 2008.

3. Alleman, T.L.; McCormick, R.L.; Deutch, S.; "2006 B100 Quality Survey Results: Milestone Report;" NREL TP-540-41549, May 2007.

4. BQ-9000 Quality Management Program, www.bq-9000.org.

5. Dunn, R.O., "Effects of monoacylglycerols on the cold flow properties of biodiesel", *J Am Oil Chem Soc*, 89 (2012), 1509-1520.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Alleman, T.L.; Chupka, G.; Fouts, L.; "Quality Parameters and Chemical Analysis for Biodiesel Produced in the United States in 2011;" In review.

IV.3 Understanding Biodiesel Low-Temperature Operability Issues

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- United Soybean Board, Chesterfield, MO

Objectives

Identify the cause and mechanism of unexpected cold weather fuel filter clogging that has been observed for some biodiesel blends.

Fiscal Year (FY) 2012 Accomplishments

- Prior work has shown that a large difference between cloud point (CP – measured in the cooling direction) and final melting temperature (FMT – measured in the warming direction) in 100% biodiesel (B100) is indicative of saturated monoglyceride (SMG) polymorphism. We have proposed that SMG polymorphism – where a metastable form precipitates from the fuel during diurnal cooling and later transforms into a more stable, higher melting temperature form – is responsible for unexpected fuel filter clogging.
- In FY 2012 the effect of biodiesel composition (saturated fatty acid methyl ester [FAME] and monoglyceride content) on CP and FMT was evaluated for a large experimental matrix. B100 from four sources was spiked with different SMG levels, and blended with four different diesel fuels at 5, 10, and 20 volume percent.
- CP and FMT were measured for this 144 sample matrix and results evaluated by regression analysis. Result indicated that:
  - SMG content has the largest effect on increasing CP, regardless of the B100 or diesel fuel.
  - At fixed SMG level, higher levels of biodiesel in the blend lower the cloud point by increasing the solubility of SMG.
  - Only at the high biodiesel blending level (20 volume percent) was saturated FAME content significant in increasing CP.
- Common belief is that saturated FAME content is the primary factor affecting biodiesel blend CP, thus these results may lead to improved strategies for wintertime biodiesel blending.
- A high FMT relative to CP was observed in many blend samples, especially for SMG content greater than 100 ppm. Analysis and additional experiments to clarify the FMT results are ongoing.

Future Directions

Further study to address the following issues is underway:

- For some B100, observation of the polymorphic phase transformation requires a significantly slower heating rate (although still faster than occurs in real world diurnal warming). Ongoing experiments are directed at understanding why this occurs.
- A related study has been initiated with industry to investigate these issues with real world, as opposed to spiked, samples.

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INTRODUCTION

Over 1 billion gallons of biodiesel was consumed in the United States in 2011 [1]. Ensuring that B100 and especially B100 in diesel fuel blends will not pose low-temperature operability issues is critical for expanded use of this important petroleum displacement fuel. Cloud point (the temperature where crystals first precipitate from the fuel) is commonly used as a conservative measure of a fuel's low-temperature operability limit. A number of studies have documented incidents of fuel filter clogging above cloud point for biodiesel blends, and in previous work we showed that polymorphs of SMGs are a likely cause [2]. SMGs are a common impurity in biodiesel. We have shown that upon cooling a less stable crystal form of SMGs initially precipitates out of the fuel [3]. This less stable form then converts to a more stable, higher melting and less soluble form that persists at temperatures above the measured CP of the fuel. Above a certain concentration or eutectic point of SMG in the B100, the CP and especially the FMT of the fuel is significantly raised. A large FMT-CP difference, of 15°C or more, is indicative of the polymorphic behavior of the SMG.

The formation of one polymorphic form over the other can be effected by several factors including the presence of other impurities, concentration of the impurity in solution, rate of cooling or heating, and the solvent or matrix which the solids are crystallized from [4]. B100 is typically blended with diesel fuel of various types which can broadly change the solvent matrix.

The objective of this study is to reveal how biodiesel and diesel fuel composition affect low-temperature performance of biodiesel blends. We measured CP and FMT when blending spiked and unspiked B100 into various diesel fuels to create various levels of SMGs in the finished blends. The B100 was blended into the diesel fuel at three different blends levels; B5, B10, and B20. Diesel fuel samples with a wide range of aromatic content and CP were employed.

APPROACH

A nominally 10% aromatic, Tier 2 certification diesel (Fuel A) and a high aromatic (37%) diesel fuel (Fuel B) were obtained from Haltermann Products. We also obtained a local (Colorado) No. 2 diesel (Fuel C) and a low cloud point No. 1 diesel from Minnesota (Fuel D). All hydrocarbon diesel fuels were ultra-low sulfur diesel meeting the requirements of ASTM D975 for their respective grades.

The B100s used for this study were a canola (B100 I) containing 6.7 wt% saturated FAME, soy (B100 II) 15 wt% saturated FAME, and two mixed feedstock animal-derived B100 (B100 III and B100 IV) with 24 wt% and 36 wt% saturated FAME, respectively. They all met the requirements of ASTM D6751 and were obtained from manufacturers. Analysis for glycerin, mono-, di-, and triglycerides was performed using ASTM D6584. FAME profile analysis was performed on an Agilent 7890 Series gas chromatograph equipped with a flame ionization detector and an HP INNOWax 30 m x 0.25 mm x 0.5 µm column. Expected monoglyceride ratios were obtained from the FAME profiles.

The B100s were manipulated to have different levels of impurities prior to blending. All four B100s were used as received. Additionally, impurities were added to all the B100s at a low level (approximately 0.1% w/w SMG), a high level (approximately 0.3% w/w SMG for B100 II, III, and IV). Note that for B100 III and IV the as received SMG content was used as the low level. For B100 II, III, and IV a third level targeted at the total glycerin specification limit was also prepared. A custom monoglyceride mix of monoolein, monopalmitin, and monostearin was made for each feedstock. Because monoolein was added with the SMG to preserve the unsaturated:saturated monoglyceride ratio, several of the high spike level samples fail the ASTM D6751 limit for total glycerin.

All diesel blends were prepared by volume using a pipette resulting in 5 mL samples. The as-received and low/high spiked samples were blended into all four diesel fuels at 5, 10, and 20 volume percent. Replicates of the low spike B100 III blends were also prepared. The specification limit B100s were blended into all four diesel fuels at 10 and 20 volume percent. This provided a total of 144 blend samples. CP by D5773 and FMT were measured using a commercial light scattering instrument with Peltier-effect cooling (Phase Technology 70X Analyzer). The experiment was conducted at 1.5°C/min heating rate.

RESULTS

Table 1 contains properties of the diesel fuels used for blending. Table 2 contains information on the B100 properties most relevant to this work.

TABLE 1. Diesel Fuel Properties

Diesel	Aromatic Content (%)[a]	CP (°C)[b]	FMT (°C)
Fuel A	9	-28.1	-22.0
Fuel B	37	-27.2	-22.9
Fuel C	25	-16.5	-14.0
Fuel D	15	-45.7	-42.5

[a]ASTM D1319; [b]ASTM D5773

TABLE 2. B100 Properties

B100	Sat FAME (%)	CP (°C)	FMT (°C)	CSFT[a] (sec)	SMG %	Total MG
B100 I	6.7	-1.2	6.8	110	0.053	0.557
B100 II	15	-1.4	5.6	91	<LOQ[b]	<LOQ[b]
B100 III	24	4.4	8.4	100	0.045	0.148
B100 IV	36	9.5	13.1	78	0.152	0.393

[a]cold soak filtration test; [b]limit of quantitation; MG - monoglyceride

The 144 blend samples prepared from both unspiked and spiked B100 I-IV were tested for CP using the D5773 method. Linear regression analysis was used to evaluate several factors affecting the blend CP. Variables analyzed and their hypothesized effects were:

- Base diesel CP: defines the temperature where petroleum wax will affect CP and also captures other base fuel properties such as average molecular weight.

- Percent aromatic content and percent biodiesel in the blend: both the presence of aromatics and biodiesel increases the solubility of relatively polar materials such as SMG.
- Percent saturated FAME and percent SMG in the blend: these species have the lowest solubility at low temperature and, along with petroleum wax, are responsible for crystal formation at CP.

Table 3 contains the coefficients and the *p*-value for each factor analyzed. The R^2 for the multiple regression was 0.70, which indicates that the model captures about 70% of the variation in CP for these samples. Four of the five factors considered were significant at 95% confidence or greater. A stepwise regression showed that removing percent aromatic content did not reduce the goodness of the fit.

TABLE 3. Linear Regression Data for Factors Affecting Blend CP

Variable	Coefficients	P-value	Variable Range	ΔCP for 10% of Range Change
Diesel CP	0.13	0.010	-45°C to -16.5°C	0.3°C
Aromatic Content	-0.096	0.083	7% to 35%	-0.3°C
% Biodiesel	-0.48	<0.001	0% to 20%	-1°C
% SMG	413	<0.001	0% to 0.085%	3.5°C
% Sat FAME	1.07	0.018	0% to 7.2%	0.8°C

SMG content had a larger effect on CP than any of the other variables. Increasing blend SMG by just 100 ppm (0.01 wt%) would increase CP by over 4°C on average. Figure 1 shows the effect of increasing amounts of SMGs in B100 II in Fuel C and Fuel D (the highest and lowest CP base fuels, respectively). This trend is similar for the other fuels tested and points to SMG being a major contributor to an increase in CP. Figure 2 examines the same data and additional data for other B100, plotted as a function of SMG content in the blend. For all fuels SMG content has a dramatic effect on CP, however there is also a clear effect of biodiesel blend level. CP is very similar for SMG content up to 100–150 ppm regardless of biodiesel blend level or saturated FAME content. Above this level the solvency effect of biodiesel is evident, with higher biodiesel content fuels exhibiting lower CP. For Fuel C blends, there also appears to be some effect of biodiesel saturated FAME content at the B20 level. Figure 2 also shows that the CP effect of a 100 ppm change in SMG can be much larger than 4°C at low SMG levels.

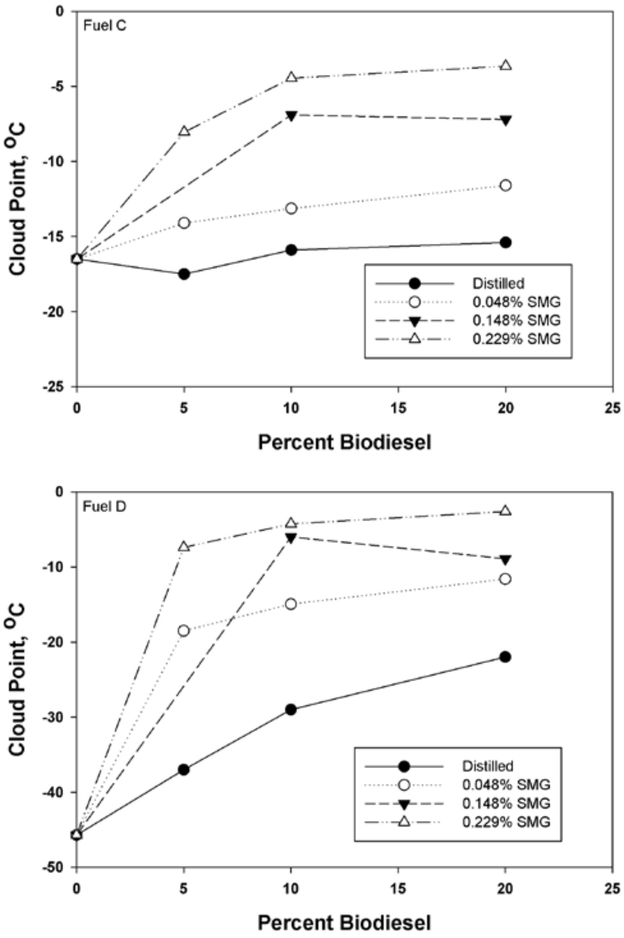

FIGURE 1. Effect of SMG content in B100 II on CP in Fuels C and D (SMG is percent in B100).

Because B100 II as received does not contain SMG at detectable levels, its blends can be used to more clearly demonstrate the effect of saturated FAME content on CP. Figure 3 shows CP for this B100 blended into all four base diesel fuels at the B5, B10, and B20 levels. In the highest CP base fuel (Fuel C) there is little effect of biodiesel blending on CP, in contrast to the situation for B100 containing SMG. Apparently petroleum wax is the first species to precipitate at temperatures greater than or equal to -16.5°C in this fuel for blends with saturated FAME content up to 3 wt%. For the lower CP diesel fuels, saturated FAME does increase CP, likely because of lower solubility at the lower temperatures of these CP experiments.

In some respects, these results are counter to industry assumptions and should lead to improved strategies for wintertime biodiesel blending. In particular, both the dominant effect of SMG content on blend CP and the solvency effect of biodiesel are not widely appreciated.

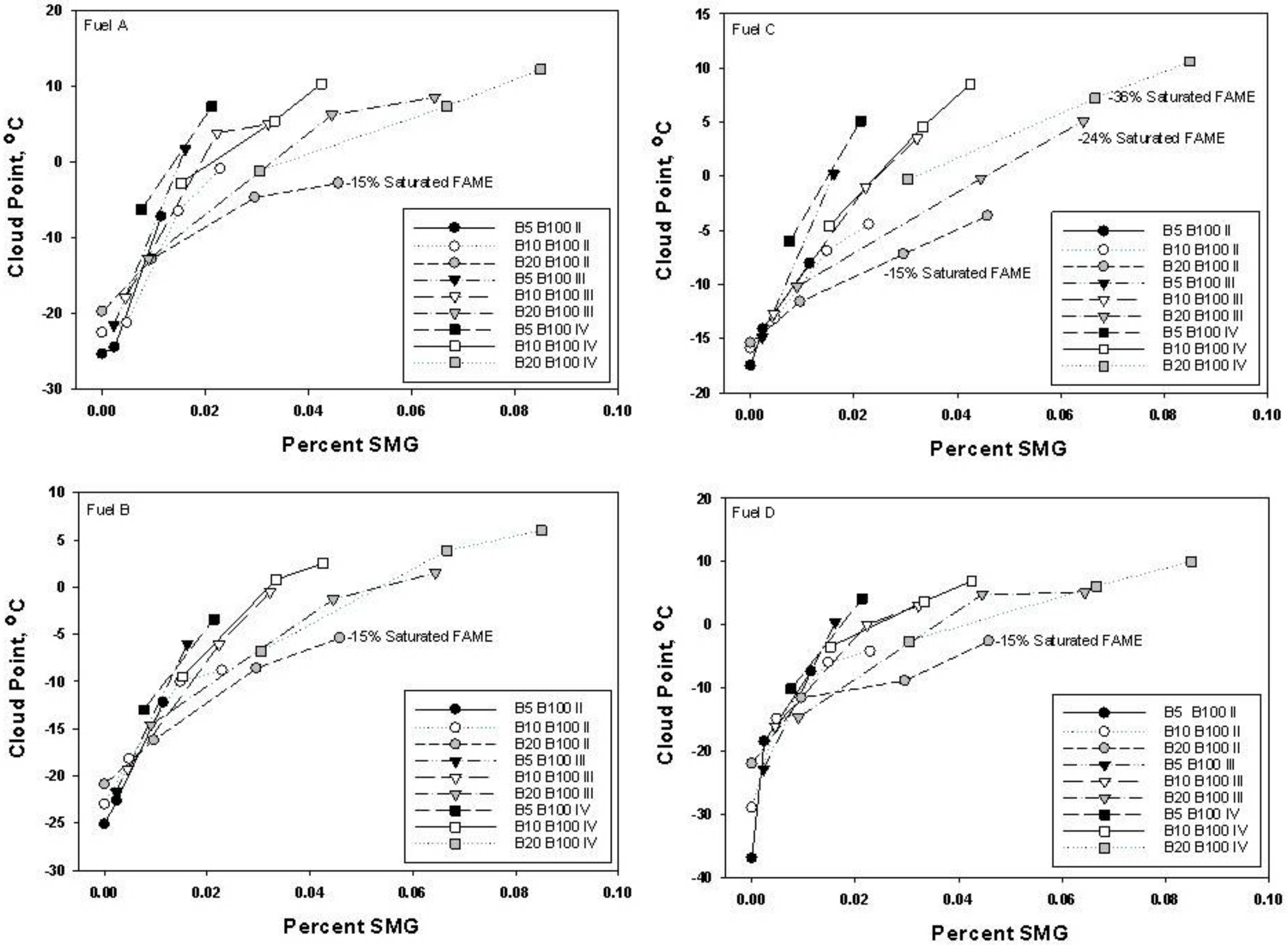

FIGURE 2. Effect of blend SMG content on CP for several B100 blended in to Fuels A-D.

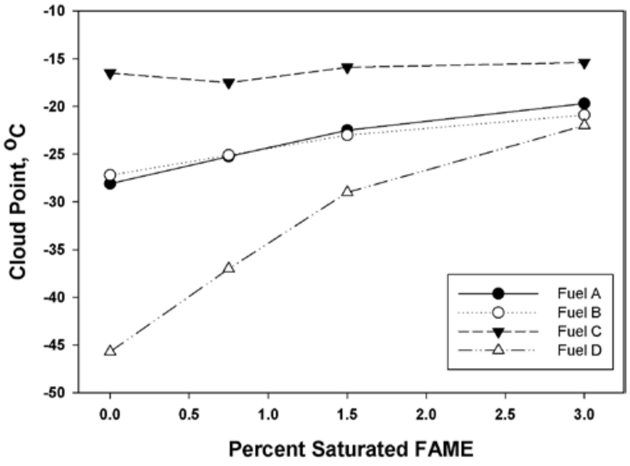

FIGURE 3. Effect of percent saturated FAME (B100 II as-received) on the CP in diesel fuels A-D.

CONCLUSIONS

- SMG content has a large effect on the CP of biodiesel blends. Unexpectedly, this effect is significantly greater than that of saturated FAME content, even though concentrations are two orders of magnitude lower.
- At fixed SMG level, increasing the biodiesel content lowers CP because of increased solubility of SMG.
- Petroleum diesel fuel CP and aromatic content have much smaller effects on CP than the factors associated with biodiesel content.

REFERENCES

1. http://www.eia.gov/totalenergy/data/monthly/query/mer_data_excel.asp?table=T10.04, Accessed on November 27, 2012.

2. Chupka, G.M., Yanowitz, J., Chiu, G., Alleman, T.A., McCormick, R.L. "Effect of Saturated Monoglyceride Polymorphism on Low-Temperature Performance of Biodiesel" *Energy Fuels*, **2011**, *25*(1), 398-405.

3. Chupka, G.M., Fouts, L., McCormick, R.L. "Effect of Low Level Impurities on Low-Temperature Performance of Biodiesel" *Energy Environ. Sci.*, **2012,** *5* 8734-8742.

4. Vippagunta, S.R., Brittain, H.G., Grant, D.J.W., "Crystalline solids" *Advanced Drug Delivery Reviews*, **2001**, *48*(1), 3-26.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Chupka, G.M., Fouts, L., Lennon, J., Alleman, T.L., Daniels, D., McCormick, R.L. "Saturated Monoglyceride Effects on Low-Temperature Performance of Biodiesel Blends" submitted.

2. Chupka, G.M., Fouts, L., McCormick, R.L. "Effect of Low Level Impurities on Low-Temperature Performance of Biodiesel" *Energy Environ. Sci.*, **2012,** *5* 8734-8742.

3. McCormick, R.L., Chupka, G.M., Alleman, T.L. "Biodiesel Cold Weather Performance Research" presented to the National Biodiesel Board Technical Committee via internet, May 31, 2012.

4. McCormick, R.L, Chupka, G.M. "Biodiesel, Cold Weather, and Polymorphic Phase Transformation" presented at Oklahoma State University, Department of Chemical Engineering, April 17, 2012.

5. McCormick, R.L, Chupka, G.M. "Biodiesel, Cold Weather, and Polymorphic Phase Transformation" presented at Colorado State University, Department of Mechanical Engineering, April 6, 2012.

6. Chupka, G.M., Chiu, G., McCormick, R.L. "Effect of Saturated Monoglyceride Polymorphism on Low-temperature Performance of Biodiesel and Biodiesel Blends" presented at Biodiesel Technical Workshop, Kansas City, MO, November 1, 2011.

IV.4 New Fuels and Lubricants Properties, Emissions, and Engine Compatibility Assessment

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Objectives

- Implement analytical methods for characterizing the combustion products from conventional and advanced combustion in order to further elucidate combustion properties of biofuels and other alternative fuels.
- Identify fuel properties and specific combustion products that may limit the implementation of biofuels and other alternative fuels.

Fiscal Year (FY) 2012 Objectives

- Improve gas chromatography – mass spectrometry (GC-MS) methods for ultra-low biofuel emissions in vehicle and engine exhaust.
- Investigate the biofuel contribution to the organic fraction of engine exhaust particulate matter (PM) emissions.

Accomplishments

- Developed a trace detection method for carbonyls, such as formaldehyde and acetaldehyde, which has a detection limit of less than 10 ppb in raw engine exhaust.
- Developed a thermal analysis of soot utilizing state-of-the-art thermal/pyrolysis GC-MS that has a 10x improvement in sensitivity over conventional solvent extraction methods.
- Developed a method for determining the total acid number for a highly polar organic matrix relevant to pyrolysis-derived biofuels.

Future Directions

- Conduct analyses with capillary electrophoresis mass spectrometry of inorganic and organic acid anions in exhaust condensates.
- Evaluate soot derived from non-petroleum-based fuel engine combustion for aromatic acids and anhydrides.

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INTRODUCTION

One of the challenges for analysis of any fuel in the diesel range and the corresponding combustion products is the semi-volatile nature of the compounds that make up the fuel. Semi-volatile compounds adsorb readily to surfaces, including PM surfaces. Consequently, analysis methods for these compounds generally use large amounts of hazardous solvents and have poor analytical recovery efficiencies, in particular for the heavier, partially-oxidized aromatic compounds. We report here on a new ORNL capability which can be used to directly transfer organic compounds from soot and other solids to the GC-MS. A comparison between solvent extraction and thermal desorption of organic compounds from soot samples is presented.

Aldehydes, and other unwanted combustion by-products, are readily oxidized to CO_2 by active three-way and oxidation catalysts, as well as diesel particulate filters. With recent advancements in aftertreatment technologies, the levels of these pollutants have decreased such that the trace-level analysis of many combustion by-products has become very difficult. The detection and quantification of carbonyl compounds such as aldehydes, which are formed during the oxidation of residual fuel species, is important not only for understanding the impact of the new technologies on ambient air, but also in understanding efficient low-temperature combustion mechanisms. One particular concern is the amount of aldehyde emissions produced during extended idling period in which the temperature of the exhaust may not be hot enough for the aftertreatment to work correctly. Current methods for the quantification of aldehydes which use a derivatization method, followed by high-pressure liquid chromatography-ultraviolet detection, cannot meet the trace-level analytical requirements of current engines. Last year, we reported on a new ORNL capability, which can be used to identify and quantitate aldehydes using high pressure liquid chromatography-ultraviolet detection-electrospray mass spectrometry. We report here on a new sample preparation technique, which allows the detection of less than 150 ng aldehydes collected.

Another technical area addressed this year was related to the quantitation of inorganic and organic acids, the total acid number (TAN). During the conversion of biomass to biofuel via the pyrolysis of biomass, a significant concentration of acids are formed, a fraction of which can remain in the fueld. The acid fraction is an important factor in determining the corrosivity of the py-oil, which plays a role in the design and materials requirements of aof fuel systems pyrolysis system. Previous attempts at determining the TAN value using a standard ASTM International method (D664) had been unsuccessful. ASTM D664 utilizes sufficiently non-polar carrier solvents to inhibit miscibility with raw and partially treated pyrolysis oils. The discrepancy between the two measurements may become more problematic for understanding the composition of pyrolysis oils, since the organic acid fraction is often higher for py-oil than mearsuredmeasured by the conventional TAN method. In the studies described below, methods were developed by our group to help understand how to achieve a better TAN value.totalacid number

APPROACH

To develop a single-shot thermal analysis of a soot sample, a comparison study was completed using subsamples from four 1-mg soot samples collected from a surrogate exhaust gas recirculation cooler tube. The solvent-extracted samples were analyzed by a direct injection method. The method was a 2-µl injection made in splitless mode and separated using a capillary column (Restek RXi-5MS 30 m, 350-µm id, 0.25-µm film). The gas chromatograph's temperature program was an initial temperature 40°C for 3 min then ramped from 40-320°C at 6°C per min at held at 320°C for 5 min. The compounds were analyzed by a mass spectrometer, which was scanned from 35 to 550 daltons at a 1-s scan rate.

During recent research on the organic extraction of non-petroleum-based fuel PM emissions, a problem arose with the interferences of non-polar compounds, such as fuel species, with the separation of aromatic anhydrides and aromatic carboxylic acids when using the capillary electrophoresis method. The solution to this problem was the implementation of a multi-shot pyrolysis injector (Frontier Laboratories, Ltd model EGA/PY-3030D) coupled to a GC-MS. This system allows the smaller more volatile compounds to be thermally removed from the soot and analyzed before the less volatile compounds are removed and analyzed thus reducing the complexity of the analysis. Also, the solvent free extraction of organic compounds from soot shortens the total analysis time and cost. For this study, the thermal analysis of the soot sample was conducted by purging the sample with helium for 30 sec then thermally desorbing it at 300°C. The desorbed compounds were then transferred into the GC-MS. and analyzed using the same GC-/MS conditions as described above.

For the trace-level carbonyl analysis, a new sample preparation step was developed. To determine the efficacy of the preparation, a comparison study was completed using aldehyde standards derivatized with di-nitrophenyl hydrazine (DNPH). The prepared standards were first dried in a 50°C water bath. The dried sample was then washed using a water/hexane (50:50) solution. This step was found to be necessary to remove the large amount of un-reacted derivatization agent (DNPH), which elutes from the sample cartridge along with the analytes. If the excess derivatization agent is not removed, its concentration is high enough to hinder the separation and detection of the analytes. The DNPH will remain in the aqueous half of the wash, and the analytes will partition into the hexane. The hexane solution is then dried, and the sample was dissolved in 100 µl of acetonitrile. The liquid chromatograph method was as follows: a 20-µl injection made onto a Restek AK column (150 mm, 2 mm) and the separation was completed using a binary gradient method of acetonitrile/water. The eluent was passed into the electrospray mass spectrometer, which was scanned, from 207 to 315 daltons at a 1-s scan rate.

The current TAN method (ASTM D664) designed for petroleum products uses non-polar solvents. Pyrolysis oil is not sufficiently miscible with the solvents. The new method developed to attain TAN values of hydrophilic bio-oils, specifically pyrolysis oils, uses the combination of an aqueous solvent system and ultrasonically-enhanced extraction to remove the acids from the sample. The extract is then divided into two aliquots; one is titrated with an aqueous base solution to pH = 11, and then assayed for inorganic acid anions, formate, and acetate. This aliquot forms the basis for the TAN value. The second aliquot is acidified and then extracted with a non-polar solvent and the organic acids are speciated with GC-MS to better evaluate the species contributing to corrosivity. Table 1 illustrates that the modified TAN methods is able to detect significant acidity in a pyrolysis oil that had been analyzed previously by ASTM D664 at a commercial laboratory with no result.

RESULTS

Figure 1 shows a small section of the chromatogram from the solvent chromatogram of results of the thermal desorption ramp of the 1-mg soot sample. Table 1 shows the 10X improved in area counts for four common oxidation products that condense on the soot particles. Thus, the increased sensitivity of this new method allows smaller, more specific, samples to be collected on engine system surfaces as well as from the exhaust. In addition, the new method eliminates the time and expense of solvent extraction.

Figure 2 is the reconstructed ion chromatograms for a 150-ppb standard mixture of aldehyde-DNPH subjected to the concentration procedure described above for trace-level carbonyl analysis. This procedure results in a 10-fold concentration, making it comparable in mass injected (30 ng) to a conventionally-prepared 1.5-ppm standard (30 ng injected on-column). Table 3 shows the recovery of the control compared to a standard of the same relative concentration. It is notable that a control solution, at 150 ppb, was prepared via the washing and selective pre-concentration method described, and it produced response comparable to that of an untreated control solution at ten-fold the concentration, i.e., 1,500 ppb. To achieve this enhancement, the significant background of unreacted DNPH present in these samples was removed via the proscribed washing and extraction method described above and developed expressly to address very low concentrations of aldehydes and ketones. Through this series of alternating organic-aqueous washes and sample concentration steps, the difference in solubility of the derivatized product

TABLE 1. A comparison of information available upon modifying the established ASTM standard for acidity of petroleum products to better accommodate the increased hydrophilicity of pyrolysis oil liquids.

Method	Test	Titrant	Titration Solvent	Result
ASTM D 664 (Commercial lab)	Total Acid Number	Potassium Hydroxide	Isopropanol/ Toluene	<0.01 mg KOH/g
ORNL ModTAN	Total Acid Number	Potassium Hydroxide	Water	79.8 mg KOH/g

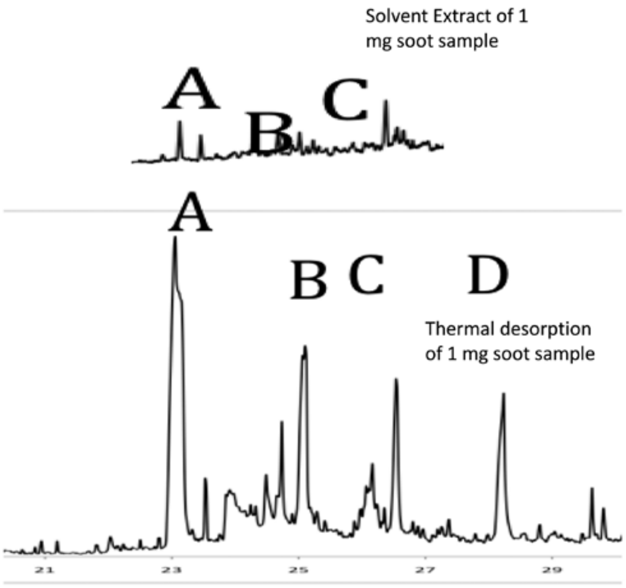

FIGURE 1. A comparison of chromatographs for solvent extract from 1 mg of soot and the direct thermal desorption of 1 mg of the same soot. Note that the signal-to-noise ratio is about 10X higher for the thermal desorbed sample and that compound D is not illustrated on the solvent extract sample. Compounds are typical oxygenated polycyclic aromatic hydrocarbons that are difficult to remove. A = 1,8 naphthalenic anhydride; B = 1-H phenalen-1-one; C = 2, 3 naphthalenedicarboxylic acid; D = 3-hydro-1, 8 naphthalenic anhydride.

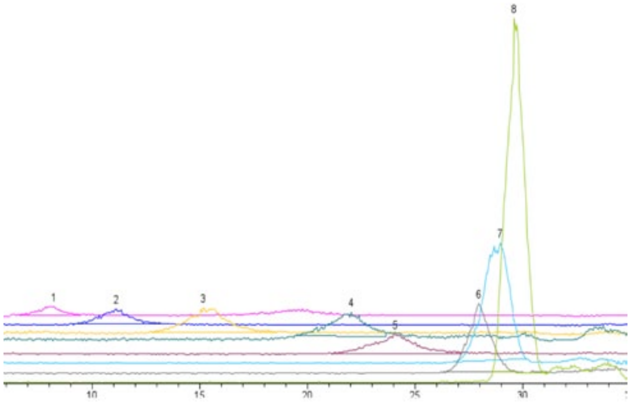

FIGURE 2. The chromatograph of 150-ppb aldehyde-DNPH standard after trace analysis preparation. 1) formaldehyde, 2) acetaldehyde, 3) acrolein, 4) unsaturated C4 aldehydes, 5) saturated C4 aldehydes, 6) benzaldehyde, 7) hexaldehyde, 8) tolualdehyde.

TABLE 2. The comparison of area counts for the thermal desorption/GC-MS analysis of a 1-mg soot sample to the direct injection/GC-MS analysis of a solvent-extracted 1-mg soot sample.

Label	Compound Name	Area Counts for Thermal Desorption GC-MS method	Area Counts for solvent extraction GC-MS method	Enhancement Percentage
A	1,8 naphthalenic dianhydride	245,438	25,703	954%
B	1-H phenalen-1-one	336,778	42,788	796%
C	2,3 naphthalenedicarboxylic acid	3424	291	1176%
D	3-hydro-1,8 naphthalenic dianhydride	189,569	23,148	818%

TABLE 3. The area counts for six aldehydes in a dilute standard, subject to the trace-level carbonyl analysis method, compared with the area counts in a standard solution of the same compounds.

Compound	Area Counts for a dilute standard concentrated to 30 ng injected	Area counts for a standard 30- ng injection	Recovery percentage (%)
formaldehyde	591,040	700,391	84
acetaldehyde	1,394,884	1,745,581	82
saturated C4 aldehydes	2,407,961	3,529,687	68
benzaldehyde	4,797,230	6,544,422	73
hexaldehyde	9,973,956	13,421,927	76
tolualdehyde	20,627,935	22,592,759	91

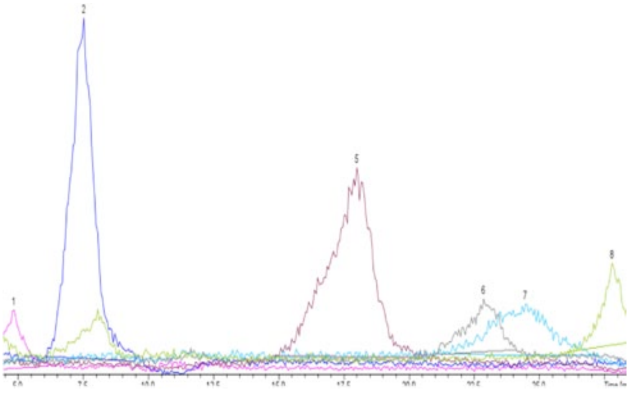

FIGURE 3. The chromatograph of a dilute exhaust sample, derivatized with DNPH, from the cold start and 30 minute idle of a model year 2011 Class 8 truck. 1) formaldehyde, 2) acetaldehyde, 5) saturated C4 aldehydes, 6) benzaldehyde, 7) hexaldehyde, 8) tolualdehyde.

complex versus the parent chromaphore was exploited. Thus, the increased sensitivity of this new method allows smaller, more specific, samples to be collected from the exhaust. In addition, the new method eliminates the time and expense of solvent extraction.

Advanced engine and aftertreatment development requires ever-greater sensitivity to facilitate the characterization of emissions speciation and performance. Figure 3 demonstrates the need to have analytical methodology capable of extremely low detection limits for state-of-the-art engines. Figure 3 shows the aldehydes recovered from the exhaust of a model year 2011 Class-8 truck during cold start and idle. Even after a thirty-fold concentration relative to the conventional collection and extraction, the detected responses still fall near the low-end of the calibration range, and represent a raw exhaust concentration of 6.2 ppb (benzaldehyde) to 500 ppb (acetaldehyde).

CONCLUSIONS AND FUTURE EFFORT

As combustion regimes and emissions control technologies improve to meet tightening regulatory standards and higher efficiency goals, it is critical to have the capability to measure exhaust constituents at low levels. In addition, novel fuel and lubricant technologies result in new combustion products that are not measured with conventional methods. The characterization methods developed under this project have been proven to detect very recalcitrant exhaust products that are relevant to fuels combustion understanding, emissions control function, and materials compatibility.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Samuel A. Lewis, Sr., John M. E. Storey, C. Scott Sluder, and Teresa L Barone. “Chemical Speciation of Soot using Thermal Desorption/ Pyrolysis Gas Chromatography/ Mass Spectrometry”, presented at Directions in Engine-efficiency and Emissions Research Conference (DEER) 2012.

2. James R.Kieser, Michael Howell, Raynella M. Connatser, and Samuel A. Lewis, “Corrosivity And Composition Of Raw And Treated Pyrolysis Oils” presented at TAPPI PEERS Conference, 2012.

3. Samuel A. Lewis, Sr., John M. E. Storey, Raynella M. Connatser, Jeremy Johnson, Doh-Won Lee, and Josias Zietsman. “Trace level Air Toxic Detection in Late-Model Heavy-Duty Trucks” accepted for presentation at 2013 CRC Mobile Source Air Toxics Workshop, 2013.

IV.5 Mid-Level Ethanol Blends Vehicle Aging Program

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DOE Technology Development Manager:
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Objectives

- Determine effects of mid-level ethanol blends – blends up to 20% ethanol in gasoline – on legacy vehicle emissions and emissions durability when aged with a dedicated fuel blend.
- Enable informed decision-making regarding Clean Air Act waiver application for increased ethanol in gasoline.

Fiscal Year (FY) 2012 Objectives

Wrap up program and publish results from vehicle studies.

Accomplishments

Published final report and several SAE International papers.

- Final Report on vehicle aging study published 2/2012.
- SAE Journal Paper on nonmethane organic gas emissions published 4/2012.
- SAE Journal paper on analysis of engine compression and leakdown measurements published 12/2011.
- SAE Journal paper on malfunction indicator lamp illumination published 12/2012.
- SAE Paper on lubricating oil consumption to publish 4/2013.

Future Directions

Program complete.

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INTRODUCTION

The United States' Energy Independence and Security Act (EISA) of 2007 calls on the nation to significantly increase its production of renewable fuels to meet its transportation energy needs [1]. The law established a new renewable fuel standard that requires 36 billion gallons of renewable fuel to be used in the on-road vehicle fleet by 2022. Given that ethanol is the most widely used renewable fuel in the United States, ethanol—both from corn and from cellulosic feedstocks—will likely make up a significant portion of the new renewable fuel requirements. The vast majority of ethanol currently used in the United States is blended with gasoline to create E10—gasoline with up to 10 volume percent (vol%) ethanol.

In light of projected growth in ethanol production, as well as the new renewable fuel standard, most analysts agree that the E10 market was essentially saturated in 2012. The U.S. produced over 13 billion gallons of ethanol in 2010 and 2011, and increased exports from 400 million gallons in 2010 to nearly 1 billion gallons in 2011. Although the U.S. Department of Energy (DOE) remains committed to expanding the flexible-fuel vehicle fuel infrastructure, that market will not be able to absorb projected volumes of ethanol in the near term. Given this reality, DOE and others have been assessing the viability of using mid-level ethanol blends (blends of gasoline with up to 20 vol% ethanol) in conventional vehicles as one way to potentially accommodate growing volumes of ethanol, thereby displacing petroleum and helping the country comply with EISA.

APPROACH

This work is a follow-on effort to previous DOE [2] and Coordinating Research Council (CRC) [3] studies to investigate the effects of aging vehicles with mid-level ethanol blends. These studies identified several high-sales-volume vehicle models that did not apply long-term (or learned) fuel trim (LFT) at open-loop conditions, and thus produced hotter exhaust and catalyst temperatures at full power operation when operated with ethanol blends compared to ethanol-free gasoline. Based on the literature, there was concern that increasing the ethanol fraction in gasoline for these vehicles could result in increased emissions over time [4,5]. Because of this concern, DOE supported the development and execution of a catalyst durability study unprecedented in size and scope.

Vehicle testing was conducted at three laboratories under subcontract to Oak Ridge National Laboratory and the National Renewable Energy Laboratory. Vehicles were aged using the Standard Road Cycle (SRC), the official Environmental Protection Agency (EPA) driving cycle used for aging whole motor vehicles for exhaust system durability [6], shown in Figure 1. Southwest Research Institute® (SwRI®, San Antonio, TX) and Environmental Testing Corporation (ETC, Aurora, CO) aged vehicles using the SRC on mileage accumulation dynamometers, while Transportation Research Center (TRC, East Liberty, OH) ran the SRC on their 7.5 mile test track.[1] Vehicles on the mileage accumulation dynamometers are shown in Figure 2, while Figure 3 shows the TRC test track.

Vehicles from the six largest vehicle manufacturers were represented in the study, including cars and light trucks from General Motors, Ford, Chrysler, Toyota, Honda, and Nissan. Eighteen Tier 2 vehicle models (i.e., vehicle models built to meet EPA's Tier 2 emission standards) from model years 2005 through 2009 and eight pre-Tier-2 vehicle models from model years 2000–2003 were aged using the SRC protocol. Emissions were tested periodically throughout the program.

Emissions tests on all vehicles were conducted using emissions certification gasoline (E0), and splash blends of this same fuel with denatured ASTM D4806 ethanol to produce "certification grade" E10, E15, and E20. Vehicle aging was conducted with retail gasoline (RE0), and this same fuel splash blended with denatured ASTM D4806 ethanol to produce RE10, RE15, and RE20; the "R" denoting retail gasoline.

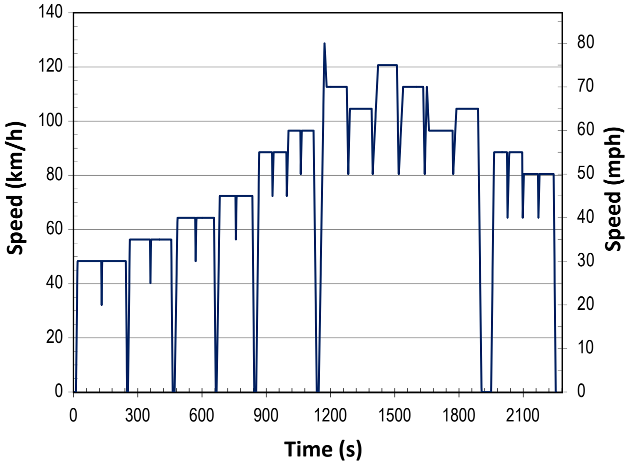

FIGURE 1. Standard Road Cycle for vehicle aging.

FIGURE 2. Vehicles on mileage accumulation dynamometers at ETC (top) and SwRI® (bottom).

FIGURE 3. Test track at TRC.

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[1] All vehicles were aged using the SRC with the exception of the 2006 Nissan Quest vehicle set, which was switched to a series of steady-speed laps on the track part way through aging. DOE directed this change to accelerate mileage accumulation.

Vehicles were purchased in matched sets of three or four vehicles with matching model year, engine family, evaporative emissions control family, powertrain control unit calibration, transmission, wheel and tire size, etc. For vehicle sets of four matched vehicles, one vehicle was aged with each of four fuels: RE0, RE10, RE15, and RE20. Five vehicle sets included all four fuels. The remaining vehicle sets of three matched vehicles omitted the RE10 vehicle (using only RE0, RE15, and RE20).

Vehicles were emissions tested using the Federal Test Procedure (FTP) at three or four points during the aging program; at the start of mileage accumulation, at one or two mid-mileage points in the program, and at the end of mileage accumulation. All vehicles of a given set were driven the same distance in the test program. The aging and emissions testing program was completed in 2011 and a final report published in 2012 [7]. Follow-on efforts in 2012 involved more detailed analysis of data from the program and preparation and publication of several technical paper/journal articles. Follow-on studies included analysis of engine compression and leakdown data [8], characterization of nonmethane organic gas emissions [9], determination of malfunction indicator lamp (MIL) threshold due to increased use of fuel ethanol in legacy vehicles [10], and analysis of lubricating engine oil consumption from the test vehicles [11].

At each emissions test interval the engine compression and leakdown were measured using established procedures. These measurements were conducted to detect any significant changes in the combustion cylinders throughout the program. Analysis of these results was published in a journal paper [8].

During the vehicle aging program, a method was developed to estimate nonmethane organic gas emissions (NMOG) based on nonmethane hydrocarbon (NMHC) emissions. Measuring and calculating NMHC emissions is straightforward and does not require comprehensive exhaust speciation, while calculation of NMOG requires more complex and detailed measurements. Some of the required NMOG measurements are often delayed compared to "test day" measurements, or can even be lost due to sampling malfunctions, despite an otherwise successful vehicle test. A journal paper was published detailing this estimation technique [9].

A follow-on study was developed to determine the MIL threshold for a subset of the test vehicles. Increasing the fuel ethanol content increases the fuel's oxygen content and decreases the fuel's energy density. One potential issue with increasing the ethanol content is the possibility of exceeding the range of authority for the engine control module to regulate the air/fuel ratio to stoichiometric conditions. EPA regulations require that the vehicle illuminate the MIL (or "check engine" display) to draw attention to a potential emissions control failure. Due to concern over nuisance MILs in vehicles fueled with mid-level blends, the study determined the MIL threshold for a subset of the test vehicles [10].

Excessive lubricating oil consumption can contribute to emissions failures due to poisoning of the exhaust catalyst; as the objective of the vehicle aging program was to determine whether the ethanol blends affected the vehicles' emissions durability, engine oil was weighed at each oil change such that oil consumption could be tracked during the program. In this way, if a vehicle displayed excessive emissions at the end of the program, the cause of the emissions failure could be appropriately attributed to the test fuel or perhaps the excessive oil consumption [11].

RESULTS

All Tier 2 vehicle emissions results for the E0 and E15 vehicles were acquired before the end of FY 2010 and made available to EPA and industry stakeholders. With the exception of four E20 vehicles, all remaining vehicle tests were completed in January 2011. Based on results of the DOE program, EPA granted partial approval to a waiver request for E15, allowing it in 2001 and newer vehicles, but denying its use in non-automotive engines such as lawn and garden equipment, snowmobiles, marine applications, etc. [12,13]. In 2012, ETC published a report detailing results from the remaining E20 vehicles tested at ETC [14].

Data analysis on the vehicle emissions data was completed in FY 2011 and the program has been detailed in a comprehensive report [5]. Median change of fuel economy and emissions with the ethanol blends, relative to E0, are shown in Figures 4 and 5 for results at start of test. Range bars show the interquartile range (25th to 75th percentile). These results are largely consistent with findings from the first DOE mid-level blends vehicle study [2,15]. Statistical analysis of the data showed that emissions increased with increasing mileage accumulation, as expected. Relative to aging with RE0, there was no fleetwide differential effect noted for aging with ethanol blends.

In addition to the emissions testing throughout the program, powertrain component inspections were performed on six of the vehicle sets at SwRI® at end of test (18 vehicles). Results for the E0 and E15 vehicles were completed by 9/30/2010 with results compiled in a draft report and pre-published in the EPA docket. Results for the E20 vehicles from those same vehicle sets were completed and a final report was published in November 2010 [16]. Powertrain component inspection included an evaporative emissions system leak check, evaporative canister working capacity test, cam lobe measurement, valve seat width and valve surface contour,

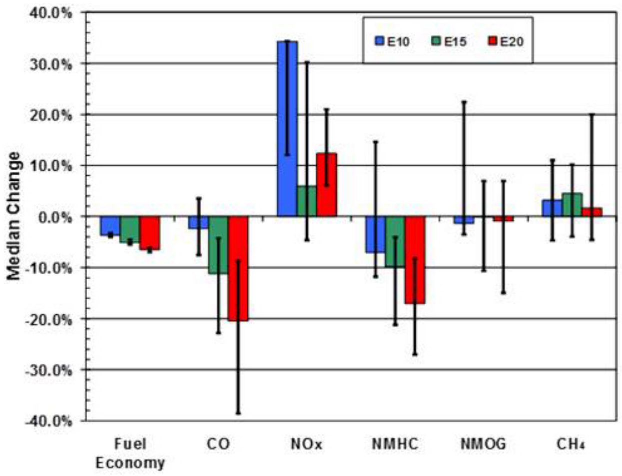

FIGURE 4. Median change in fuel economy and CO, NOx, NMHC, NMOG and CH$_4$ emissions relative to E0. Range bars show interquartile range (25th to 75th percentile). Results for Federal Test Procedure at start-of-test.

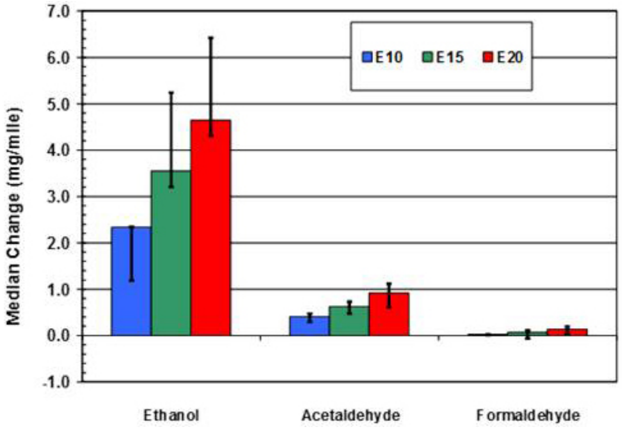

FIGURE 5. Median change in ethanol, acetaldehyde, and formaldehyde emissions relative to E0. Range bars show interquartile range (25th to 75th percentile). Results for Federal Test Procedure at start-of-test.

valve stem height, intake valve deposit mass, engine oil analysis, fuel injector flow measurements, fuel pump flow measurement and fuel pump disassembly and inspection. Vehicles aged with ethanol blends were found to have higher intake valve deposit mass. Although retail top-tier gasoline[2] was used for the aging fuels, the detergent additive concentrations were not adjusted in consideration of adding ethanol to the fuel, thus the dilution of the additive package is believed to be the contributor to the higher intake valve deposit mass.

Analysis of the compression and leakdown data from the vehicle program suggest that the existing measurement techniques are not well suited to monitor incremental changes in cylinder leakage due to normal aging (such as on the SRC). Leak-down and compression tests are adequate, in their present form, to identify and diagnose power cylinders with gross failures. There were no correlations found between compression and leakdown nor any clear trends showing changes of either measurement with increased mileage accumulation. These conclusions result from the fact that the majority of the leak-down results from tests conducted during the mileage accumulation campaign could not be classified as significant changes, regardless of whether the change was positive or negative in nature. For more detail on this analysis, see reference 8.

The NMOG estimation technique developed for this program showed that the NMOG/NMHC ratio is a function of the ethanol blend level. Given an ethanol blend level and a valid NMHC emission measurement, the technique allowed for NMOG to be estimated for test cases in which all necessary exhaust constituent measurements were not available. Figure 6 shows the NMOG estimation results versus the measured results. Over 95% of the estimates have errors of 1.5 ± 7.4 mg/mile (for reference, the Tier 2, Bin 5 NMOG standard is 90 mg/mile) [9].

The MIL study showed that LFT threshold values for the 22 vehicles studied ranged from 18% to 38%. Using statistical information about mean values of LFT and LFT variability from a recent CRC in-use vehicle study [17], estimates of MIL activation frequency were developed. Figure 7 shows the estimated MIL rates for the 22 vehicles (number of occurrences per million vehicles). The bars show the range of MIL occurrences expected, based on two estimates; the more conservative estimate results in more MIL occurrences. For example, per one million units of vehicle model number 11, between 117 and 12,100 vehicles are projected to experience MIL illumination with E15 fuel. For the bars that extend to the bottom of the chart, the less

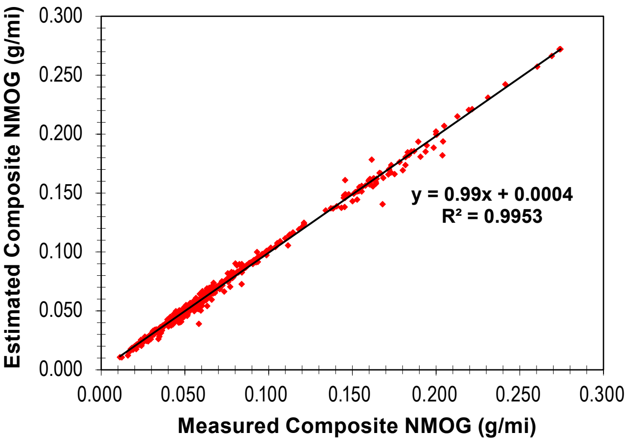

FIGURE 6. Estimated NMOG versus measured NMOG.

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[2] Top-tier gasoline contains more deposit-control additives than the EPA minimum requirements (http://www.toptiergas.com/).

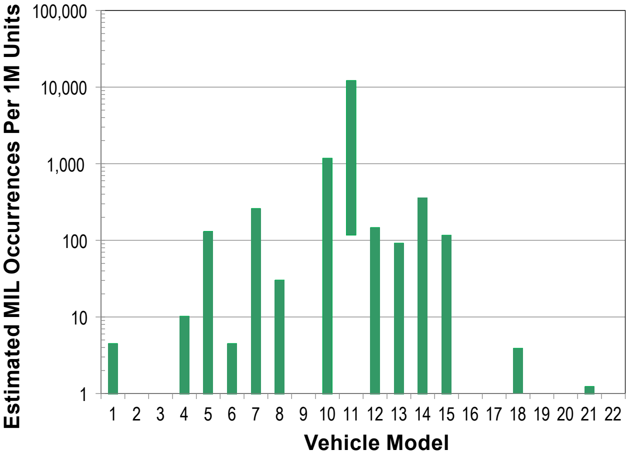

FIGURE 7. Estimated MIL illuminations with E15 fuel.

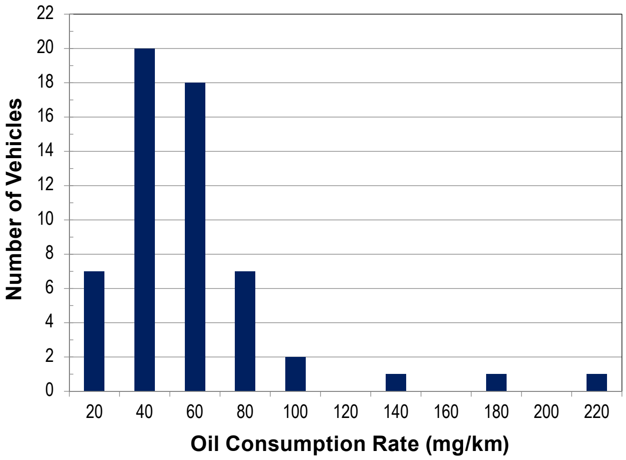

FIGURE 8. Oil consumption rate histogram for all vehicles.

conservative estimate is that less than one vehicle per million units will experience a MIL. For cases with no bar shown, both estimates are below 1 unit per million. For more detail on the MIL study, please see reference 10.

Oil consumption rates for the matched sets of properly functioning vehicles aged on the SRC in this program ranged from 0.015 to 0.090 g/km. Figure 8 shows a histogram of the oil consumption rates for the vehicles. The three outliers to the right of the chart are vehicles with known oil problems. Statistical analysis of the data found no statistically significant differences in oil consumption attributed to the ethanol level in the aging fuel. Further, no correlations between oil consumption rate and emissions were noted. For more detail on the oil consumption analysis, please see reference 11.

CONCLUSIONS

Examination of powertrain components from Tier 2 vehicles aged with RE0, RE15 and RE20 showed no signs of increased corrosion or wear from the use of ethanol blends compared to gasoline. Vehicles aged with ethanol blends did have higher intake valve deposit mass, however detergent additive concentrations were not adjusted in consideration of adding ethanol to the fuel [16].

Statistical analysis of emissions test results determined the following:

- Aging vehicles on the SRC increased emissions over time, as expected.
- Aging with ethanol blends did not affect emissions changes over time differently than aging with ethanol-free gasoline.
- Whether vehicles applied LFT under open-loop conditions did not affect emissions and fuel economy results.
- Addition of 10% to 20% ethanol to certification gasoline caused the following general fleetwide changes in measured tailpipe emissions and fuel economy compared to gasoline. (These immediate effects are largely consistent with findings of the DOE V1 study [2,15].)
  - Median CO emissions decreased by 0.03 to 0.14 g/mile.
  - Median NMHC emissions decreased by 0.002 to 0.008 g/mile.
  - Median oxides of nitrogen emissions increased by 0.001 to 0.004 g/mile.
  - Median ethanol emissions increased by 2.3 to 4.6 mg/mile.
  - Median acetaldehyde and formaldehyde emissions increased slightly (by less than 1 mg/mile).
  - NMOG and methane emissions were largely unchanged.
  - Fuel economy was decreased by about 3% to 7%, consistent with the energy density of the test fuel.

Several follow-on studies have been published. In summary:

- Compression and leakdown measurements, in their current form, are not well-suited to monitor incremental changes in cylinder leakage due to normal aging on the SRC.

- The NMOG/NMHC ratio for vehicles is a function of the ethanol blend level of the fuel. An effective method for estimating NMOG when only NMHC and ethanol level are known has been developed.
- Threshold values of LFT at which MILs are illuminated vary by vehicle model and manufacturer. Some vehicle models are not expected to illuminate MILs with E15 or E20, while some other more sensitive models will likely have thousands of occurrences per million units.
- Lubricating oil consumption is not correlated with vehicle emissions or the ethanol level in the aging fuel. Oil consumption of properly-functioning modern vehicles on the SRC range from 0.015 to 0.090 g/km.

REFERENCES

1. Energy Independence and Security Act of 2007, H.R. 6, 110th Congress, 2007-2008.

2. K. Knoll, B. West, W. Clark, R. Graves, J. Orban, S. Przesmitzki, T. Theiss, “Effects of Intermediate Ethanol Blends on Legacy Vehicles and Small Nonroad Engines, Report 1 – Updated,” ORNL/TM-2008/117, NREL/TP-540-43543, February 2009.

3. “Mid-Level Ethanol Blends Catalyst Durability Study Screening,” CRC Report No. E-87-1, Coordinating Research Council, Alpharetta, GA, 2009.

4. R. Bechtold et al., *Technical Issues Associated with the Use of Intermediate Ethanol Blends (>E10) in the U.S. Legacy Fleet: Assessment of Prior Studies,* ORNL/TM-2007/37, Oak Ridge National Laboratory, August 2007, available at http://info.ornl.gov/sites/publications/files/Pub7767.pdf.

5. Orbital Engine Company, *Market Barriers to the Uptake of Biofuels Study; Testing Gasoline Containing 20% Ethanol (E20),* Phase 2B Final Report to the Department of the Environment and Heritage, Australia, May 2004.

6. Code of Federal Regulations, 40CFR Part 86, Appendix V.

7. B.H. West, C.S. Sluder, K.E. Knoll, J.E. Orban, J. Feng, “Intermediate Ethanol Blends Catalyst Durability Program,” ORNL/TM-2011/234, February 2012.

8. Sluder, C. Scott, and Brian West, “Limitations and Recommended Practice In the Use of Compression and Leak-Down Tests to Monitor Gradual Engine Degradation,” *SAE Int. J. Engines* 4(3):2767-2777, 2011, doi:10.4271/2011-01-2427, December 2011.

9. Sluder, C. Scott, and Brian West, “NMOG Emissions Characterization and Estimation for Vehicles Using Ethanol-Blended Fuels,” *SAE Int. J. Fuels Lubr.* 5(2):721-732, 2012, doi:10.4271/2012-01-0883, April 2012.

10. Sluder, C. Scott, Brian West, and Keith Knoll, “Investigating Malfunction Indicator Light Illumination Due to Increased Oxygenate Use in Gasoline,” *SAE Int. J. Fuels Lubr.* 5(3):1360-1371, 2012, doi:10.4271/2012-01-2305, December 2012.

11. West, Brian, and C. Scott Sluder, “Lubricating Oil Consumption on the Standard Road Cycle,” SAE Paper 2013-01-0884, April 2013.

12. *Federal Register*/Vol. 75, No. 213/ November 4, 2010/ Notices, “Partial Grant and Partial Denial of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator”.

13. *Federal Register*/Vol. 76, No. 17/January 26, 2011/Notices, “Partial Grant of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent; Decision of the Administrator”.

14. Vertin, Keith, Gerard Glinsky, and Aaron Reek, “Comparative Emissions Testing of Vehicles Aged on E0, E15, and E20 Fuels,” NREL/SR-5400-55778, August 2012.

15. Keith Knoll et al., “Effects of Mid-Level Ethanol Blends on Conventional Vehicle Emissions,” SAE paper 2009-01-2723, SAE International, Warrendale, Pennsylvania, November 2009.

16. B.A. Shoffner, R.D. Johnson, M.J. Heimrich, M.D. Lochte, “Powertrain Component Inspection from Mid-Level Blends Vehicle Aging Study,” ORNL/TM-2011/65, November 2010.

17. “Impact of E15/E20 Blends on OBDII Systems - Pilot Study,” CRC Report No. E-90, Coordinating Research Council, Alpharetta, GA, March 2010.

FY 2012 PUBLICATIONS

1. B.H. West, C.S. Sluder, K.E. Knoll, J.E. Orban, J. Feng, “Intermediate Ethanol Blends Catalyst Durability Program,” ORNL/TM-2011/234, February 2012.

2. Sluder, C. Scott, and Brian West, “Limitations and Recommended Practice In the Use of Compression and Leak-Down Tests to Monitor Gradual Engine Degradation,” *SAE Int. J. Engines* 4(3):2767-2777, 2011, doi:10.4271/2011-01-2427.

3. C. Scott Sluder and Brian H. West, *NMOG Emissions Characterizations and Estimation for Vehicles Using Ethanol-Blended Fuels,* ORNL/TM-2011/461, Oak Ridge National Laboratory, October 15, 2011, available at http://info.ornl.gov/sites/publications/Files/Pub33272.pdf.

4. Sluder, C. Scott, and Brian West, “NMOG Emissions Characterization and Estimation for Vehicles Using Ethanol-Blended Fuels,” *SAE Int. J. Fuels Lubr.* 5(2):721-732, 2012, doi:10.4271/2012-01-0883.

5. Sluder, C. Scott, Brian West, and Keith Knoll, “Investigating Malfunction Indicator Light Illumination Due to Increased Oxygenate Use in Gasoline,” *SAE Int. J. Fuels Lubr.* 5(3):1360-1371, 2012, doi:10.4271/2012-01-2305.

6. West, Brian, and C. Scott Sluder, “Lubricating Oil Consumption on the Standard Road Cycle,” SAE Paper 2013-01-0884, April 2013.

FY 2012 PRESENTATIONS

1. Brian West, et al., "Potential Paths to EISA Compliance," SAE Government Industry meeting, January 25, 2012, available at: http://www.sae.org/events/gim/presentations/2012/brian_west.pdf.

2. Scott Sluder, "NMOG Emissions Characterization and Estimation for Vehicles Using Ethanol-Blended Fuels," SAE World Congress, April 2012.

IV.6 Unconventional Hydrocarbon Fuels

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Kevin Stork

Objectives

- Facilitate the successful introduction of future fuel feedstocks which will help in the reduction of U.S. dependence on foreign oil, while being compatible with future advanced combustion engines.
- Develop analytical approaches correlating fuel component molecular structure to fuel properties and fuel performance.

Fiscal Year (FY) 2012 Objectives

- Facilitate transition of fuels derived from unconventional hydrocarbons into the market by developing a fundamental understanding of ‘fit for service’ properties.
- Develop analytical tools to characterize fuels derived from unconventional hydrocarbons, focusing especially on chemistry-based predictive models to support future advanced combustion/emission technologies.
- Develop the correlations between chemistry-based predictive models and fuel properties established by engine and ASTM International[†] tests that will assist in defining refinery acceptance criteria of the fuel as a blend stock.
- Obtain and analyze biomass pyrolysis oil derived fuels, extending the developed analytical framework to these bio-derived fuels.

Accomplishments

- Completed PNNL report [1] detailing ^{13}C and ^{1}H nuclear magnetic resonance (NMR) sub-structure analyses and assignments for three Fuels for Advanced Combustion Engine (FACE) diesel blends developed under guidance from the Coordinating Research Council (CRC).
- Completed the ^{13}C and ^{1}H NMR sub-structure analyses and assignments for over 20 diesel and renewable fuels of various origins.
- Developed new NMR approaches for identifying structure-property relationships of diesel fuels, including diffusion-ordered spectroscopy (DOSY), as well as two dimensional NMR techniques, such as single-bond proton-carbon correlation (heteronuclear single quantum coherence, or HSQC) and multiple-bond proton-carbon correlation (heteronuclear multiple bond correlation, or HMBC) experiments.
- Obtained initial quantities of a pyrolysis oil and a pyrolysis oil ultra-low sulfur diesel (ULSD) blend, and completed ^{13}C and ^{1}H NMR sub-structure analyses.
- Continued work identifying molecular structures utilizing advanced analytical techniques, e.g., NMR, gas chromatography field ionization mass spectrometry (GC-FIMS) and 2-dimensional gas chromatography (2D-GC) analysis, which are being shown to provide significant correlation with diesel-range fuel lubricity.

Future Directions

- Continue to develop structure-property correlations built upon data obtained from current fuel sets.
- Identify key molecular structure features in unconventional fuels which have the greatest impact on fuel properties and performance.
- Continue to coordinate the interaction with Natural Resources Canada (CanmetEnergy) on analytical correlation of fuel properties and material compatibility investigations.
- Continue collaborative work with members of the CRC’s FACE Working Group and the alternative and surrogate fuels subcommittees.
- Acquire biomass-derived pyrolysis oil samples from disparate sources, having different degrees of upgrading, particularly processed samples with significantly reduced oxygen and acid content, to extend the analysis and correlation chemistry of bio-based fuels.

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[†] Formerly known as the American Society for Testing and Materials.

INTRODUCTION

The objective of this project is to ensure that our chemical knowledge of future, unconventional fuels is sufficient to support advanced combustion engine technology. Future diesel fuels derived from unconventional resources, e.g., upgraded pyrolysis oil, biodiesel, oil sands, or shale oil, can exhibit chemistries and molecular structures significantly different from conventional hydrocarbon resources. Because of strict fungibility requirements for pipeline transporting, unconventional hydrocarbon fuels will possibly be limited to regional areas, resulting in high concentrations of fuels with various combinations of hydrocarbon species entering the fuel market. A preliminary investigation into bulk properties, e.g., cetane, has shown that property-performance correlations based on conventional fuels are unreliable predictors for unconventional fuels.

Chemistry and structural differences that occur with unconventional fuels can result in unpredictable problems with engine and fuel system components, and can impact our understanding of advanced combustion and after-treatment performance. PNNL will work collaboratively with other laboratories in developing a full suite of analyses and engine tests for unconventional fuels, notably upgraded shale oil, upgraded bitumen from oil sands, and upgraded pyrolysis oil. PNNL will develop correlations between NMR data, bulk fuel properties, and ‘fit for service’ performance of these unconventional fuels, e.g., lubricity and seal swell. PNNL will also investigate other infrastructure and material compatibility issues such as cold temperature performance, crankcase oil compatibility and storage stability, where engine performance failures resulting from unexpected adverse performance could be devastating to the introduction of these fuels. The goal is to eliminate industry’s dependence on costly and empirically-derived engine and rig tests which have poor predictive capabilities with regard to material performance with new engine fluids, as well as develop predictive capabilities based upon molecular structure regarding fuel properties and performance.

APPROACH

Renewable and unconventional diesel samples from a variety of sources were obtained through our collaborations with other national laboratories and with Advanced Vehicle/Fuel/Lubricants Committee members as part of our activities with the CRC. Fuels analyzed include representative samples of renewable diesels, commercially available diesels, Fischer-Tropsch diesel, oil sand and shale oil-derived diesels, and pyrolysis oil-derived samples. Also examined were reblends of three FACE diesel fuels.

Based upon our previous experience with shale oil-derived samples, a series of analyses were undertaken with an emphasis on quantitative NMR measurements, and a secondary focus on building new analytical capabilities. New capabilities under development include the use of DOSY; two-dimensional NMR techniques, such as HSQC, and HMBC; and two-dimensional gas chromatography. DOSY is expected to provide diffusional information that is related to the molar volume distributions of the components and is expected to correlate with lubricity, soot formation, kinematic viscosity, and cloud point. Two-dimensional NMR techniques better define average structural components within the fuel and their interrelationships. Better identification of these structural features may also permit superior correlation with cetane number, lubricity, and other properties critical to engine performance. Similarly, two-dimensional gas chromatography provides resolution of the chemical components contained within a fuel sample, which can then be further correlated with fuel properties and performance. To gain full benefit from these analysis tools it will be necessary to: 1) incorporate all analytical data sets into one format to assist advanced engine development and for fuel blending modeling; 2) establish property correlations to ensure engine system compatibilities with existing engines; and 3) expand molecular-based blending models to ensure the transparency of fuels from alternate feedstocks entering into the market. While these analysis techniques are complex, once key parameters are identified, the analyses can be streamlined to select for them.

RESULTS

Through our collaborations with other national laboratories we have successfully validated the use of one-dimensional ^{1}H and ^{13}C NMR as a means of identifying fuel composition (i.e., aromatic, naphthenic, and paraffinic carbons), as well as making substructural assignments (i.e., alkyl-substituted aromatic carbons, methyl and ethyl groups attached to aromatic carbons, *n*-paraffinic carbons, and others). These successes have led to a PNNL report detailing the analysis of three reblended FACE diesel fuels [1], which we expect to be developed into a peer-reviewed publication. Similarly, nearly 20 additional fuels from renewable sources (e.g., pyrolysis oil, algae-derived, plant-derived), unconventional sources (e.g., oil sands, shale oil, gas-to-liquid), and commercial sources, have been analyzed for carbon types and the results of the analyses are expected to be reported in FY 2013. We anticipate using these data as a means of developing structure-property/performance correlations, and continuing our work in refining structure-lubricity correlations.

Building upon our successes with one-dimensional NMR (quantitative ^{13}C and ^{1}H NMR), we have sought NMR techniques that are more discriminating, and have spent the better part of FY 2012 validating the utility of those techniques. Because of the increased complexity of these approaches, it has been necessary to start with simplified fuel systems. Fortunately, two suitable simplified, or "surrogate," fuels have been under development as part of a CRC activity we are participating in, led by Dr. Charles Mueller of Sandia National Laboratories and William Cannella of Chevron [2]. Briefly, the surrogate fuels serving as our models contain eight or more pure chemical components that provide sufficient structural variability to span the NMR spectrum, and have a carbon-type composition selected to match a target diesel fuel unique to each surrogate. Analyses of these fuels assist in validating the utility of our new quantitative approaches by a providing a simplified data set with known parameters, as well as a complementary diesel fuel which each surrogate attempts to mimic.

Figure 1 shows the aromatic region of an HSQC NMR spectrum of the certification fuel surrogate, one of two surrogate fuels, where only three of the eight components have aromatic groups. Figure 2 shows the chemical structures of those three components, as well as the carbon number that corresponds to a peak in the HSQC spectrum. For HSQC spectra, only protons and carbons directly bound to each other are correlated, and the correlation is shown in a two-dimensional plot similar to a topographic map. Carbons without an attached proton do not appear. The critical question being examined was whether the intensity of the correlated peaks could be related to the mole fraction of each of the molecules in the surrogate fuel. Since the surrogate fuel is a mixture of known amounts of each component, this serves as an excellent system for validating the HSQC pulse sequence as a quantitative NMR approach. Table 1 provides a comparison of the calculated mole fraction with the actual mole fraction of each component for the two available surrogate fuels. The calculated values are based upon the peak integration results from the HSQC spectra, similar to Figure 1, and the actual values were measured when the surrogate fuel was mixed. From these results, it is clear that the calculated and actual values are exceptionally close, and are well within the expected precision for quantitative NMR measurements, demonstrating that HSQC spectra can be used quantitatively. Similar results may be obtained for the aliphatic region of the HSQC spectra. We are in

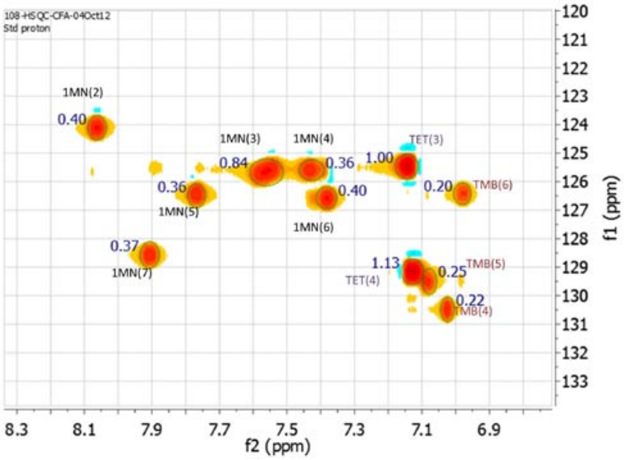
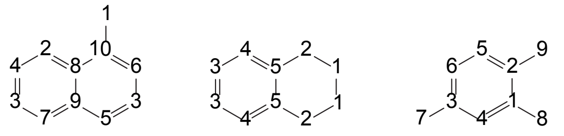


FIGURE 1. Aromatic region of a certification diesel surrogate fuel HSQC NMR spectrum [2]. This two-dimensional NMR spectrum is a contour plot showing the correlation of protons attached directly to carbons of the surrogate fuel components. Each peak has an integration zone showing relative intensity, as well as an assignment to one of three pure components making up the surrogate fuel. Note that each peak corresponds quantitatively to the relative mole fraction of that component in the surrogate fuel, as well as to the ratios of unique carbons within a molecule (see assignments).



(a) 1-methylnaphthalene (1MN)

(b) tetralin (TET)

(c) 1,2,4-trimethylbenzene (TMB)

FIGURE 2. Carbon assignments associated with the surrogate fuel spectrum shown in Figure 1. For example, the #3 carbon in tetralin (TET) has a ^{13}C chemical shift of 125.5 ppm and a ^{1}H chemical shift of 7.15 ppm. While each of these peaks can be individually resolved and integrated in the 1-dimensional ^{13}C NMR because there are a limited number of components, for diesel fuels having many components, this would not be true. Only carbons having chemical shifts in the aromatic region are shown. Note that carbons without attached hydrogen atoms are not observed in HSQC spectra. Note also that numbering associated with naming conventions do not necessarily correlate with numbering associated with NMR assignments.

TABLE 1. HSQC Aromatic Region Integration Results for Two Surrogate Fuels

	Certification Diesel Surrogate		FACE 9A Diesel Surrogate	
Component[a]	Calculated[b] Mole % C	Actual[c] Mole % C	Calculated[b] Mole % C	Actual[c] Mole % C
TMB	7.6	7.5	18.7	18.8
TET	15.1	15.4	11.5	11.3
1MN	14.5	14.4	5.7	5.8

[a] Where TMB is 1,2,4-trimethylbenzene, TET is tetralin, and 1MN is 1-methylnaphthalene.
[b] Calculated from two-dimensional NMR integration results.
[c] Values obtained from mixing the surrogate fuel from pure components.

the process of examining these surrogate fuels using additional two-dimensional NMR techniques such as HMBC (multiple-bond proton-carbon correlation NMR spectroscopy), as well as several other correlation techniques that might provide useful structural correlation information. This work is significant in that two-dimensional NMR spectra are not routinely used to obtain quantitative information, regarding composition of a mixture or for substructural quantitation, and have rarely been used for fuels analyses and then only qualitatively.

We have also applied HSQC to fuels from a variety of sources, including mildly hydrotreated shale oil, shale oil-derived diesel #2, oil sands-derived diesel, and a commercial diesel. We have found that these fuels have many features in common. Figure 3 shows the aromatic region for a commercially available, ultra-low sulfur diesel fuel. As described for the diesel surrogate in Figure 1, the plot is a contour map showing only the single-bond hydrogen-carbon correlation spectrum for this fuel. Substructural features circled in red are major contributing chemical structures held in common for each of the fuels of widely disparate origins, although in differing proportions for each of the fuels. Based on our knowledge gained with the surrogate fuels described above, it is possible to understand the relative contribution of each of these features to each fuel, and make comparisons between the fuels. Additionally, from the perspective of identifying key structure-property correlations, these comparisons may become important, allowing the impact of common structures and less common structures to be factored and assessed independently. We expect that these relationships will be critical to understanding and predicting fuel properties and performance.

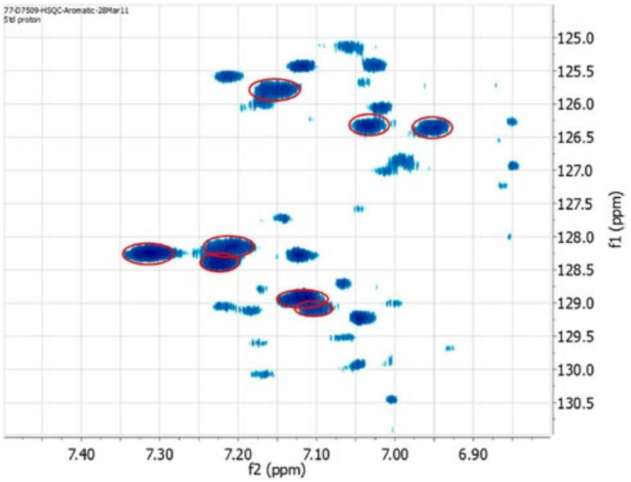


FIGURE 3. HSQC NMR spectrum of the aromatic region of a commercial ULSD. Major substructures common with diesel fuels from unconventional and conventional sources are circled in red. Other substructures represent a combination of minor components and components which do not appear consistently in other diesel fuels.

Over the course of the year we have examined a series of fuels using the NMR to evaluate the diffusion of different components within a fuel mixture. DOSY has been used to probe the properties of asphaltenes [3], as well as several complex mixtures [4], but has not found use in general fuel analysis. We have applied DOSY and a simpler pulse-gradient spin echo (PGSE) technique to examine the diffusional behavior of components within a subset of fuels, such as a mildly hydrotreated shale oil at several concentrations, and two blended diesel fuels. Interestingly, the PGSE spectra revealed time-dependent resonance patterns unique to each fuel, suggesting that there are clear differences in the constituents, and that those constituents have measurably different diffusion parameters. The different diffusion parameters may originate from differences in constituent molar volume, i.e. larger molecules diffuse more slowly, or differences in interaction between constituents, i.e. depending upon the solvent-solute interactions, some molecules may tend to cluster, as has been observed in the precipitation of asphaltenes [3c]. The ability to distinguish these differences may have critical implications to understanding fuel properties and performance, and because PGSE is a relatively simple experiment, PGSE or similar techniques may be amenable to online/in situ NMR analysis during the upgrading process. We expect to more thoroughly investigate this analysis approach during the coming year, obtaining quantifiable data from which to make stronger assertions.

Figure 4 shows a quantitative $^{13}C\{^1H\}$ NMR spectrum of a pyrolysis oil, with the overall carbon-type compositional breakdown reported in Table 2. Areas of interest that separate the pyrolysis oil from conventional diesel fuels are circled in red and are composed mainly of oxygenates, although other heteroatoms may also be represented. These chemical substructures are the origin of many of the undesirable properties associated with pyrolysis oil including residual acidic species, which contribute to corrosivity, and ethers and alcohols, which contribute to longer term stability issues and moisture issues. These functional groups can be difficult to observe using gas chromatography-based techniques since some of the polar components can be retained by the column, can contribute to column degradation, and can influence retention times for other fuel components. NMR spectroscopy is not susceptible to these limitations, and can provide quantitative analytical information, although quantitation is limited to components having minimum quantities of between 1 and 2 % mole fraction.

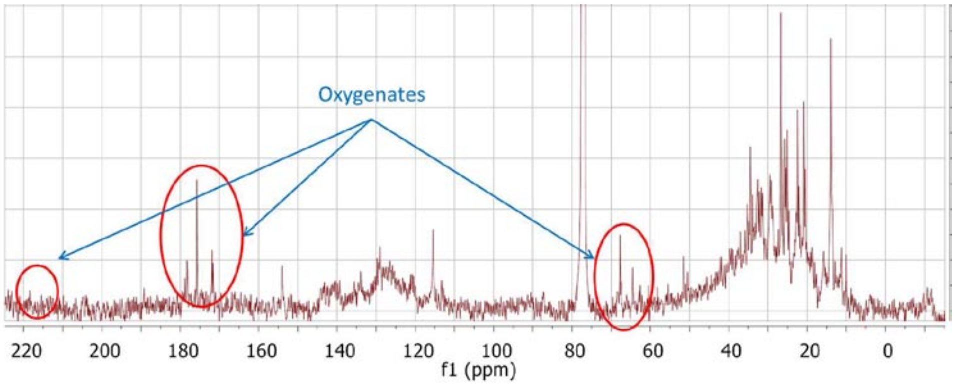


FIGURE 4. Quantitative $^{13}C\{^1H\}$ NMR spectrum of a pyrolysis oil sample. Features not typically observed in commercial diesel fuels are circled in red and reflect carbons adjacent to a heteroatom, most commonly oxygen.

TABLE 2. Carbon Type Analysis for a Pyrolysis Oil Sample

	Mole % Carbon
General Carbon Types	
Aromatic Carbon	26.4
Aliphatic Carbon	66.6
Oxygenates (carbons adjacent to oxygen)	7.0
CH Carbon	8.5
CH_2 Carbon	40.5
CH_3 Carbon	17.7
Aromatic Carbon Breakdown	
Total Aromatic Carbon	26.4
Carbonyl Carbon	4.1
Carboxyl Carbon	1.1
Phenolic Carbon	1.1
CH_2/CH Substituted Aromatic Carbon	6.9
Naphthene Substituted Aromatic Carbon	1.1
CH_3 Substituted Aromatic Carbon	1.5
Internal (Bridgehead) Aromatic Carbon	1.9
Peripheral Unsubstituted Aromatic Carbon	13.2
Heteroaromatic Carbon	4.1
Naphthenic Carbon Breakdown	
Total Naphthenic Carbon	37.0
Naphthenic CH	6.2
Naphthenic CH_2	26.2
Naphthenic CH_3	4.6
Paraffinic Carbon Breakdown	
Total Paraffinic Carbon	29.6
n-Paraffin Character of Sample	0.8
iso-Paraffin Character of Sample	97.3

CONCLUSIONS

- Two-dimensional NMR can provide quantitative structural and substructural information, particularly by allowing the deconvolution of overlapping NMR resonances. From our HSQC measurements, common substructural components can be observed among fuels from disparate sources, but these fuels are also distinguishable by their dissimilar components. The latter may be expected to distinguish one fuel from another, potentially influencing some of fuel properties or performance.
- Diffusion measurements, providing correlation to molecular size and fuel viscosity, have been shown to differ among fuel samples and promise to provide an additional source of information correlating structure and property.
- We are developing a "toolkit" of approaches that can be used as needed, depending on the level of detail needed for the application.
- As we correlate structural composition to fuel properties, we can moderate our level of analysis to accommodate the needs of the model.

REFERENCES

1. Bays, J.; King, D.; O'Hagan, M. *Carbon-Type Analysis and Comparison of Original and Reblended FACE Diesel Fuels (FACE 2, FACE 4, and FACE 7)*; PNNL-21955; Pacific Northwest National Laboratory: Richland, WA, 2012.

2. Mueller, C.J.; Cannella, W.J.; Bruno, T.J.; Bunting, B.; Dettman, H.D.; Franz, J.A.; Huber, M.L.; Natarajan, M.; Pitz, W.J.; Ratcliff, M.A.; Wright, K., Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics. *Energy & Fuels* **2012,** *26* (6), 3284-3303.

3. (a) Durand, E.; Clemancey, M.; Quoineaud, A.A.; Verstraete, J.; Espinat, D.; Lancelin, J. M., H-1 diffusion-ordered spectroscopy (DOSY) nuclear magnetic resonance (NMR) as a powerful tool for the analysis of hydrocarbon mixtures and asphaltenes. *Energy & Fuels* **2008,** *22* (4), 2604-2610; (b) Kozhevnikov, I.V.; Nuzhdin, A.L.; Martyanov, O.N., Transformation of petroleum asphaltenes in supercritical water. *Journal of Supercritical Fluids* **2010,** *55* (1), 217-222; (c) Miknis, F.P.; Pauli, A.T.; Michon, L.C.; Netzel, D.A., NMR imaging studies of asphaltene precipitation in asphalts. *Fuel* **1998,** *77* (5), 399-405.

4. (a) Socha, A.M.; Kagan, G.; Li, W.B.; Hopson, R.; Sello, J.K.; Williard, P.G., Diffusion Coefficient-Formula Weight Correlation Analysis via Diffusion-Ordered Nuclear Magnetic Resonance Spectroscopy (DOSY NMR) To Examine Acylglycerol Mixtures and Biodiesel Production. *Energy & Fuels* **2010,** *24*, 4518-4521; (b) Gil, A.M.; Duarte, I.; Cabrita, E.; Goodfellow, B.J.; Spraul, M.; Kerssebaum, R., Exploratory applications of diffusion ordered spectroscopy to liquid foods: an aid towards spectral assignment. *Analytica Chimica Acta* **2004,** *506* (2), 215-223; (c) Kapur, G.S.; Findeisen, M.; Berger, S., Analysis of hydrocarbon mixtures by diffusion-ordered NMR spectroscopy. *Fuel* **2000,** *79* (11), 1347-1351; (d) Colbourne, A.A.; Morris, G.A.; Nilsson, M., Local Covariance Order Diffusion-Ordered Spectroscopy: A Powerful Tool for Mixture Analysis. *Journal of the American Chemical Society* **2011,** *133* (20), 7640-7643.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Bays, JT; King, DL; O'Hagan, MJ. Carbon-Type Analysis and Comparison of Original and Reblended FACE Diesel Fuels (FACE 2, FACE 4, and FACE 7). Pacific Northwest National Laboratory Report, PNNL-21955, October 2012.

2. Mueller, C.J.; Cannella, W.J.; Bruno, T.J.; Bunting, B.; Dettman, H.D.; Franz, J.A.; Huber, M.L.; Natarajan, M.; Pitz, W.J.; Ratcliff, M.A.; Wright, K., Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics. Energy & Fuels 2012, 26 (6), 3284-3303.

IV.7 Alternative Fuels Infrastructure Development

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DOE Technology Development Manager:
Kevin Stork

Objectives

To provide analysis and in-country support for the development of alternative fuel infrastructure in the United States and abroad.

Fiscal Year (FY) 2012 Objectives

To provide analysis and in-country support for the development of alternative fuel infrastructure in the United States and abroad.

Accomplishments

This project profiled the progress of ethanol production and consumption in Thailand in 2012 as compared to the situation reported in previous years with a concentration on 20% ethanol in gasoline (E20) production and use.

Future Directions

Follow the changes that are occurring in alternative fuel use in Thailand with an emphasis on the issues being encountered with distribution and use of higher ethanol blends of E20 and 85% ethanol in gasoline (E85).

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INTRODUCTION

Thailand has produced gasohol in the country since 2001—beginning with 10% ethanol in gasoline (E10), then E20 in January 2008, and E85 in the third quarter of 2008. After a decade of introducing gasohol to the market, gasohol consumption has continued to increase due to price incentives that the Thai government has created. Ethanol production has continued to increase in 2011 since the ethanol plants are on line to operate at their planned capacities. However, gasohol consumption in 2011 might not be increased at as a significant rate as in previous years. The new government, which came in power in August 2011, terminated the levy on gasoline to lower gasoline prices resulting in a jump of gasoline consumption at an expense of gasohol consumption.

APPROACH

This research reviews the status of alternate transportation fuels development and utilization in Thailand.

RESULTS

The ethanol fuels available in the Thai market are E10, E20 and E85. E10 is blended in Octane 91 and Octane 95 and are sold as Gasohol 91 and Gasohol 95, respectively. E20 and E85 are both blended only in Octane 95 and are sold as Gasohol E20 and Gasohol E85, respectively.

Sales of gasohol in Thailand had been increasing continually since it was commercially available in the market but the sales slightly decreased in 2010 and 2011. The average sales of gasohol in 2010 were 12.01 mL/d as compared to 12.21 mL/d in 2009, a decline of 1.6%, and the average sales of gasohol in 2011 were 11.50 mL/d, a decline of 4.2% from 2010. Average sales of gasohol per day from January to July 2012 are 11.51 mL/day as compared to 12.57 mL/d during the same months in 2011, a drop of 8.4% (see Table 1). In 2010, due to the economic downturn, both gasoline and gasohol consumption slightly dropped. Consumption of gasohol dropped further in 2011 because of the government policy to terminate the levy on gasoline to lower gasoline prices resulting in a jump of gasoline consumption and a decline of gasohol consumption.

All gasoline sold in Thailand is unleaded in Octane 91 (regular gasoline) sold as ULR 91RON or in Octane 95 (premium gasoline) sold as ULG 95RON. ULR91RON dominates the market having a market share of 42% of total gasoline and gasohol sales. The government has planned to phase out ULG91 from the market on October 1, 2012. However, it is most likely that the phase out date will be postponed due to the resistance of the oil refineries.

In contrast, sales of Gasohol E20 and Gasohol E85 have risen due to strong support of the government in reducing excise tax rates for E20-compatible cars and for flexible fuel vehicles (FFVs) and in keeping prices of Gasohol E20 and Gasohol E85 competitive with prices of gasoline. Sales of Gasohol E20 increased from 137.4 million liters in 2010 to 222 million liters in 2011. So far in 2012 (from January to July) about 166 million liters of Gasohol E20 has been sold. The sales of Gasohol E85 have also increased substantially since it was available in 2008. The total amounts of Gasohol E85 sold in 2008 were 0.021 million liters, in 2009 were 0.3 million liters, in 2010 were 2.1 million litters, and in 2011 were 9.1 million liters. Total sales of Gasohol E85 in 2012 are expected to be double those of 2011. Sales of gasohol as compared to gasoline are shown in Table 1.

As the government has pushed to increase the demand for high-content ethanol fuels, demand for Gasohol E20 and Gasohol E85 has risen, and consequently the numbers of pumps. Since last reported in August 2011, there are 217 more Gasohol E20 pumps in Thailand making it a total of 968 pumps that are selling Gasohol E20. Pumps for Gasohol E85 also increased, from 24 pumps in August 2011 to 49 pumps as of July 2012. Most recent data (December 2010) showed total numbers of Gasohol 91 pumps were at 2,821 and those of Gasohol 95 were 4,109 pumps.

The government has structured oil pricing to make retail prices of gasohol lower than retail prices of gasoline, and gasohol with higher ethanol contents is less expensive than gasohol with lower ethanol contents. For example, at the same octane, price of Gasohol E20 is the most competitive as compared to price of Gasohol 95 (E10) and price of ULG 95RON; and price of Gasohol E85, the highest ethanol content fuel, is lower than prices of other fuels. This goal has been accomplished by using money from the Oil Fund to subsidize gasohol producers and keep gasohol prices low.

There was a brief period after August 2011, when the new government (the Yingluk Administration), took power, that the levy collection to the Oil Fund on gasoline sold in the market was terminated. Thus it made prices of gasoline vastly drop. For example, the price of ULG 95 RON on August 26, 2011 before the levy termination was 47.34 baht per liter and on October 13, 2011 after the levy termination it was 40.82 baht per liter. As of September 2012, the levy collection to the Oil Fund on gasoline was re-imposed. For example, on September 14, 2012, a levy at a rate of 6.8 baht/liter was collected on ULG 95RON and 5.5 baht/liter on ULG 91RON, making price of ULG 95RON go up to 48.90 baht/liter and price of ULG91 RON go up to 43.05 baht/liter. At the same time, the levy is being collected at a smaller rate (1.1 baht/liter) on Gasohol 95, and a subsidy with the money from the Oil Fund was given to the producers of Gasohol 91 (1.2 baht/liter), Gasohol E20 (1.5 baht/liter) and Gasohol E85 (12.4 baht/liter). The current prices of Gasohol 95, Gasohol 91, Gasohol E20 and Gasohol E85 (on September 14, 2012) are 37.63, 35.18, 34.18, and 21.98 baht/liter, respectively.

Sales of E20 (known as Gasohol E20) have continued to rise since its introduction to the Thai market on January 1, 2008. About 29.03 million liters of E20 were sold in 2008, 83.4 million liters in 2009, 137.4 million liters in 2010, and 222 million liters in 2011. The Department of Energy Business reported the sales of E20 in 2012 from January to July at a total of 166 million liters, or about 0.78 million liters per day, as compared to 0.61 million liters per day in 2011.

At present all new cars in Thailand are E20-compatible cars. More than 300,000 of E20-compatible vehicles have been sold in Thailand so far.

To promote greater use of cars capable of utilizing E20, excise tax rates of E20 cars have been reduced to be 5% lower than regular cars at the same cylinder capacity. The current excise tax rates for E20 cars are as follow:

- Cars with cylinder capacity less than 2,000 cc and engine power not over 220 HP are subject to 25% excise tax rate (regular cars 30%).
- Cars with cylinder capacity between 2,000 cc to 2,500 cc and engine power not over 220 HP are subject to 30% excise tax rate (regular cars 35%).

TABLE 1. Sales of Gasoline and Gasohol

Unit: Million Liters

	Sales						
	2007	2008	2009	2010	2011	2011 (Jan-July)	2012 (Jan-July)
ULR 91RON	4,467	3,388	2,877	2,958	3,077	1,621	1,929
ULG 95RON	1,107	341	177	77	42	22	26
Gasohol 91 (E10-Octane 91)	244	924	1,415	1,552	1,860	1,106	1,178
Gasohol 95 (E10-Octane 95)	1,519	2,439	2,972	2,692	2,122	1,427	1,084
Gasohol E20		29.03	83.4	137.4	222	128	166
Gasohol E85		0.021	0.25	2.1	9.1	4.3	14.3

Source: Department of Energy Business (www.doeb.go.th/info/data/datadistribution/y_sale.xls)

- Cars with cylinder capacity over 2,500 cc but less than 3,000 cc and engine power not over 220 HP are subject to 35% excise tax rate (regular cars 40%).

E85 was introduced to Thailand in 2008. PTT and Bangchak are presently the only E85 distributors. As of July 2012, there are total of 49 petro stations selling E85—of which 30 stations are located in Bangkok and vicinities. PTT owns 10, and Bangchak owns 39 of the E85 stations. PTT and Banchak cited that each E85 dispenser required an investment of 3 million baht and the problem for their investment in more E85 pumps was due to relatively low demand for E85 in the Thai market. The companies committed to distribute more E85 if demand grew.

Five FFV models are available in Thailand at present—Volvo C 30 1.8F, Volvo S80 2.5 FT, Volvo S80 Business Line, Mitsubishi Lancer EX, and, just coming to the market in July 2011, Chevrolet Captiva. The Volvo C30 1.8 F is an imported model available in the Thai market since the beginning of 2008 at the price tag of 1.89 million baht (no additional new Volvo C30 were imported to Thailand in 2011). The Volvo S80 2.5 FT model has being manufactured in Thailand since November 2008. The Lancer EX model is a mass production FFV model in Thailand by Mitsubishi which was launched in October 2009. The Lancer EX is powered by two engines – 1.8 and 2.0 liter, and costs from 831,000 baht to 1.034 million baht. In the last quarter of 2010 the Volvo company added another model of Volvo—Volvo S80 Business Line. Chevrolet Captiva has been in the market since July 2011 with the price ranging between 1.2 -1.7 million baht. By the end of September 2011, there are a total of 6,554 FFVs being used in Thailand of which the majority is the Lancer EX since it is the most affordable one.

E85 consumption has continued to increase as more FFVs are available in the Thai market especially since the mass production of Lancer EX hit the market at a more reasonable price. A total of 9.1 million liters of Gasohol E85 were sold in 2011. Sales of E85 were reported to be at 14.3 million liters between in January to July 2012, more than double the amount of 4.3 million liters which were sold during January to July 2011.

The government has focused on promoting domestically manufactured FFVs of all cylinder capacities. More tax incentives are offered to domestically manufactured FFVs as compared to imported FFVs. A high import duty has been imposed on all imported cars including FFVs.

At present the government has lowered the excise tax of FFVs by another 3% from the previous rates for all cylinder capacity: 22% for FFVs with cylinder capacity not over 2,000 CC; 27% for FFVs with cylinder over 2,000 cc but not over 2,500 cc; and 32% for FFVs with cylinder capacity over 2,500 cc but not over 3,000 cc. These made the current excise tax rates of FFVs 3% lower than those of E20-compatible cars, and 8% lower than regular cars, of the same cylinder capacity.

CONCLUSIONS

The Thai government has announced various ethanol and gasohol-support measures in both supply side and demand side in order to achieve its ethanol target, with an ultimate goal of having Thailand become the ethanol hub in the Association of Southeast Asian Nations.

The total capacity of ethanol production (as of November 2011) is at 3.065 mL/d with an additional 2.420 mL/d expected by the end of 2012. However, less than half of the total installed capacity is being used.

In the new 10-Year Alternative Energy Development Plan (ADEP) (2012-2021) which replaced the previous 15-year Renewable Energy Development Plant (2008-2022), the government has set a target for ethanol consumption at 9 mL/d in 2021.

The AEDP also sets a new aggressive goal of 25.0 mL/day for second generation biofuels by 2021. The second generation fuels are meant to provide a replacement for diesel, and the feedstocks under discussion are bagasse, jatropha, and algae. Together, these support an overall 2021 ADEP renewable transport fuel target of 44%.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. *Cary Bloyd, Ethanol Production and Utilization in Thailand—2012 Update*, September 2012, PNNL Whitepaper.

2. Cary Bloyd, *Asia-Pacific Economic Cooperation Environmental Friendly Vehicles Activities*, Presented (Invited Speaker) at 5th International Environmentally Friendly Vehicle Conference, Baltimore, MD on September 12, 2012. PNNL-SA-90533.

IV.8 Decision Analysis Tool to Compare Energy Pathways for Transportation

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Objectives

- To develop an agile decision-analysis tool to enable rapid analysis of a wide range of transportation fuel pathways and vehicle technologies.
- To evaluate fuel and vehicle technologies on multiple criteria, including, greenhouse gas emissions, cost of transportation, food security, energy security, and criteria pollutant emissions.
- To create an online resource for sharing and reviewing estimates and forecasts of key quantities used for energy analysis.

Fiscal Year (FY) 2012 Objectives

- To evaluate the oil price shock on vehicle fleet.
- To expand analysis of biofuels futures including updating biomass supply curves and extending the biofuels production technologies.
- To perform alternative transportation pathway analysis and screen technology topics for policy briefs.
- Update the Analytica Transportation Energy Assessment Model (ATEAM) user interface and documentation using an online framework to include the current ATEAM user documentation as an integral part of the operating model.
- To develop an online database for energy analysts to find, review and share estimates of key quantities used in energy analysis, named Megajoule.org.

Accomplishments

- Oil price shocks were investigated by extending and applying ATEAM to explore its impacts on the U.S. vehicle fleet and correspondingly the potential for new fuel and vehicle technologies, such as compressed natural gas vehicles (CNGVs) and battery electric vehicles (BEVs) and other competitive alternative fuel technologies, to reduce the U.S.'s vulnerabilities to such changes.
- Potential market penetration of various fuels including compressed natural gas (CNG), liquefied natural gas (LNG), liquefied petroleum gas and methanol in light-duty, medium-duty and heavy-duty vehicles was analyzed.
- Four different methods were explored to compute the early adopter penalty for advanced vehicle technologies to address the diffusion of new technology as the technology becomes more prevalent in the market.
- A recursive feedback loop was used to forecast the development of fueling infrastructure endogenously, where the previous year's stock of alternative fuel vehicles affects the availability of alternative fuels.
- Modules for scenario analysis, sensitivity analysis, and uncertainty analysis have been built to identify which assumptions matter to the results and why.
- A list of nine important transportation issues and scenarios were submitted for screening to prepare the series of six technology briefs. Initial study was conducted on the effect of the modification of the Renewable Fuel Standard on the droughts and preliminary results were submitted as a letter to the Environmental Protection Agency.
- An online energy information hub Megajoule.org was implemented and expanded as an online database for energy analysts. In addition to improve the user interface and internal structure of Megajoule, introductory materials and new estimates and sources, probabilistic projections obtained from expert elicitations of a series of technologies were added.

Future Directions

- Incorporate the estimates for various biomass costs to update biomass supply curves. Compare cellulosic ethanol and other advanced biofuels pathways, including "drop-in fuels" that need less distribution infrastructure. Examine the portfolio effects of uncertainty results from research and development on biofuels.

- Develop a Web-based ATEAM document using direct links from the ATEAM model to corresponding webpages, and cross links with the guide and make it easier to access and navigate.
- Develop a series of two to four page technology briefs and a paper demonstrating ATEAM capabilities.
- Move the main hosting of Megajoule to another platform to enhancing the visibility by search engines. Expand the dataset with data from both research and collaborating information-sharing resources and continue to improve the user-friendliness and flow of the user interface.

* * * * *

INTRODUCTION

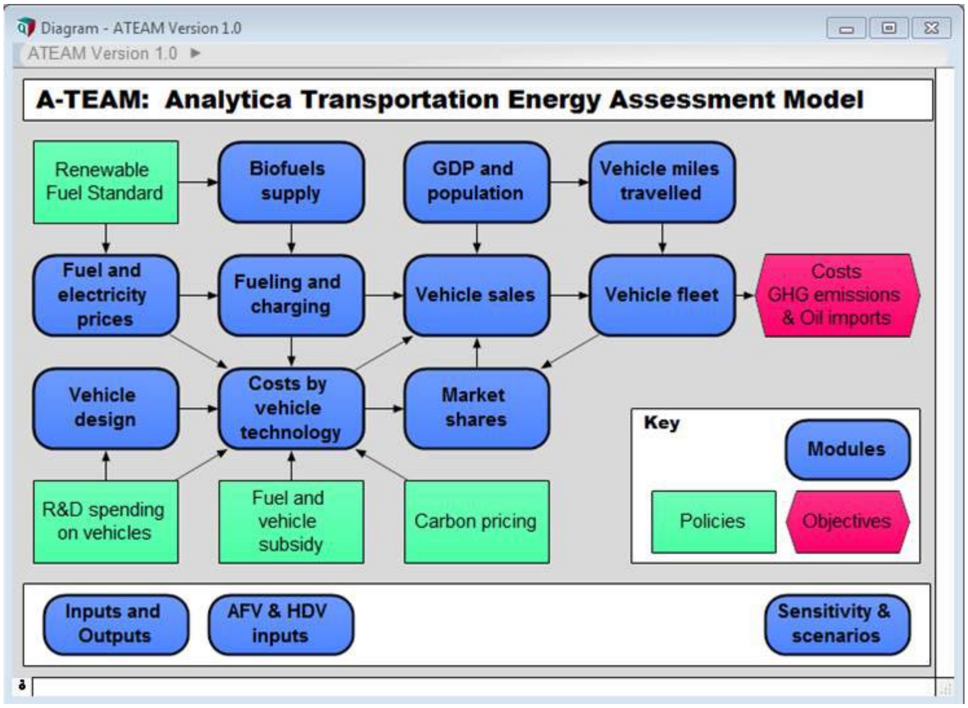
New biofuels, lower-cost batteries, plug-in hybrid electric vehicles (PHEVs), CNG/LNG, and light-weighting are just a few of the new automotive technologies being developed, with the goal of reducing greenhouse gas emissions, transportation costs, and oil imports. Given the time it takes for the U.S. vehicle fleet to turn over, and interactions among these innovations in the market place, it can be difficult to estimate the scale and timing of their effects. In this project, we have developed ATEAM (Figure 1) as a scenario decision-analysis tool to assist policy makers, program managers, and others to more rapidly explore these issues and understand their interactions.

Our goal is to make the model public domain, open source, and extensible, so that interested groups from government, academe, industry, and non-governmental organizations can use ATEAM to explore and compare their perspectives on these important, and sometimes controversial issues.

APPROACH

The focus of the previous phase was on U.S. light-duty and heavy-duty vehicle fleet. In this phase, we expanded and applied ATEAM to analyze select high importance transportation issues and scenarios.

To refine scenario analysis, we included a more sophisticated treatment of various types of alternative vehicle fuels. We compiled a more comprehensive database of key quantities associated with each technology. We focused primarily on automotive applications for CNG, LNG, liquefied petroleum gas and methanol in heavy-duty, medium-duty and light-duty vehicles. To analyze the potential market penetration of these fuels under various circumstances, we looked primarily for incremental vehicle costs (converted



GHG – greenhouse gas; AFV – alternative fuel vehicle; HDV – heavy-duty vehicle

FIGURE 1. Top level ATEAM Influence Diagram as User Interface

or manufacturer-supplied), infrastructure costs, fuel costs, market penetration potential, fuel availability and scalability and relevant tax incentives. Among the different type of costs, we expanded our study on the early adopter penalty cost using four different methods to address the intangible early adopter cost represents consumer preference and the tendency for the social costs or innovation penalty of switching to a new technology. In our first method, we use the levelized life cycle cost per mile of conventional internal combustion vehicles to compute an implied levelized life cycle cost per mile for advanced technologies. The difference of the implied cost and the actual cost without early adopter penalty will be the cost of the advanced technologies' early adopter penalty. The other three methods are based on the CIMS model [1], a scheme from University of California at Davis [2], and the MA3T model [3], respectively.

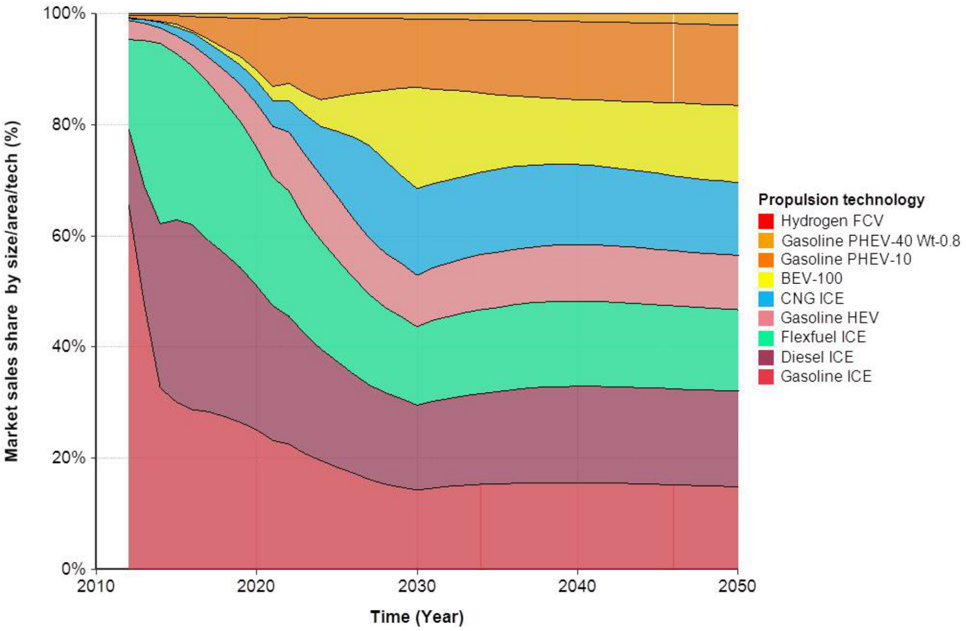
Megajoule.org

A large and growing community of energy analysts at universities, industry, government, and NGOs are involved in quantitative projections relating to energy. We have developed a Web-accessible database for energy analysts to find, review, critique, and share their estimates and projections for such quantities, named Megajoule.org. Megajoule represents a taxonomy for forms of energy (oil, gas, coal, solar, electricity, hydrogen, ethanol, and so on), energy technologies (such as lithium-ion batteries, plug-in hybrid vehicles), metrics (such as efficiency, capital cost, levelized cost of energy), sources (such as articles, technical reports, books), and specific estimates, such as the efficiency of a photovoltaic modules projected from a particular article. Users can search to find estimates of the quantities of interest to them, and, if they sign up as contributors, rate their credibility, add comments, and add their own estimates. Contributors cannot be anonymous to encourage them to take responsibility for their contributions.

In this phase, we expanded the previous version of Megajoule.org. We improved the user interface and internal structure of Megajoule, add introductory materials and populated new estimates and sources, probabilistic projections.

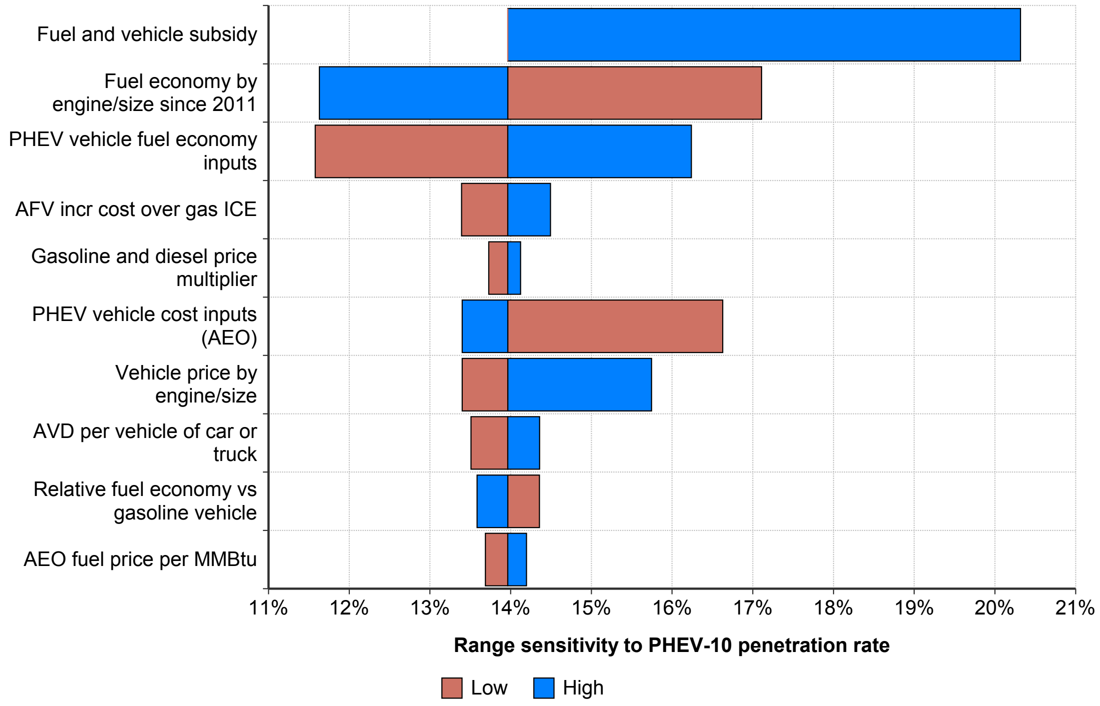
RESULTS

The adoption of alternative fuel vehicles is quite sensitive to the increment fuel cost, vehicle cost and infrastructure cost. The ATEAM prototype model enables the evaluation of market penetration rates of different vehicle technologies (Figure 2). ATEAM is designed to be agile and transparent to explore the sensitivities and uncertainties to find out what assumptions matter and why. Users can select the parameters and methods for sensitivity analysis. An example of sensitivity analysis on the penetration rate of PHEVs with 10-mile all-electric range (PHEV-10) is shown in Figure 3.



PHEV-40 – PHEV with 40-mile all-electric range; FCV – fuel cell vehicle; BEV – battery electric vehicle; ICE – internal combustion engine; HEV – hybrid electric vehicle

FIGURE 2. Projected Market Shares by Technology for a Select Scenario



AEO – Annual Energy Outlook; AVD – annual vehicle distance

FIGURE 3. Range Sensitivity Analysis of PHEV-10 Penetration Rate to Key Input Variables

For Megajoule, we have made several improvements to the user interface and internal structure. The graphing engine now supports two new formats, a college scarves bar chart and a simple scatter plot using the Analytica Cloud Player. The college scarves plot displays low and high uncertainty values for each point and allows users to sort the selected data by several different criteria. Figure 4 shows an example of capital cost per energy of lithium battery.

CONCLUSIONS

In this phase of the project, we expanded our previous ATEAM prototype to analyze a select high importance transportation issues and scenarios. The prototype can assess sensitivities and the effects of uncertainty on key model parameters. We have expanded the modeling of the impact of oil price shock on vehicle fleet, early adopter penalty for advanced vehicle technologies and conducted initial analysis on the impact of change to Renewable Fuel Standard on the droughts. Next steps are to apply the refined model to develop a series of six policy briefings on selected technology issues.

REFERENCES

1. Jonn Axsen, Dean C. Mountain, Mark Jaccard, *Combining stated and revealed choice research to simulate the neighbor effect: The case of hybrid-electric vehicles*, Resource and Energy Economics 31 (2009) 221-238.

2. Sonia Yeh, *An empirical analysis on the adoption of alternative fuel vehicles: The case of natural gas vehicles*, Energy Policy 35 (2007) 5865-5875.

3. Zhenhong Lin, David Greene, 2009, *The MA3T model: Market Adoption of Advanced Automotive Technologies*, (2009).

FY 2012 PUBLICATIONS/PRESENTATIONS

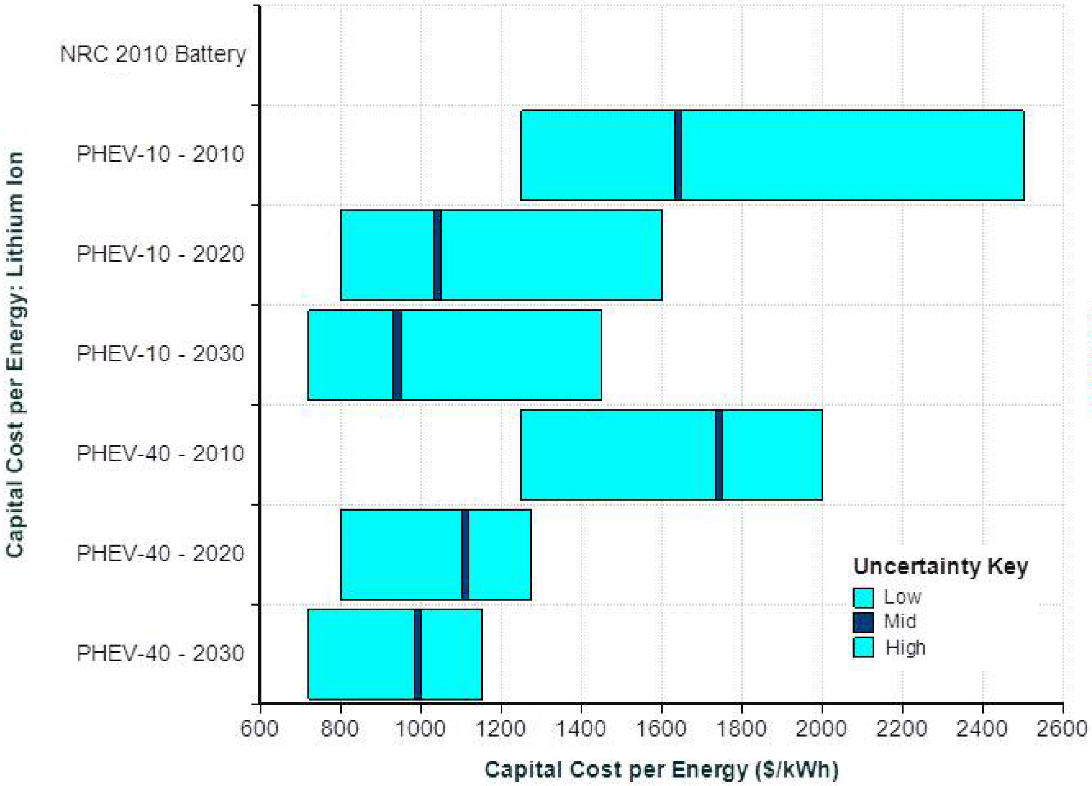
1. “Exploratory Decision Analysis & Surprises: The Future of the Automobile”, Max Henrion, the Society for Decision Professionals, March 21, 2012.

3. “Exploring the future of the automobile in the USA with ATEAM and Megajoule.org” Department of Engineering & Public Policy, Carnegie Mellon University. April 11, 2012.

3. An Introduction to Analytica Transportation Energy Assessment Model. Web demonstration. Pacific Gas & Electric. May 15, 2012.

4. “An introduction to Megajoule.org”, Max Henrion, Energy Modeling Forum, Snowmass, CO, Aug 1, 2012.

5. “ATEAM User Guide”, version 2.0, September, 2012



NRC – National Research Council

FIGURE 4. Capital Cost per Energy of Lithium Battery Generated Using Megajoule.org with selected data

6. “Uncertainty and Surprise in Energy Forecasts: The Cost of Photovoltaics” Max Henrion, Evan Sherwin. INFORMS 2012, Phoenix AZ, Oct 15, 2012.

7. “Transparency in Transportation Energy Analysis Modeling”, Max Henrion, California Energy Commission, Sacramento, Nov 20, 2012.

IV.9 Performance of Biofuels and Biofuel Blends

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Objectives

Measure the impact of new biomass-derived fuels on gasoline performance properties and light-duty vehicle exhaust emissions.

Fiscal Year (FY) 2012 Objectives

Quantify the impact of butanol isomers, as well as blends of butanol with ethanol, on gasoline fuel properties and tailpipe emissions.

Accomplishments

- The effect of isobutanol, 1-butanol, 2-butanol, and blends of these with ethanol on gasoline vapor pressure and anti-knock index (octane number) was quantified over a range of blend levels.
- At 5.5% oxygen in the fuel (equivalent to 15 vol% ethanol in gasoline, or E15) a blend of 12% isobutanol, 7% ethanol caused no increase in final blend vapor pressure relative to the hydrocarbon blendstock. This blend also exhibited anti-knock index higher by one octane number than the corresponding 5.5% oxygen butanol-only blend.
- The largest effect on regulated emissions was a reduction in CO from 0.40 g/mile for neat gasoline (E0) to 0.28 g/mile from E15. Isobutanol marginally reduced CO relative to E0. There was no significant effect on oxides of nitrogen (NO_x).
- E15 produced the highest unburned alcohol emissions (average of 1.38 mg/mile ethanol). Despite blending at higher concentration than E15, both butanols produced much lower unburned alcohol emissions (0.17 mg/mile 1-butanol, and 0.30 mg/mile iso-butanol).
- The lower alcohol emissions were offset by higher emissions of carbonyl compounds from the butanol blends. Emissions of butyraldehyde were significantly higher from 1-butanol while emissions of acetone and methacrolein were significantly higher from iso-butanol.
- The 12% iso-butanol/7% ethanol blend significantly reduced non-methane organic gases (NMOG) emissions relative to E0 because both carbonyl and unburned alcohol emissions were lower than for blends containing the individual alcohols.

Future Directions

- Expansion of this work should include testing of these blends in one or more additional cars as well as assessment of evaporative emissions.
- Future work may also examine the performance of other cellulosic biomass-derived oxygenates such as methyl pentanoate and furan-based compounds.

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INTRODUCTION

Higher alcohols have been the subject of increased interest because they may provide significant advantages over ethanol, including higher energy density, lesser effect on gasoline/blend vapor pressure, lower affinity for water, and improved material compatibility. Properties of various alcohol blend fuels have been the subject of a recent study [1]. Vapor pressure and distillation characteristics have been determined for alcohol−gasoline blends containing 5−85% by volume of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, i-butanol (2-methyl-1-propanol), and t-butanol (2-methyl-2-propanol) by Andersen and coworkers [2,3].

The effect of ethanol on tail-pipe emissions has been well studied in vehicles from the early 1980s to recent low-emission and super-low-emission vehicles. Early studies [4] showed a general reduction in tailpipe emissions of hydrocarbons, CO, benzene and 1,3-butadiene when tested with nominal 10% ethanol, and an increase in formaldehyde and acetaldehyde. Results for NO_x emissions were mixed. More recent studies confirm these general trends with the exception that engines capable of adapting to actual fuel ethanol content during open-loop operation exhibited no impact on regulated pollutant emissions with increased ethanol content [5-7]. Data on emissions from butanol blends is sparse. Older emissions testing [8,9] on various mixed alcohol blends including ethanol, butanol and methanol had mixed results, although CO was consistently lower. In more recent studies, BP measured emissions on 16% butanol in gasoline blends for in-use cars and found no significant change in emissions of CO or NO_x and a slight reduction in hydrocarbon emissions in comparison to a base fuel [10]. Other researchers have also observed little effect of butanol on emissions [6,7].

We examined ethanol and butanol isomers, as well as mixtures of ethanol and butanol, blended into gasoline at 5.5 wt% oxygen. Gasoline blends studied include E15, iso-butanol and n-butanol at 23.5 vol% (iBu24 and nBu24), and an alcohol mixture with iso-butanol at 12 vol% and ethanol at 7.4 vol% (iBu12E7). Fuel properties and tailpipe emissions were measured, with a focus on emissions of NMOG.

APPROACH

Source Gasolines and Alcohols: Three gasoline blendstocks for oxygenate blending (BOBs) were acquired from a petroleum refiner and used for the mixed butanol-ethanol blend property measurements. Properties of these blendstocks have been reported previously [1]. Certification gasoline was used for the vehicle emissions tests, both neat (E0) and as the blendstock for the alcohol blends. Neat alcohols were reagent grade.

Preparation of Blends: For the gasoline property study, the BOBs and alcohols were cooled overnight in a freezer prior to blending to minimize loss from evaporation. Mixtures of ethanol with butanol in the BOBs were prepared over a range of composition to investigate the effect on vapor pressure. Results were compared to estimates derived using the Wilson ternary model for ethanol, gasoline, and 1-, 2-, or iso-butanol, with the constants derived from our previous work [1]. The emission test fuel blend compositions are shown in Table 1. Vapor pressures of the alcohol/gasoline mixtures were measured following ASTM D5191. Research and Motor Octane numbers were measured by ASTM D2699 and D2700, respectively. Alcohol concentrations were measured by ASTM D5599.

Vehicle Description: The test vehicle was a 2009 Honda Odyssey. The vehicle has a 3.5-L V-6 calibrated to meet the Tier 2 Bin 5 federal emission standard. This same vehicle was previously used in an ethanol emissions evaluation [11]. The mileage on the vehicle odometer at the start of testing was 120,594 miles. In preparation for emissions testing an on board diagnostics scan was performed, the exhaust system was leak checked, and the dynamometer road load coefficients were derived. The vehicle was stored in a temperature and humidity controlled soak area throughout the duration of testing.

TABLE 1. Composition of Blended Fuels Used for Vehicle Emission Tests

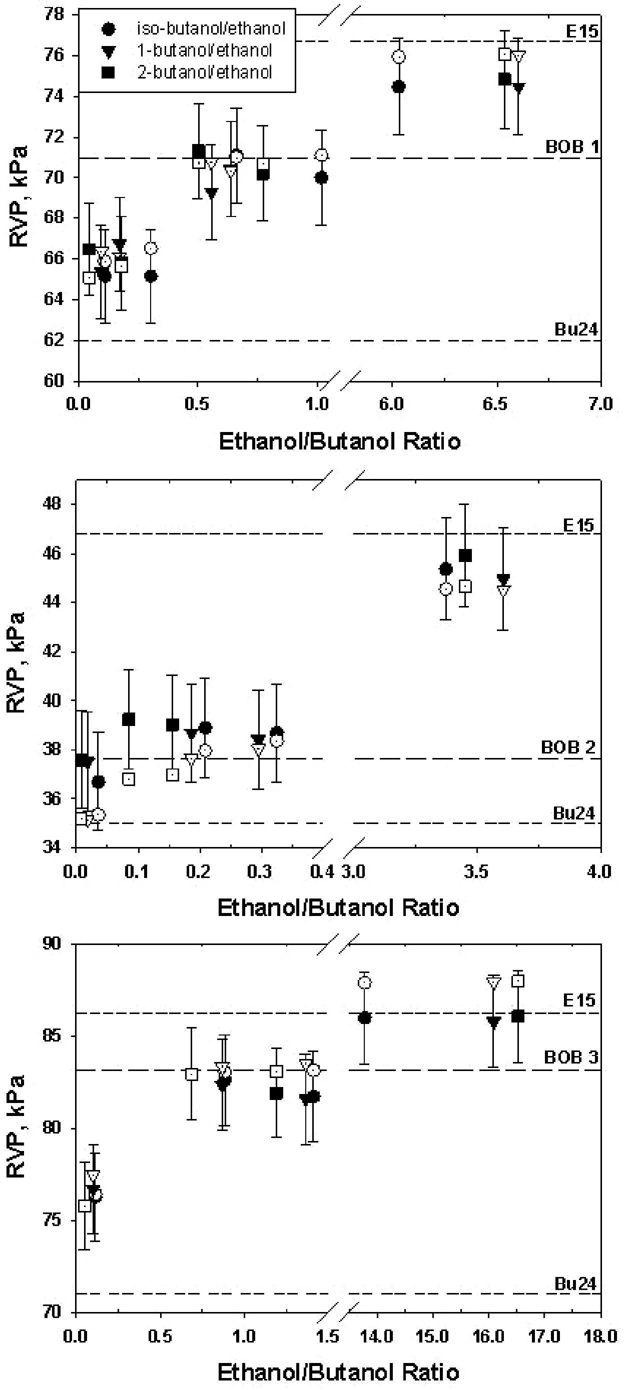
Alcohols	Blends/Component Volume %			
	Ethanol (E15)	n-Butanol (nBu24)	Isobutanol (iBu24)	Isobutanol/ Ethanol (iBu12E7)
Ethanol	15.0			7.4
n-Butanol		23.5		
Isobutanol			23.5	12.0
Certification Gasoline	85.0	76.5	76.5	80.6

Emissions Measurement: Testing was conducted in triplicate over the California Unified Cycle, also known as the LA92. The vehicle was operated in a temperature and humidity controlled environment on a Burke Porter chassis dynamometer with 48" rolls. Dilute bag samples were collected using a constant volume sampling system. CO and CO_2 were analyzed by non-dispersive infrared analyzers, NO_x was analyzed using by chemiluminescence, total hydrocarbons were analyzed using a flame ionization detector, and methane by gas chromatograph-flame ionization detector. Background correction was made by analysis of a simultaneously collected ambient sample.

Water impingers were used to collect unburned alcohols from dilute vehicle exhaust. These were analyzed using a modified version of the California Air Resources Board (CARB) Non-Methane Organic Gas Test Method #1001: Determination of Alcohols in Automotive Source Samples by Gas Chromatography. Ethanol and butanol recovery experiments were performed to validate this sampling approach. The dilute bags were analyzed for C1 to C8 hydrocarbons. The analysis method was a modified version of the CARB Non-Methane Organic Gas Test Method #1002: Determination of C_2 to C_5 Hydrocarbons in Automotive Source Samples by Gas Chromatography. Analysis of the aldehyde and ketone components was performed by derivatizing the compounds of interest using 2,4-dinitrophenylhydrazine with Waters Sep-Pak Silica cartridges. Analysis was by a modified version of CARB Non-Methane Organic Gas Test Method #1004: Determination of Aldehyde and Ketone Compounds in Automotive Source Samples by High Performance Liquid Chromatography.

RESULTS

Fuel Blend Properties: Vapor pressure results for the ethanol/butanol/gasoline blends are presented in Figure 1. Model predictions of the D5191 vapor pressure are within the uncertainty of the test method, with only a few exceptions for blends with BOB 2, the lowest vapor pressure BOB. These results were used to design the iBu12E7 gasoline blend used for vehicle emission tests; this blend's ethanol/isobutanol ratio was 0.58. When blending ethanol and butanol together to 5.5 wt% oxygen (equivalent to an E15), the required volumes of alcohols produce an octane rating exceeding that of an E10 blend, but fall short of the octane of E15 (see Figure 2).



RVP - Reid Vapor Pressure

FIGURE 1. Vapor pressure results (ASTM D5191) for gasoline blends as a function of ethanol/butanol ratio. Dotted symbols are the results of model predictions. Solid symbols are measured vapor pressures. Error bars are the stated reproducibility (95% confidence interval) of ASTM D5191.

Regulated Emissions: Figure 3 shows the measured regulated exhaust emissions; error bars are 95% confidence levels for the triplicate tests. With a few notable exceptions, the alcohol blended fuels did not affect the NO_x, CO, or NMOG within the measurement error. The largest emissions effect was that E15 caused a statistically signification 29% reduction of CO, from 0.395 g/mi for the E0 certification fuel to 0.282 g/mi. In the case of the mixed alcohol blend iBu12E7, NMOG emissions decreased 25% to 0.018 g/mi from 0.024 g/mi for E0.

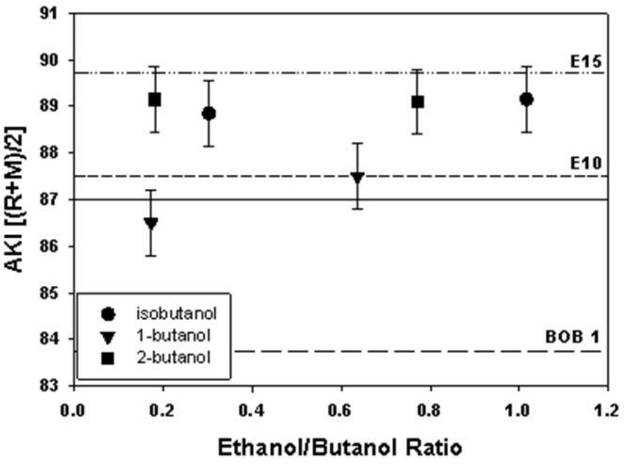


FIGURE 2. Octane rating of BOB 1 blends with ethanol and butanols at approximately 5.5 wt% oxygen. Error bars are the reproducibility (95% confidence) for anti-knock index (AKI), stated in ASTM D4814.

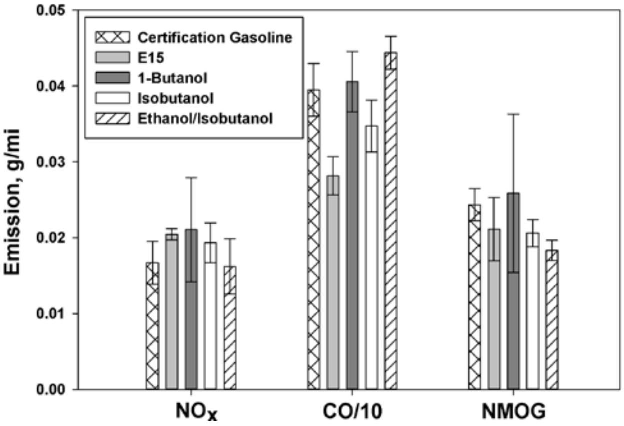


FIGURE 3. Regulated emission rates, error bars are 95% confidence based on three replications.

Unburned Alcohol and Carbonyl Emissions: E15 produced the highest levels of unburned alcohols, despite being blended at the lowest alcohol concentration. Table 2 compares amounts of alcohols and key carbonyls measured from the different fuel blends tested. The data show that in the cases of nBu24 and iBu24 the low amounts of alcohols measured were offset by carbonyl products of incomplete combustion, such that the combined totals of alcohol plus carbonyls for the two butanol blends and E15 are approximately the same.

For E15, formaldehyde was emitted at approximately the same rate as from E0, but acetaldehyde more than doubled from 0.35 mg/mile to 0.87 mg/mile. Butyraldehyde is the expected first oxidation product from n-butanol and Table 2 show the strong butyraldehyde response measured from nBu24 tests. Other noteworthy exhaust carbonyls produced from nBu24 include acetaldehyde, comparable in emission rate to that from E15, as well as an increase in formaldehyde emission relative to E0 and E15. Isobutanol produced total carbonyl emissions comparable to n-butanol, primarily as formaldehyde, acetone and methacrolein. As might be expected, the total carbonyls from the mixed alcohol blend iBu12E7 are lower than from iBu24. Part of the reason iBu12E7 reduced NMOG emissions can also be discerned in Table 2. This blend produced total carbonyls comparable to E15, but with a much lower alcohol emission rate. Thus the combined total was lower than any other alcohol blended fuel tested. This result, added to the lowest NMHC emission rate, led to the reduction in NMOG.

Hydrocarbon Emissions: Important conclusions from the data are that 1,3-butadiene emissions did not increase from any fuel blend tested, and appear to have actually decreased by about 45% for iBu12E7 relative to E0. Benzene emissions appear to have decreased as a function of gasoline dilution with alcohol, although within the 95% confidence interval, only iBu24 produced lower benzene emissions than E0. Similar observations are made for iso-octane and toluene, all of which behaved as unburned gasoline emissions.

CONCLUSIONS

- The CO reduction from ethanol was much larger than observed for isobutanol, 1-butanol or the isobutanol/ethanol blend. There was little fuel effect on NO_x emissions.
- Unburned alcohol emissions were highest for E15 (1.38 mg/mi ethanol). Despite fuel blending at higher concentration than E15, both butanols produced much lower unburned alcohol emissions (0.17 mg/mi 1-butanol, and 0.30 mg/mi iso-butanol).
- This was offset by higher total emissions of carbonyl compounds from the butanol blends. Emissions of butyraldehyde were significantly higher from 1-butanol while emissions of acetone and methacrolein were significantly higher from iso-butanol. Thus, NMOG was unaffected.
- Emissions of 1,3-butadiene were generally unaffected.
- The 12% iso-butanol/7% ethanol blend significantly reduced NMOG emissions relative to E0 because both carbonyl and unburned alcohol emissions were lower than for blends containing the individual alcohols.

REFERENCES

1. Christensen, E., Yanowitz, J., Ratcliff, M., McCormick, R.L. "Renewable Oxygenate Blending Effects on Gasoline Properties" *Energy Fuels* **2011**, *25*(10): 4723-4733.

2. Andersen, V.F., Anderson, J.E., Wallington, T.J., Mueller, S.A., Nielsen, O.J. "Vapor Pressure of Alcohol-Gasoline Blends" *Energy Fuels* **2010**, *24*(6): 3647-3654.

3. Andersen, V.F., Anderson, J.E., Wallington, T.J., Mueller, S.A., Nielsen, O.J. "Distillation Curves for Alcohol−Gasoline Blends" Energy Fuels 2010**,** 24(4): 2683-2691.

4. Reuter, R.M., Benson, J.D., Burns, V.R., Gorse, R.A., Hochhauser, A.M., Koehl, W.J., Painter, L.J., Rippon, B.H., Rutherford, J.A. "Effects of Oxygenated Fuels and RVP on

TABLE 2. Summary of Alcohol and Key Carbonyl Emissions (composite mg/mile)

Fuel Blend	mg/mile							
	Form-aldehyde	Acet-aldehyde	Acetone	Meth-acrolein	Butyr-aldehyde	Carbonyl Total	Alcohol Total	Combined Total
E0	0.80	0.35	0.29	0.16	0	1.60	0	1.60
E15	0.86	0.87	0.17	0.14	0	2.04	1.38	3.42
nBu24	1.06	0.91	0.17	0.19	0.57	2.90	0.17	3.07
iBu24	1.28	0.39	0.65	0.40	0.13	2.85	0.30	3.15
iBu12E7	0.95	0.54	0.26	0.34	0	2.09	0.47	2.56

Automotive Emissions - Auto/Oil Air Quality Improvement Program" SAE Techn. Pap. No. 920326, 1992.

5. Knoll, K., West, B., Huff, S., Thomas, J., Orban, J., Cooper, C. "Effects of Mid-Level Ethanol Blends on Conventional Vehicle Emissions" SAE Techn. Pap. No. 2009-01-2723, 2009.

6. Stansfield, P.A., Bisordi, A., OudeNijeweme, D., Williams, J., Gold, M., Ali, R. "The Performance of a Modern Vehicle on a Variety of Alcohol-Gasoline Fuel Blends" SAE Techn. Pap. No. 2012-01-1272, 2012.

7. Schulz, M., Clark, S. "Vehicle Emissions and Fuel Economy Effects of 16% Butanol and Various Ethanol Blended Fuels (E10, E20 and E85)" DOI: 10.1520/JAI103068, February 2011.

8. Gautam, M., Martin, D.W., Carder, D. "Emission characteristics of higher alcohol/gasoline blends" Proc. Inst. Mech. Engrs. 2000, 214, Part A:165-182.

9. Furey, R., King, J.B. "Emissions, Fuel Economy, and Driveability Effects of Methanol/Butanol/Gasoline Fuel Blends" SAE Techn. Pap. No. 821118, 1982.

10. Wilks, C. "Butanol – The Advanced Biofuel" Presented to Japanese Petroleum Institute Symposium, November 2008.

11. Vertin, K., Glinsky, G., Reek, A. "Comparative Emissions Testing of Vehicles Aged on E0, E15 and E20 Fuels" Subcontract Report NREL/SR-5400-55778, August 2012.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Tao, L., Aden, A., He, X., Tan, E.C.D., Zhang, M., Zigler, B.T., McCormick, R.L. "Techno-economic Analysis and Life-cycle Assessment of Cellulosic Iso-Butanol and Comparison with Cellulosic Ethanol and n-Butanol" in preparation.

2. Ratcliff, M., Luecke, J., Williams, A., Christensen, E., Yanowitz, J., McCormick, R.L. "Air Pollutant Emissions from a Tier 2 Bin 5 Vehicle Fueled with Higher Alcohol Blends" in preparation.

3. Knoll, K., Kemper, J., Yanowitz, J., Luecke, J., McCormick, R.L. "The Impact of Adaptation on Flex-Fuel Vehicle Emissions When Fueled with E40" submitted.

IV.10 Assessment of Bi-Fuel CNG Light-Duty Passenger Vehicles with Home Refueling

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Objectives/Fiscal Year (FY) 2012 Objectives (single-year project)

- Take concepts successfully developed for plug-in hybrid vehicles (PHEVs, also considered a “bi-fuel” vehicle) that estimate in-use customer electric driving fractions and apply them for bi-fuel compressed natural gas (CNG)/gasoline vehicle assessments.
- Estimate the incremental vehicle costs for a bi-fuel vehicle compared to a conventional gasoline vehicle based upon the most current public data and estimates from leading supplier experts.
- Estimate the amount of fuel displaced and fuel costs using the PHEV-derived analysis tools.
- Use various vehicle design parameters and use case scenarios as inputs, calculate the net costs and cost savings and/or payback periods.

Accomplishments

- A sophisticated analysis spreadsheet was developed that can calculate vehicle costs, home compressor costs, fuel usage, and ultimately, payback periods and net savings based upon a large list of input assumptions.
- Fuel savings and net costs were analyzed for both a midsized vehicle and a full-sized pickup truck based upon both driving statistics (total fleet) and usage case scenarios (e.g. short and long commuter case).
- Analysis shows that significant gasoline savings in both vehicle cases, is appreciated with modest sized tanks (75-100 miles range). However, only the full-sized pickup truck results in net cost savings with current technology costs.
- However, if the Advanced Research Projects Agency-Energy (APRA-E) goal of $500 for a consumer home refueling appliance (HRA) is achieved, net cost savings can also be realized for the bi-fuel mid-size passenger car.

Future Directions

- Further analysis should include improved input assumptions based upon the most contemporary data. For example:
  - A state-of-the-art bi-fuel VW Passat from Europe will be dynamometer tested. Test and analyze the best data that demonstrate bi-fuel efficiency penalties. This data will update input assumptions that estimate relative rates of gasoline and CNG fuel consumption (including real-world driving patterns).
  - The testing and results from initial test results from the APRA-E HRAs can be used to further refine input assumptions.
- This analysis is focused on Type-1 steel tanks, further development could include cost models for new generation composite tanks to find weight/size savings compared to costs.

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INTRODUCTION

Although much progress has been made in recent years, battery-powered vehicles suffer from limited range due to low energy density of batteries compared to combustion fuels. In the 1990s the PHEV was proposed as a compromise solution that could achieve electric operation for most of daily driving without meeting maximum daily driving (range) requirements. Analysts knew that even a range of 40 miles could satisfy a reasonably high percentage of miles traveled if the vehicle is recharged (refueled) at home every night. Based upon transportation surveys of a large population in the U.S., the percentage of miles for a given PHEV range can be estimated, this is called the “Utility Factor.” These calculations are the basis for SAE International standards J1711 and J2841 that provide the percentage weighting for charge-depleting operation mode for a given range of that mode. For example, 20 miles electric-only range provides an estimated 40% electric utility, 40 miles range provides 62% and if the range were 100 miles, the utility is as high as 86% for a PHEV.

The bi-fuel CNG vehicle has many similar properties to the PHEV with regards to initial higher costs, challenging energy storage issues, home refueling (recharging) and reduced alternative energy usage costs. By refueling every night and only including tank storage for a reasonable alternative fuel range, the "bang-for-the-buck" can be fine-tuned based upon a number of vehicle attributes. The objective of this project was to study these attributes as they affect vehicle costs, fuel cost savings and the potential fuel savings of bi-fuel vehicles as an early adoption CNG strategy. The advantage is that one does not need to wait for widespread refueling infrastructure to begin displacing fuel in the largest petroleum market segment, the light-duty passenger car.

APPROACH

A sophisticated analysis spreadsheet was used to calculate overall results for a large set of input parameters and assumptions chosen by the user. The CNG consumption is based upon the baseline vehicle gasoline fuel economy (an efficiency penalty is built-in based upon current bi-fuel vehicles). The tank size is an input parameter that along with the CNG fuel consumption assumption determines range. Costs from a tank cost model (based upon the tank size input) are added to fixed fuel system hardware and HRA costs to define the bi-fuel vehicle's added initial costs. The range determines the amount of CNG and gasoline consumption (based upon a utility factor analysis). The respective vehicles fuel costs are compared to total initial costs and HRA maintenance costs to determine if there are ownership savings during the first five years (during a typical purchase loan payback period). Given that more than half of new cars are purchased using financing, a new vehicle choice should provide cost savings throughout this period of ownership.

Although any particular vehicle can be analyzed, two specific cases of high-volume light-duty vehicles were examined in detail. One was a mid-size passenger car (similar to Ford Fusion, or Toyota Camry), the other a full-size pickup (similar to Ford F-150, Chevy Silverado, or Dodge Ram, which combined account for 42% of sales of the top ten light-duty vehicles sold in the U.S.). As tank size is increased, CNG fuel use increased (i.e. cost savings). However, the tank and compressor costs also increase. Tank optimums for both vehicles were found to provide roughly 100 miles CNG range (higher than our initial 75-mile range assumption). Current bi-fuel vehicles are not necessarily designed for home refueling and thus they tend to have much greater CNG range capabilities (with significant weight and cost penalties). The 100-mile capable CNG tanks size were found to be manageable with little overall design changes. This was verified with test cars fitted with cardboard dummy tanks in the appropriate sizes in a Ford Fusion in the trunk area and the Ford F-150 pickup under the bed.

RESULTS

The fleet utility factor (UF) is the percentage of miles driven by a large fleet of PHEVs or bi-fuel vehicles for a given electric or CNG range. Figure 1 shows the UF from SAE J2841 for ranges from 0 to 150 miles (100 miles noted by the red dot). Note that as the range approaches 150 miles, the additional utility gained for each additional mile range has diminished considerably.

The utility factor analysis shows dramatic fuel savings for a modest 100-mile CNG range. For the mid-size vehicle, this equates to a CNG tank that holds 4.0 gasoline-equivalent gallons of CNG, the full-size pickup CNG tank holds 5.5 equivalent gallons. The 86% petroleum savings is substantial, comparing the baseline mid-size vehicle to other technologies; the bi-fuel can displace more gasoline than any of the other advanced technologies listed in Figure 2, including the smaller-sized Chevy Volt.

A vehicle purchase and operational cost model for the two bi-fuel CNG vehicles cases were compared to their baseline counterparts. The accumulated savings scenarios (positive and negative) are plotted over time for new vehicle purchase with financing over a 5-year payback period. Virtually all vehicle design options and assumptions were able to payback the added costs before the end of useful vehicle life. However, for wide-spread consumer interest, the move to a new technology will have to be associated with net cost savings throughout ownership. In other words, will the bi-fuel CNG customer be paying less in ownership (higher car payments

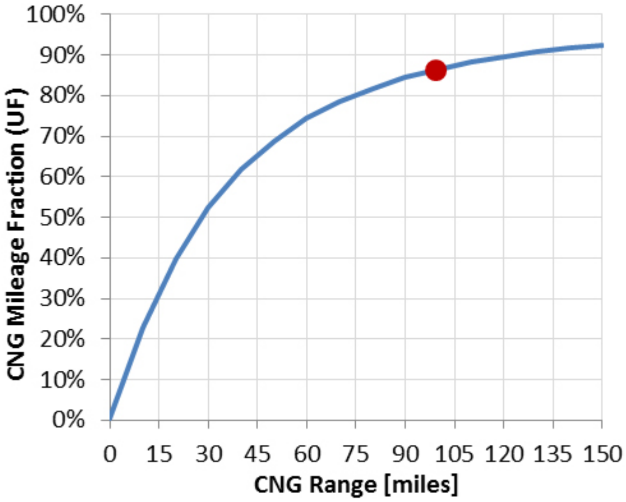


FIGURE 1. UF Curve – Bi-fuel vehicles with 100 miles CNG range are expected to drive 86% of their miles on CNG.

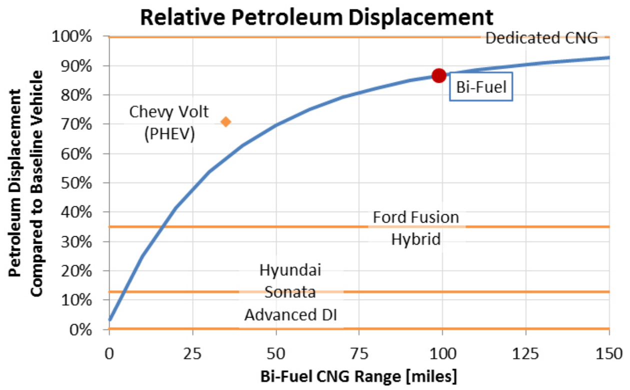
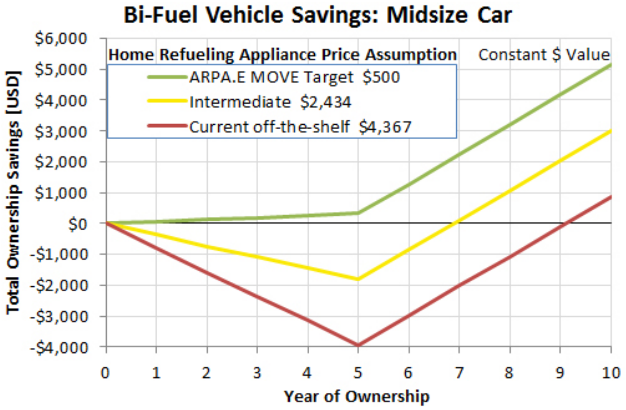


FIGURE 2. Petroleum displacement of bi-fuel vehicles and other advanced technologies compared to the baseline gasoline mid-size vehicle.

and lower fuel costs) per month than the conventional vehicle (with lower payments and higher fuel costs)? The analysis presents "typical" results (driver-weighted probability) according to another PHEV analysis tool termed the "Individual Utility Factor." Figures 3 and 4 are the calculated total ownership savings for the mid-size car and the full-size pick-up respectively. The payback is most sensitive to HRA cost assumptions, thus the analysis was made for three cost cases, one is current costs (modest volumes), another is the $500 Advanced Research Projects Agency-Energy (ARPA-E) cost target, and the third is an intermediate cost.

Given that not all customers drive "typical" daily distances, some potential consumers may achieve net savings under longer-distance commuting scenarios. The analysis tool developed allows for calculating yearly operating cost savings based upon a particular commuting scenario. One-way commuting distances with conservative weekend miles provides the results shown in Figure 5. These results are a guide to what part of the market could be able to achieve a reasonable payback period. Although an average commuter in a midsize vehicle has only a yearly savings of around $1,000, this amount doubles if we consider one-way daily commuters over 43 miles.

Without any cost breakthroughs the bi-fuel vehicle with home refueling is roughly $7,500 more than a baseline conventional counterpart. However, if the home refueling appliance cost is reduced to $500, and the other additional component costs can also be squeezed, it is estimated that the initial costs could be as low as $2,500, an amount low enough for widespread customer overall cost savings in the pickup market. A combination of breakthrough HRA cost reductions and slightly longer-than-average commutes would extend savings into the midsize market segment.



USD - U.S. dollars

FIGURE 3. Typical ownership savings for bi-fuel midsize car (only positive if ARPA-E cost targets met).

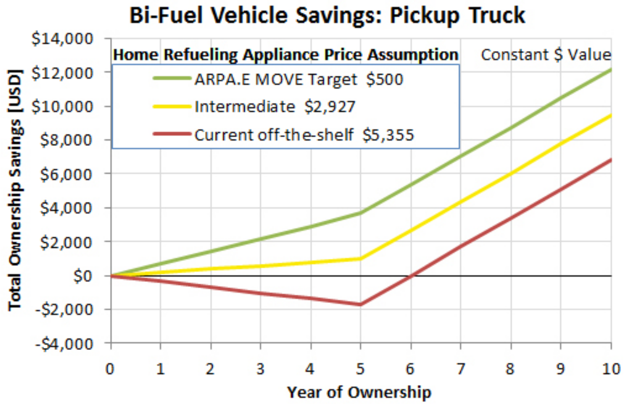


FIGURE 4. Typical ownership savings for bi-fuel full-sized pickup truck – positive if existing home compressors were significantly reduced.

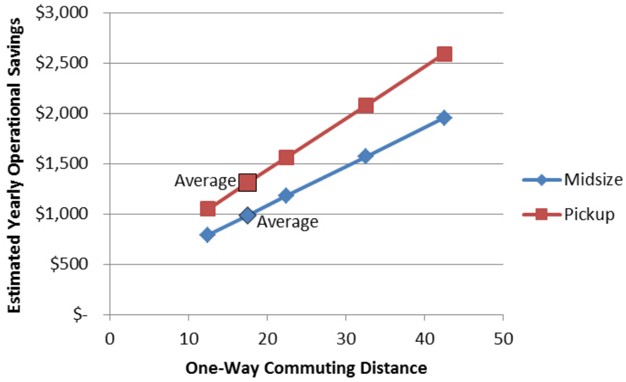


FIGURE 5. Cost savings with varying on-way commuting distances.

CONCLUSIONS

This study utilized some established methods for PHEV analysis and the best cost data available to look at the feasibility of bi-fuel CNG vehicles with home refueling as a cost-attractive option for light-duty vehicles. Bi-fuel vehicle cost attractiveness has been validated with medium-duty bi-fuel CNG trucks as they are now being marketed to fleets by several manufacturers. However, given the huge fuel displacement potential in the light-duty market, this cost/design study was undertaken.

The principal deliverable of this project was the highly complex spreadsheet model that provides net costs based upon dozens of input assumptions and variables. The analysis is easily repeated for any known light-duty vehicle. Two cases were closely studied to illustrate the potential of the home-refueled bi-fuel CNG light-duty vehicle.

The findings of the study reveal the following:

- Using the utility factor curve as a guide, the required CNG range for significant fuel displacement and thus the required tank size is not terribly demanding. Inexpensive steel tanks are assumed in this study for CNG operation of 75-100 miles range.
- Although many factors are involved with finding an "ideal" or "optimum" CNG tank size, reduced gasoline savings above 100 miles does not provide enough cost savings to warrant tanks providing greater than a 100 mile range (4.0 to 5.5 gallon gasoline equivalent).
- A large fleet of bi-fuel vehicles with 100 miles CNG range is estimated to displace 86% of the gasoline fuel usage. This is a higher fuel displacement than PHEVs (with less than 95 miles range) and battery electric vehicles (BEVs, with less than 135 miles range, see SAE 2013-01-1474 [3] for the BEV utility factor data).
- Steel tank costs are well understood. However, there are significant uncertainties in vehicle fuel system and home refueling appliance costs. The incremental costs for a high-volume, manufacturer-supplied bi-fuel vehicle compared to a conventional baseline are roughly $1,500 for the vehicle components, and $3,500 for the refueling compressor (plus installation).
- Although fuel costs savings are very favorable, high HRA costs drive the payback dynamics.
- With high-volume vehicle components and current home refueling technology, cost savings is not found in either the passenger car or full-size pickup.
- With a 50% cost reduction in the home refueling appliance, savings is found in the pickup truck (but not the passenger car).
- A breakthrough in low-cost refueling devices will completely change the cost drivers. If the $500 ARPA-E HRA target cost is met, cost parity is found in the passenger car and significant additional savings is found in the pickup truck.
- Without cost reductions in the home refueling appliance, cost savings is only possible for customers with longer-distance commutes. Only modestly longer distances are needed for pickup truck customer cost savings. However, the passenger car customer must commute very long-distances (>60 miles each way) to achieve cost parity. Although the market fraction of the long-distance commuter is limited, the proportion of fuel consumed by this market is quite significant.

REFERENCES

1. SAE International Surface Vehicle Recommended Practice, "Recommended Practice for Measuring the Exhaust Emissions and Fuel Economy of Hybrid-Electric Vehicles, Including Plug-in Hybrid Vehicles," SAE Standard SAE J1711, Rev. June 2010.

2. SAE International Surface Vehicle Recommended Practice, "Utility Factor Definitions for Plug-In Hybrid Electric Vehicles Using 2001 U.S. DOT National Household Travel Survey Data," SAE Standard SAE J2841, Rev. March 2009.

3. Duoba, M., "Developing a Utility Factor for Battery Electric Vehicles," SAE Technical Paper 2013-01-1474, 2012.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Duoba, M., "Bi-Fuel Home Refueling ("Piped-in NGV") Assessment," presentation given to DOE VT fuels staff, August 8, 2012.

IV.11 Emissions and Operability of Gasoline, Ethanol, and Butanol Fuel Blends in Recreational Marine Applications

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Objectives

- Assess suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications.
- Ensure engine operability on butanol blends for a wide range of recreational marine engine applications.
- Quantify emissions of recreational marine engines operated on butanol blends compared to gasoline and ethanol blends.
- Demonstrate durability of recreational marine engines when operated on butanol blends.

Fiscal Year (FY) 2012 Objectives

- Establish detailed performance and emissions baseline of commonly used recreational marine engines using ethanol and butanol blends employing laboratory engine testing.
- Collect in-use emissions data of commonly used recreational 2- and 4-stroke marine engines employing field vessel testing.
- Evaluate the impact of fuel dilution on the lubrication performance of marine engine oil.

Accomplishments

- Engine lab testing with 10% ethanol in gasoline (E10) and 16 vol% gasoline iso-butanol (iso-But16) showed a 20-40% decrease in CO emissions relative to Indolene for the 4-stroke and 2-stroke direct injection engines. Reduction in CO using E10 was slightly higher compared to the iso-B16 alcohol blend. Oxides of nitrogen (NOx) emissions increased for both engines by 10-30% using alcohol blends. Overall net emissions were similar between the E10 and iso-But16 alcohol blends for each engine technology.
- In-use vessel testing with Indolene, E10 and iso-But16 showed a 20, 70 and 10% reduction in CO, NO, and total hydrocarbon (THC) emissions for 2-stroke engines when using alcohol blends. 4-stroke engines showed a 5-20% reduction in CO emissions but a 10-40% increase in NO emissions. No significant emissions differences between E10 and iso-But16 were found regardless of engine technology.
- Friction, wear and scuffing tests suggest that the presence of bio-based components (E10, iso-But16) in the fuel results in a slight friction reduction but a noticeable reduction in scuffing load compared to the baseline case.

Future Directions

- Conduct end-of-life performance and emissions laboratory tests upon completion of run-time accumulation.
- Perform laboratory engine testing with focus on engine cold start performance and particulate matter emissions assessment.
- Extend test matrix to include tri-fuel blend (gasoline/ethanol/butanol) combustion analysis and emissions on laboratory engine as well as tri-fuel blend field evaluation.
- Assess the wear mechanisms in samples tested with clean engine oils and oils contaminated with different levels of fuel for E0, E10 and iso-But16 fuels. If possible, wear mechanisms in engine components after teardown will also be evaluated. Attempt to develop a correlation of wear mechanisms in laboratory tested samples and engine tested components.

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INTRODUCTION

The Renewable Fuel Standard under the Energy Independence and Security Act of 2007 mandates an increase in the volume of renewable fuel to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022 [1]. This mandate is estimated to result in a hypothetical ethanol blend ratio of 24-29 vol-% in 2022 [2]. In order to further increase the renewable fuel fraction in transportation fuels, the U.S. Environmental Protection Agency recently granted a waiver for use of 15 vol-% ethanol blends (E15) in model year 2001 and newer light-duty motor vehicles [3].

The impact of extended ethanol blends and other alcohol fuels on recreational marine engines and vessels is widely unknown. However, given the dominant engine control strategies employed and materials used in the legacy marine fleet, it is suspected that increased ethanol levels can have detrimental effects on engine and vessel operation, performance, durability and emissions. Therefore, this project investigates the potential of iso-butanol as an alternative to ethanol as a blend component for recreational marine applications.

APPROACH

The project is designed to provide a comprehensive assessment of the impact of iso-butanol as a blending agent for a range of recreational marine engine applications. The assessment includes laboratory and in-use vessel testing of engine performance and emissions at several stages during the useful life of typical recreational marine 2-stroke and 4-stroke engines. Several test engines as well as vessels are operated for extended periods of time to evaluate the effects of iso-butanol on engine durability compared to certification gasoline and typical ethanol blends. Upon completion of the durability runs, engines are inspected and torn down to evaluate the fuel impact on engine components. In parallel, tests are conducted to assess the impact of ethanol and butanol blends on oil dilution and the lubrication performance of marine engine oil.

RESULTS

The initial phase of this project focuses on a relative comparison of gasoline-ethanol blends and gasoline-butanol blends compared to neat gasoline reference fuel (Indolene) as a baseline. Currently alcohol content in transportation fuels is limited by oxygen content and E10 is widely used throughout the United States.

Butanol exists in four isomers that differ in structure resulting in a variation of fuel properties. Due to its higher knock resistance compared to the other isomers, iso-butanol is being promoted by several fuel producers (e.g. BP, Gevo) and was selected for this study. Butanol is a four-carbon alcohol and has an oxygen content of 21.6 wt% compared to 34.7 wt% of ethanol. Therefore the iso-But16 blend was selected since it has equal oxygen content (3.5 wt%) to E10.

Engine Lab Testing

Three engine models from three different marine engine manufacturers were selected for laboratory emissions testing and useful life endurance testing. The engines include (2) 10 H.P Tohatsu 4-stroke carbureted outboards, (2) 90 H.P Mercury 4-stroke fuel-injected outboards and (2) 200 H.P Evinrude 2-stroke direct fuel-injected outboards. All engines operate open-loop without the use of lambda feed-back sensors. The Mercury and Evinrude engines were each baseline tested in the emissions laboratory according to the International Council of Marine Industry Associations (ICOMIA) test cycle (ISO8178) using three fuels, Indolene, E10 and iso-But16. The ICOMIA test is a 5-mode test that includes full load (Mode 1), engine idle (Mode 5) as well as three additional points covering the entire engine load and speed range. The emissions values for the operating points are weighted at 40% for idle, 25, 15 and 14% for the mid-load points and 6% for full load to provide one result value per test. Baseline emissions were recorded for each test fuel using an AVL i60 five-gas emissions analyzer.

Figure 1 shows the changes in CO, NOx and THC emissions with E10 and iso-But16 operation relative to the Indolene baseline for the Mercury and Evinrude engine. The Mercury engine showed a reduction in CO emissions of 35% and 38 % with iso-But16 and E10 respectively as compared to the Indolene baseline. The Evinrude showed a reduction in CO emissions of 15% and 22% with iso-But16 and E10 respectively relative to the Indolene baseline test fuel. The NOx emissions increased by approximately 30% for the Mercury and by approximately 12% for the Evinrude relative to the baseline Indolene test fuel. THC emissions showed a slight reduction for both the Mercury and the Evinrude using both alcohol fuels.

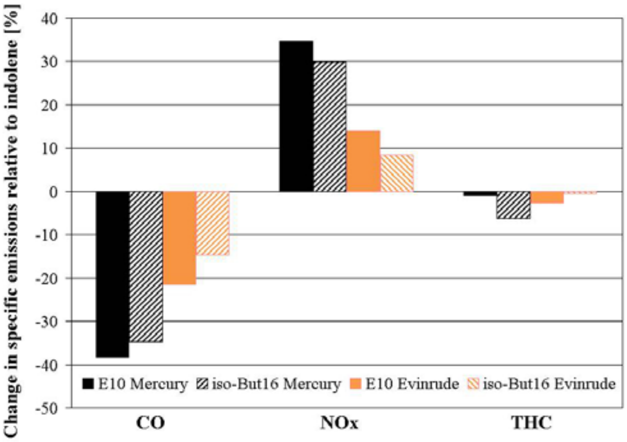

FIGURE 1. Average change in laboratory cycle-weighted emissions for E10 and iso-But16 operation compared to Indolene.

Engine endurance testing is ongoing with one engine from each set of engines operating on E10 and the other engine from each set operating on iso-But16. Upon completion of endurance testing, all engines will be emissions-tested and then torn-down to inspect and compare engine components.

In-Use Vessel Testing

Three vessel/engine combinations were selected for the in-use testing performed in May and September 2012 near Annapolis, MD. The tested engines include an INDMAR 6.0-l L96 V8 4-stroke engine in a Malibu Wakesetter Ski Boat, a Volvo Penta 5.7-l Gxi V8 4-stroke engine in an Alamar Aluminum Hull boat and an OMC Johnson Legacy 2.6-l, 6-cylinder 2-stroke outboard engine in a Promarine Fiberglass Inc "Intruder" boat. The vessels were tested according to the ICOMIA test cycle (ISO8178) and a Marine Portable Bag Sampling System [4] and Sensors, Inc. Semtech-DS Onboard Vehicle Emissions Analyzer were used to collect emissions data.

Figure 2 shows the changes in CO, NO and THC emissions with E10 and iso-But16 operation relative to the Indolene baseline for the INDMAR, Volvo Penta and OMC Johnson engines. The INDMAR engine showed a reduction in CO emissions of approximately 4% with E10 as well as iso-But16 compared to the Indolene baseline while the other two engines showed an approximately 20% reduction regardless of alcohol used for blending. The NO emissions increased for the two 4-stroke engines while a significant decrease was observed for the 2-stroke engine. THC emissions showed an inconclusive trend for the 4-stroke engines and a slight decrease for the 2-stroke engine. Overall emissions for the iso-butanol blend are equal or slightly lower compared to the ethanol blend.

The emissions trends are likely caused by variations in air/fuel ratio. Typical emissions trends for spark ignition engines include a reduction of THC and CO emissions with leaner operation and an NO peak at $\lambda \sim 1.05$. The two 4-stroke engines employ closed-loop feedback control to maintain stoichiometric air/fuel ratios in order to maximize the efficiency of the aftertreatment system. At full-load conditions the engine controller deviates from stoichiometric operation and operates fuel-rich to reduce exhaust temperatures and prevent engine knock. The OMC Johnson 2-stroke engine uses a carburetor, has no closed-loop feedback control and no emissions aftertreatment system.

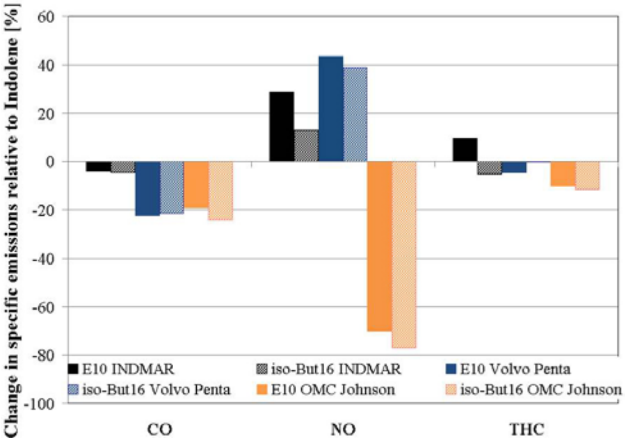

FIGURE 2. Change in cycle-weighted emissions for E10 and iso-But16 operation compared to Indolene.

Figure 3 shows the relative air/fuel ratio for all three engines at the different modes throughout the ICOMIA test. The INDMAR and Volvo Penta 4-stroke engines operate at close to stoichiometric air/fuel ratios regardless of fuel except for full load operation (Mode 1). Thus the changes in emissions shown in Figure 2 likely result from leaner operation at full load when using alcohol blends compared to Indolene. The OMC Johnson engine operates open-loop and air/fuel ratios using alcohol blends are generally leaner compared to Indolene operation except for engine idle (Mode 5). The increased air/fuel ratios are consistent with a decrease in CO and THC emissions as shown in Figure 2. The significant reduction in NO emissions is inconsistent with the general emissions trend and could be due to additional charge cooling from the alcohol fuel, uncertainties in the

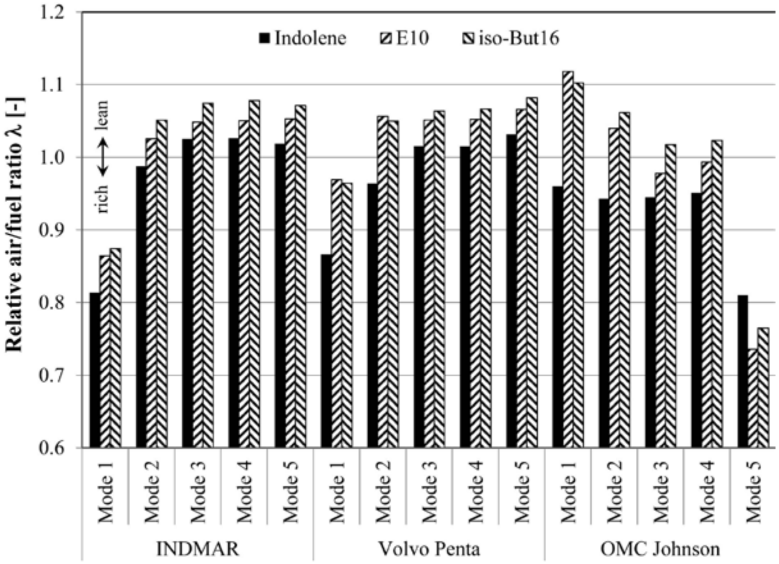

FIGURE 3. Relative air/fuel ratio for E10 and iso-But16 operation compared to Indolene.

air/fuel ratio determination of the modal data as well as the richer operation at the heavily weighted idle point.

Lubricants Testing

Four different types of bench top friction and wear tests were conducted to assess the impact of fuel dilution on the lubrication performance of marine engine oil. The tests included unidirectional and reciprocating sliding and 4-ball test for friction and wear as well as block-on ring for scuffing. Three groups of engine oils were used for the tests including fresh engine oil (Yamalube 4M 10W30), surrogate model oils with 5, 10, 20, 30 and 50% of fuel (E0, E10 and iso-But16) added as well as used engine oil from a Yamaha test boat subjected to a sequence of 60 cold-start cycles with oil samples taken at 15-cycle intervals.

The tests on the surrogate oils suggest that average friction for all the oils is nearly identical and that fuel dilution resulted in a slight reduction of scuffing load and increased wear in proportion to fuel content regardless of fuel type compared to fresh oil.

The analysis of the oil generated from the cold-cycle tests showed a nearly linear reduction in viscosity as well as an increase in fuel dilution of the engine oil with increasing number of test cycles with no significant differences between E0, E10 and iso-But16.

Figure 4 shows the results of the 4-ball test and Figure 5 shows the scuffing test results for fresh oil as well as the oils from the Yamaha test boat cold start cycles. It appears that the presence of bio-based components (E10, iso-But16) in the fuel results in a slight friction reduction compared to the baseline case. However, oil dilution by bio-based containing fuels (E10 and iso-But16) also resulted in a noticeable reduction in scuffing load. No significant differences between E10 and iso-But16 were discovered.

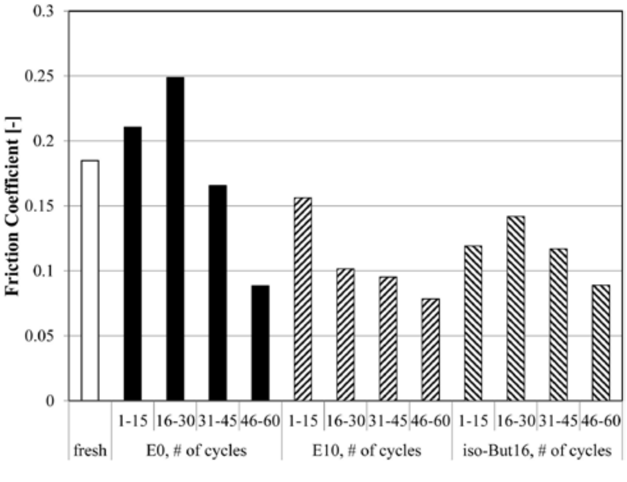

FIGURE 4. 4-ball test friction results for used oils from Yamaha engine tests.

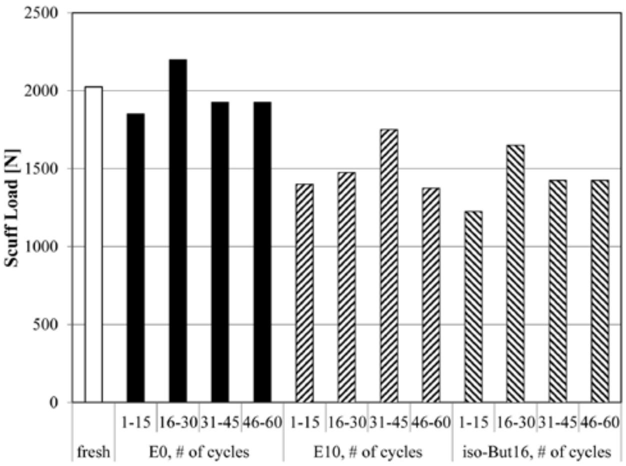

FIGURE 5. Scuffing test results for used oils from Yamaha engine tests.

CONCLUSIONS

- Engine lab testing with E10 and iso-But16 showed a decrease in CO emissions relative to Indolene for the 4-stroke and 2-stroke direct injection engines. Reduction in CO using E10 was slightly higher compared to the iso-B16 alcohol blend. NOx emissions increased for both engines using alcohol blends. Overall net emissions were similar between the E10 and iso-B16 alcohol blends for each engine technology.
- In-use vessel testing with Indolene, E10 and iso-But16 showed a reduction in NO, THC and CO emissions for 2-stroke engines when using alcohol blends. 4-stroke engines showed reduced THC and CO emissions but increased NO emissions. No significant emissions differences between E10 and iso-But16 were found regardless of engine technology.
- Friction, wear and scuffing tests suggest that the presence of bio-based components (E10, iso-But16) in the fuel results in a slight friction reduction but a noticeable reduction in scuffing load compared to the baseline case.

REFERENCES

1. Section 201-202 Renewable Fuel Standard (RFS) Energy Independence and Security Act of 2007 (Pub.L. 110-140, originally named the CLEAN Energy Act of 2007).

2. Ickes, A. 'Improving Ethanol-Gasoline Blends by Addition of Higher Alcohols' 18th Directions in Engine-Efficiency and Emissions Research (DEER) Conference. Dearborn/MI. 2012.

3. Environmental Protection Agency (EPA) 'Partial Grant of Clean Air Act Waiver Application Submitted by Growth Energy To Increase the Allowable Ethanol Content of Gasoline to 15 Percent'; Federal Register Vol. 76, No. 17. 2011.

4. Wasil, J., McKnight, J., Kolb, R., Munz, D. et al., 'In-Use Performance Testing of Butanol-Extended Fuel in Recreational Marine Engines and Vessels,' SAE Technical Paper 2012-32-0011, 2012, doi:10.4271/2012-32-0011.

FY 2012 PUBLICATIONS/PRESENTATIONS

1. Sevik, J. 'Exhaust emissions of low level blend alcohol fuels from two-stroke and four-stroke marine engines' Master Thesis. 2012.

2. Wasil, J. '1991 – 2011: A 20 Year History of Biofuels policy and the impact on the Recreational Marine Industry' Seminar 409: 'Boat Fuel and Fuel Systems: Designing Boats to Meet EPA Rules' The International BoatBuilders' Exhibition & Conference. Louisville, KY. 2012.

3. Wallner, T. 'Butanol Blends as Marine Fuels - An Overview' Seminar 409: 'Boat Fuel and Fuel Systems: Designing Boats to Meet EPA Rules' The International BoatBuilders' Exhibition & Conference. Louisville, KY. 2012.

4. Wasil, J., McKnight, J., Kolb, R., Munz, D. et al., 'In-Use Performance Testing of Butanol-Extended Fuel in Recreational Marine Engines and Vessels,' SAE Technical Paper 2012-32-0011, 2012, doi:10.4271/2012-32-0011.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. In-use testing work featured in an article and video on www.boats.com by Lenny Rudow http://blog.boats.com/2012/05/butanol-the-next-great-biofuel-for-boats/

2. Press release published on www.boatingindustry.com on May 9, 2012 http://www.boatingindustry.com/news/2012/05/09/brp-to-begin-testing-next-generation-biofuel/

3. 'Isobutanol Testing, Round Two' published in Boat U.S. Magazine's News From The World Of American Boating in August/September 2012 http://www.boatus.com/magazine/2012/august/BoatUS-Reports-Jurisdictions-Target-Boat-Gatherings.asp

V. Acronyms, Abbreviations and Definitions

η_{th}	Thermodynamic cycle efficiency
γ	Ratio of specific heats
μl	Micro-liter
ϕ	Fuel/air-equivalence ratio
$\eta_{f,ig}$	Gross indicated fuel-conversion efficiency
°F	Degrees Fahrenheit
% w/w	% weight/weight
1-D	One-dimensional
2D-GC	2-dimensional gas chromatograph
2-D	Two-dimensional
AC&F	Advanced Combustion and Fuels
ADC	Advanced distillation curve
AF	Air/fuel ratio
AFR$_{st}$	Stoichiometric air/fuel ratio
AMN	Alpha methyl naphthalene
APBF	Advanced petroleum-based fuels
API	American Petroleum Institute
ARPA-E	Advanced Research Projects Agency-Energy
ASTM	ASTM International, a standards setting organization
atdc, ATDC, aTDC	After top-dead center
ATEAM	Analytica Transportation Energy Analysis Model
a.u.	Arbitrary units
AVFL	Advanced Vehicles Fuels and Lubricants
AW	Anti-wear
B6	6% biodiesel
B20	20% biodiesel
B100	100% biodiesel
BDC	Bottom dead center
BET	Named after Brunauer, Emmett and Teller, this method for determining the surface area of a solid involves monitoring the adsorption of nitrogen gas onto the solid at low temperature and, from the isotherm generated, deriving the volume of gas required to form one monolayer adsorbed on the surface. This volume, which corresponds to a known number of moles of gas, is converted into a surface area though knowledge of area occupied by each molecule of adsorbate.
BEV	Battery electric vehicle
BMEP	Brake mean effective pressure
BOB	Blendstock for oxygenate blending
BSFC	Brake specific fuel consumption
BTE	Brake thermal efficiency
Bxx	Biodiesel blend containing xx volume percent biodiesel
CA50	Crank angle at which 50% of the combustion heat release has occurred
CARB	California Air Resources Board
CDC	Conventional diesel combustion
CFD	Computational fluid dynamics
CFPP	Cold filter plugging point
CI	Compression ignition
CL	Chemiluminescence
CLCC	Closed-loop combustion control
CLEERS	Cross-Cut Lean Exhaust Emissions Reduction Simulations
CME	Canola methyl ester
CMOS	Complementary metal-oxide semiconductor
CN	Cetane number
CNG	Compressed natural gas
COV	Coefficient of variation
CP	Cloud point
CPChem	Chevron-Phillips Chemical Company
CR	Compression ratio
CRADA	Cooperative Research and Development Agreement
CRC	Coordinating Research Council
CSM	Colorado School of Mines
CSFT	Cold soak filtration test
CT	Carbon-bond type
CuME	FAME derived from Cuphea oil
DCN	Derived cetane number
DEER	Diesel Engine Emissions Reduction
degCA	Degrees crank angle
DI	Direct-injection
DISI	Direct-injection spark ignition
DNPH	2,4-dinitorophenylhydorazine
DOC	Diesel oxidation catalyst
DOSY	Diffusion-ordered spectroscopy
DPF	Diesel particulate filter
DRIFTS	Diffuse reflectance infrared Fourier-transform spectroscopy

DSC	Differential scanning calorimetry
E15	15% ethanol, 85% gasoline fuel blend
E20	20% ethanol, 80% gasoline fuel blend
E50	50% ethanol, 50% gasoline fuel blend
E85	Nominally 85% ethanol/15% gasoline blend which can actually range from 51–83% per ASTM D5798
ECM	Engine control module
ECS	Emission control system
ECU	Electronic control unit
EDS	Energy-dispersive X-ray spectroscopy
EEPS	Engine exhaust particle sizer
EGO	Exhaust gas oxygen
EGR	Exhaust gas recirculation
EHL	Elastohydrodynamic lubricant
EISA	Energy Independence and Security Act of 2007
EIVC	Early intake valve closing
ELOC	Extended lift-off combustion
EOI	End of injection
EPA	Environmental Protection Agency
EPMA	Electron probe microanalysis
η_{th}	Thermodynamic cycle efficiency
ETC	Environmental Testing Corporation
ETE	Ethyltetrahydrofurfuryl ether
Exx	xx% ethanol, 100-xx% gasoline fuel blend
FACE	Fuels for Advanced Combustion Engines
FAME	Fatty acid methyl ester
FE	Fuel economy
FFV	Flexible-fuel vehicle; flex-fuel vehicle
FID	Flame ionization detector
FMC	Ford Motor Company
FMT	Final melting temperature
FSN	Filter smoke number
FTP	Federal Test Procedure
FTP-75	Federal Test Procedure for LD vehicles
FU	Fleet utility
GC	Gas chromatography
GC-FID	Gas chromatography/flame ionization detector
GC-FIMS	Gas chromatography field ionization mass spectrometry
GC-MS	Gas chromatography – mass spectrometry
GDI, GDi	Gasoline direct injection
GHG	Greenhouse gas
GTDI	Gasoline turbocharged direct injection
GTL	Gas to liquid
HC	Hydrocarbon
HCCI	Homogeneous charge compression ignition
HD	Heavy-duty
HECC	High-efficiency clean-combustion
HFET	Highway Fuel Economy Test
HFRR	High frequency reciprocating rig
HMBC	Heteronuclear multiple bond correlation
HMN	Heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane, a diesel primary reference fuel)
HPLC	High-performance liquid chromatography
HRA	Home refueling appliance
HRR	Heat release rate
HRTEM	High-resolution transmission electron microscopic
HSDI	High-speed direct injection
HSQC	Heteronuclear single quantum coherence
HTHS	High-temperature high-shear
HVA	Hydraulic valve actuator
ICOMIA	International Council of Marine Industry Associations
IL	Ionic liquid
ILSAC	International Lubricants Standardization and Approval Committee
$IMEP_{gross}$	Indicated mean effective pressure, gross
$IMEP_{net}$	Indicated mean effective pressure, net over all four strokes
IQT™	Ignition Quality Tester
ISFC	Indicated specific fuel consumption
ISCO	Indicated specific carbon monoxide
ISHC	Indicated specific hydrocarbons
$ISNO_X$	Indicated specific emissions of nitrogen oxides
ITE	Indicated thermal efficiency
IVD	Intake valve deposit
kPa	Kilopascals
KIVA	Combustion analysis software developed by Los Alamos National Laboratory
LC/MS	Liquid chromatography with mass spectrometric detection
LED	Light-emitting diode
LEV	Low Emission Vehicle
LFT	Learned fuel trim (or long-term fuel trim)

LHV	Lower heating value; latent heat of vaporization
LIVC	Late intake valve closing
LL	Liquid length
LNG	Liquefied natural gas
LTC	Low-temperature combustion
LTFT	Low temperature flow test; long-term fuel trim
LTHR	Low temperature heat release
MAG	Monoglycerides
MBT	Maximum (spark advance) for best torque
MCE	Multi-cylinder engine
MECA	Manufacturers of Emission Controls Association
μl	Micro-liter
MFB	Mass fuel burned
MFB50	Crank angle where 50% of heat release has occurred
MFC	Model Fuels Consortium, a consortium run by Reaction Design to improve kinetic modeling tools and fuels and engine modeling tools.
MIL	Malfunction indicator lamp
MIT	Massachusetts Institute of Technology
ML	Mixed lubrication
MLEB	Mid-level ethanol blend
MOAT	Morris one-at-a-time
ng	Nano-gram
NHD	N-hexadecane
NMHC	Non-methane hydrocarbon
NMOG	Non-methane organic gases
NMR	Nuclear magnetic resonance
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
NVO	Negative valve overlap
OA	Oleic acid
ODT	Octadecane thiol
OEM	Original Equipment Manufacturer
OSC	Oxygen storage capacity
PAG	Polyalkylene glycol
PAH	Polycyclic aromatic hydrocarbon
PAO	Polyalphaolefin
PCCI	Pre-mixed charge compression ignition
% w/w	% weight/weight
PFI	Port fuel injection, port fuel injected
PGM	Platinum group metal
PGSE	Pulse-gradient spin echo
PHEV	Plug-in hybrid electric vehicle
PIONA	Paraffins, iso-paraffins, olefins, naphthenes, and aromatics
PL	Pyrolysis liquids
PLIF	Planar laser induced fluorescence
PM	Particulate matter
PMEP	Pumping mean effective pressure
PN	Particulate number
POM	Polyoxometallate
ppb	Parts per billion
PRR	Pressure rise rate
RCCI	Reactivity-controlled compression ignition
RCM	Rapid compression machine
RD	Reaction Design
REx x	xx% ethanol, 100-xx% retail gasoline fuel blend
RFS	Renewable Fuel Standard
RFS2	Renewable Fuel Standard 2
RON	Research Octane Number
RPM, rpm	Revolutions per minute
SA	Spark assist, spark assisted
SA-HCCI	Spark-assisted homogeneous charge compression ignition
SCORE	Sandia Compression-ignition Optical Research Engine
SCR	Selective catalytic reduction
SEM	Scanning electron microscopy
SI	Spark ignition
SIDI	Spark ignition direct injection
SME	Soy methyl ester
SMG	Saturated monoglyceride
SMPS	Scanning mobility particle scanner
S_L	Laminer flame speed
SOC	Start of combustion; soluble organic compound
SOF	Soluble organic fraction
SOI	Start of injection
SRC	Standard Road Cycle
ST	Spark timing
SULEV	Super ultra-low emissions vehicle
SwRI®	Southwest Research Institute®
T_{bdc}	Bottom-dead-center temperature
T50	Temperature for 50% evaporated
TAN	Total acid number

TDC	Top-dead center
TDC_{exc}	Top-dead center (of gas-exchange strokes)
TDO	Thermal deoxygenation
TET	Tetralin
TGA	Thermo-gravimetric analysis
THC	Total hydrocarbon
THF	Tetrahydrofuran
TMB	1,2,4-trimethylbenzene
TPD	Temperature-programmed desorption
TPGME	Tri-propylene glycol methyl ether
TPO	Temperature-programmed oxidation
TRC	Transportation Research Center
TSI	Threshold sooting index
TWC	Three-way catalyst
UL	Underwriters Laboratory
ULEV	Ultra-low emission vehicle
ULG 91 RON	Unleaded gasoline 91 Research Octane Number
ULG 95 RON	Unleaded gasoline 95 Research Octane Number
ULSD	Ultra-low-sulfur diesel
UTG	Unleaded test gasoline
VOF	Volatile organic fraction
vol%	Volume percent
V-P	Viscosity-pressure
VVA	Variable valve actuation
WOT	Wide-open throttle
XRD	X-ray diffraction
XRF	X-ray fluorescence
ZDDP	Zinc dialkyl-dithiophosphate

VI. Index of Primary Contacts

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