Fuel & Lubricant Technologies

2013

VEHICLE TECHNOLOGIES OFFICE
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I. INTRODUCTION
I. Subprogram Overview and Status

I.1 ADVANCED FUELS AND LUBRICANTS FOR AN EFFICIENT, CLEAN, AND SECURE U.S. VEHICLE TRANSPORTATION SYSTEM

On behalf of the U.S. Department of Energy’s Vehicle Technologies Office (VTO), we are pleased to introduce the Fiscal Year (FY) 2013 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, about 35% of which is currently imported. Advanced lubricants improve vehicle fuel efficiency, helping to reduce fuel consumption.

- **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. Advanced lubricants are more environmentally friendly and reduce oil additive effects on emissions control equipment.

- **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. Advanced lubricants improve engine durability, allowing longer life and superior in use performance.

The Fuel & Lubricant Technologies Program supports fuels and lubricants research and development (R&D) to provide vehicle manufacturers and 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 starch-based ethanol, biomass-derived fuels, 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 can be further optimized by matching fuel composition to the combustion system, in addition to helping compliance with new emissions standards. The Fuel & Lubricant Technologies Program activities focus on the properties and quality of the finished fuels derived from these sources, not primarily on their production.

The goals of the Fuel & Lubricant Technologies Program are (1) to enable advanced combustion regime engines and emission control systems to be more efficient while meeting current and future emissions and durability standards; and, (2) to reduce reliance on conventional, petroleum-based fuels through direct fuel substitution by emerging fuels and 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.

Recently, the Fuel and Lubricant Technologies Program conducted a large verification program in partnership with EPA and others to verify the use of higher level ethanol blends in vehicles. This work was required to meet aggressive goals for renewable fuels established in the Energy Independence and Security Act (EISA) of 2007. The joint work resulted in EPA granting a partial waiver for E15 to be used on 2007 and newer light-duty vehicles (2010) and a second partial waiver for 2001 to 2006 light-duty vehicles (2011). The Fuel & Lubricant Technologies Program 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 as part of this work. Materials compatibility, evaporative emissions, and vehicle driveability were also investigated. More recently, the Fuel & Lubricant Technologies Program has focused on how higher ethanol content fuels can be used to improve engine efficiency by raising compression ratio and advancing spark timing to take advantage of ethanol’s inherently higher octane and charge cooling effects.

The Fuel & Lubricant Technologies Program is an integral part of the U.S. DRIVE 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. In 2013, a U.S. DRIVE fuels technology team was initiated and is beginning work in 2014.
I. Introduction

Initial focus will be on advanced biofuels and natural gas. Issues related to codes and standards, fuel quality, infrastructure, and engine efficiency will be addressed and recommendations for pre-competitive research will be developed. 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 Program works closely with the Advanced Combustion Engine Program 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 Program 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.

Subprogram Goals

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

The 2013 goal was met by demonstrating peak thermal efficiencies of greater than 50% and high efficiency combustion over 85% of an engine operating map by combining advanced combustion engines and fuels of economic importance. The advanced engines evaluated included spark-assisted homogeneous charge compression ignition (HCCI), partially premixed compression ignition (PCCI), and reactivity controlled compression ignition (RCCI). The fuels studied included conventional gasoline and diesel, intermediate and high level ethanol blends, biodiesel, and natural gas.

For the 2015 goal, the Fuel & Lubricant Technologies Program will continue to collaborate 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 Program also works closely with other DOE programs (e.g., the Advanced Combustion Engine Program and the Biomass Energy Program) to ensure that engines and fuels resulting from their R&D are optimized to work in conjunction with each other for maximum efficiency and durability.

Transportation Fuels and Energy Security

Petroleum-derived fuels account for 97% of all fuel used in the U.S. heavy-duty 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.

Barring a significant change in events going forward, it is likely that the U.S. will likely be faced with continuing high transportation fuel prices with the possibility of supply disruptions lasting from days to weeks. 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 about as much petroleum as is produced in the U.S. The increase in U.S. crude oil production in the Gulf of Mexico and from shale formations, combined with increasing biofuel and coal-to-liquids production, is expected to reduce the need for imports over the longer term. Vehicles and the refueling infrastructure will need to adapt to these changes in fuel resources and resource location.
Research sponsored by the Fuel & Lubricant Technologies Program 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. Natural gas is another resource that has increased significantly in the U.S., which is near to reaching full natural gas independence with no net imports. Natural gas needs to be exploited for heavy-duty transportation and multiple research needs have been identified by industrial and trade groups.

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 85% ethanol and 15% gasoline (E85), gasoline, or any blend in between. These E85 vehicles are currently optimized for gasoline operation. The Fuel & Lubricant Technologies Program is sponsoring the development of engines for the next generation of flexible-fuel vehicles designed specifically to exploit the desirable fuel properties of E85 (high octane and charge cooling ability) which will increase the fuel economy of vehicles running on 20% ethanol to 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, continuing quality problems with biodiesel resulted in filter-clogging problems and cold weather operating problems in many trucks. As a result of this and similar problems with the quality of U.S. biodiesel, the Fuel & Lubricant Technologies Program partnered with the National Biodiesel Board to improve ASTM International (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 Program in 2005, 2007, 2008, 2010, 2011, and 2012 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 Program 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 CO₂, 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 CO₂ during their growth.

Emissions of harmful pollutants and GHGs 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 Program 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 Program-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. EPA has also recently announced new regulations for gasoline sulfur at 10 ppm average which will enable lean engine and aftertreatment operation and provide resulting improvements in vehicle fuel economy.

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. still represents a large portion 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 Program 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 Program greatly improves the prospects for advanced fuels and advanced vehicle technologies.

Subprogram Laboratory Capabilities

The Fuels, Engines, and Emissions Research Center (FEERC) at Oak Ridge National Laboratory (ORNL) is a comprehensive laboratory for internal combustion engine technology, specializing in research on high efficiency combustion, emissions controls, emissions chemistry, renewable fuels, and lubricant technologies. The applications include engines for transportation, distributed energy, and portable power. FEERC performs research on all system levels spanning basic chemistry and materials to components to engine systems to full vehicle applications. This research leverages one-of-a-kind expertise and facilities at ORNL in the areas of leadership computing, neutron sciences, materials characterization, advanced manufacturing, and biosciences. FEERC is part of the ORNL National Transportation Research Center, a comprehensive DOE National User Facility spanning virtually all vehicle technologies.

FEERC contains seven engine dynamometer laboratories that range from 10 to 450 kW, a 225 kW full vehicle dynamometer, and has access to Vehicle Systems Integration laboratory, a comprehensive propulsion laboratory which will accommodate full engine-transmission configurations and has a 400-kW battery emulator with full transient vehicle simulation. The vehicle laboratory and many of the engine laboratories are approved for fuels spanning natural gas, gasoline, diesel, and similar. All engine setups have full-pass engine control systems which provide complete engine control access to integrate engine functions with aftertreatment systems, and enable research in high-speed intelligent combustion controls for enabling new combustion regimes. Fully developed setups are available for research focused on advanced combustion including RCCI, partially premixed combustion, PCCI, and high dilution gasoline direct injection. Example setups which are available for a range of combustion, emissions controls, fuels, and lubricant research are described below.

- 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 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 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.
I. Introduction

- 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) with full controls using a microprocessor-based controller supports research on lean exhaust aftertreatment systems.

FEERC has extensive emissions characterization and catalyst expertise with instrumentation capable of conducting speciation of exhaust constituents in great detail with fast time resolution. Several configurations of mass spectrometers and chromatographs are in daily operation, as well as Fourier Transform Infrared Spectroscopy. Capillary electrophoresis enables analysis of urea decomposition products. An extensive collection of sampling techniques and separation methods enable speciation and quantification of volatile and semi-volatile emissions. Exhaust particle characterization is accomplished through various methods, including time-integrated mass measurement on filters by tapered element oscillating microbalance, particle sizing by micro-orifice uniform deposit impactor system and scanning mobility particle sizer, composition analysis, and transmission electron microscopy for particle morphology. In addition to supporting emission characterization, the three analytical labs in FEERC house flow benches and surface spectroscopy instruments for studies of catalyst kinetics and aging mechanisms. FEERC has examples of a very rare and effective configuration of diffuse reflectance infrared spectroscopy and a well-equipped chemisorption apparatus. FEERC scientists also have access to transmission electron microscopy when needed, through the microscopy labs at NTRC and the High Temperature Materials Laboratory. FEERC also has a long history of developing unique diagnostics and methods. Examples are described below.

- The SpaciMS, or “spatially resolved capillary inlet mass spectrometry,” is an example of a diagnostic tool developed by FEERC staff that has provided extraordinary insights for numerous engine systems and catalyst devices. This analytical tool enables the spatial and temporal resolution of species in functioning environments such as catalyst channels, engine intake/exhaust runners, and fuel cells. It is complemented by fiber-optic based phosphor thermometry, allowing simultaneous species and temperature measurements in catalyst channels. SpaciMS received a 2008 R&D 100 Award, and the technique has been expanded to function via gas detection with Fourier Transform Infrared spectroscopy (“SpaciFTIR”) to improve sensitivity for NH3 and other gases difficult to measure with mass spectrometry.

- 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 gasoline direct injection engines.

- A laser-induced fluorescence technique for measuring fuel dilution of oil enables on-line analysis of lubricants during engine operation for rapid feedback to combustion engineers optimizing fuel injection timing and controls.

The FEERC team is highly engaged in both industry and government research on fuels, engines and emissions technologies. They provide leadership with industry through the Crosscut Lean Exhaust Emissions Reduction Simulations (www.CLEERS.org) team, and they participate in the U.S. DRIVE and the 21st Century Truck Partnership.

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 Alternative Fuels, Direct-Injection (DI), Spark-Ignition (SI) Engine Lab. Research in this lab is being conducted in a single-cylinder, 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 2013 include: 1) Results from an unprecedented parametric study of fuel property effects on advanced mixing-controlled heavy-duty diesel combustion strategies indicate that fuel-induced efficiency and emissions changes cannot be fully explained using gross fuel properties and conventional diagnostics alone. Quantification of in-cylinder processes such as the flame lift-off length as well as detailed fuel composition also appear to be required. The database developed includes over 25,000 replicates and 10 simultaneous (13 total) diagnostics on five chemically and physically well-characterized reference fuels. 2) The effects of gasoline/ethanol-blend ratio, spark timing, and load on soot and NOx emissions were quantified for an advanced stratified DISI operating mode. Measured exhaust soot emissions and in-cylinder combustion imaging were used to clarify soot-formation pathways for various fuel blends and operating strategies. These results provide guidelines for achieving clean operation of these fuel-efficient spray-guided engines as the fuel composition changes. 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.

The Renewable Fuels and Lubricants (ReFUEL) Lab at the National Renewable Energy Laboratory (NREL) is dedicated to future fuels and advanced vehicle powertrain research. It features a heavy duty chassis dynamometer test cell capable of testing the performance and emissions of vehicles weighing from 8,000 to 80,000 lbs. The heavy-duty chassis dynamometer has recently been used in research programs to evaluate fuel consumption and emissions from medium and heavy-duty advanced technology vehicles and vehicles utilizing bio-fuels. The lab also features two engine dynamometer test cells. One is a 600 HP AC engine dynamometer test cell capable of certification-quality emissions research and altitude simulation though air handling systems that provide pressure, temperature, and humidity controls capable of simulating conditions from sea-level to the mile-high environment of Denver. A 2012 Cummins ISL 8.9-L engine is currently installed in the heavy-duty engine test cell; however, engines can be swapped out quickly for other testing. The second engine test cell has a light duty 75-hp AC dynamometer capable of running transient test cycles. It is currently setup for long term testing on a single-cylinder gasoline research engine.

Emissions measuring equipment at the ReFUEL Laboratory includes a Horiba MEXA 7100 gas analyzer, Horiba 1170 NOx and NH$_3$ analyzer, CAI raw gaseous analyzer bench, Thermo Scientific Fourier transform infrared instrument, gravimetric particulate filter collection system and a clean room for measurements, Dekati FPS4000 two-stage dilution for particulate matter measurements, TSI fast mobility particle sizer, and an AVL particulate matter Microsoot Sensor. Data acquisition systems in each test cell record data for testing, including a high-speed data acquisition system used for in-cylinder measurement of combustion and analysis. A portable emissions monitoring system is available for on-road or in-the-field emissions measurements. In conjunction with ReFUEL, the NREL Fuel Chemistry Laboratory provides high-quality measurements of gasoline and diesel fuel performance properties, as well as detailed fuel compositional analysis. The NREL Combustion Laboratory features small-scale, relatively high throughput measurements on ignition kinetics.
I.2 HIGHLIGHTS OF SIGNIFICANT FY 2013 ACCOMPLISHMENTS

The following presents highlights of the Fuel & Lubricant Technologies project accomplishments in 2013.

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

The objective of this program 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. In FY 2013 they: (1) Demonstrated that accelerating the exposure of the emissions control system to fuel metal content that is above 14x leads to deactivation mechanisms that are not commensurate with normal aging; and (2) Established a stoichiometric gasoline aging system and evaluated the compatibility of a novel lubricant additive with three-way catalysts. (Toops)

- ORNL is quantifying exhaust gas recirculation (EGR) system performance when using non-petroleum-based fuels and identifying fuels or fuel properties that may reduce the effectiveness of the EGR system through problematic deposit formation. In FY 2013 they resolved an important modeling issue by showing that effectiveness “stabilization” does not necessarily require that the deposition rate reaches zero, showed that the prevailing conditions during deposition determine the fouling outcome (either stabilization or plugging) by their influence on the deposit layer temperature and density, and provided recommendations for avoiding plugging through minimizing hydrocarbon deposition during low-temperature cooler conditions. (Sluder)

- Argonne National Laboratory (ANL) is developing accurate and reliable correlations between benchtop tests used to evaluate friction and wear performance to engine tests that measure fuel economy, durability, and reliability of engine tests. In FY 2013 they identified benchtop tests that best simulate friction, wear, and failure mechanisms; developed test protocols (load, time, temperature, speed, lubricant, materials, finish, etc.) that replicate engine environment; performed baseline tests on candidate lubricants and additives and materials; established collaborations with academia and industry; and 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 FY 2013 they: (1) Developed a thermally activated procedure to control the structure of tribochemical films that exhibit greater than 50% reduction in friction from the same lubrication additive; (2) Measured the mechanical durability (load-carrying capacity) of tribochemical films with different structures; (3) Identified a pathway to increase load-carrying capacity of the film by more than 2X; and (4) Measured the nano-mechanical properties of hardness and elastic modulus for films with different structures. Results need further studies to better elucidate the observed behaviors. (Ajayi)

- ANL is seeking to develop lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in legacy vehicles. In FY 2013 they established friction and wear benchmarks for nano-additive systems, evaluated and identified several nano-particulate additive systems with frictional and wear performance equivalent to or superior to the benchmark, and assessed the impact of encapsulation for time release attributes, as well as the effect of temperature and concentration on the tribological performance of many additive systems. (Ajayi)

- ANL is developing lubricants that would provide reduction in friction and wear and serve as a drop-in solution to existing systems. In FY 2013 they found that the most beneficial additives reduced the average coefficient of friction by almost 20% but wear remained high, and the highest performing additives were ones that produced a conductive or semi-conductive tribo-film for the length of the reciprocation test. (Demas)
I. Introduction

- ORNL is developing oil-soluble ionic liquids (ILs) as engine oil additives to demonstrate 10% improvement in mechanical efficiency of internal combustion engines, and is exploring potential advantages and disadvantages of this new category of additives through systematic lab experiments, modeling, engine dynamometer tests, and field tests. In FY 2013: (1) Multiple groups of quaternary structured ILs were designed and synthesized; (2) Oil solubility, corrosion behavior, thermal stability, and compatibility with other oil additives were used to screen candidate ILs; (3) Tribological bench tests demonstrated up to 96% wear reduction in boundary lubrication and up to 50% friction reduction in mixed lubrication when adding ILs into a gas-to-liquid base oil (at a phosphorus content of 800 ppm); (4) Two top candidate ILs have been identified for further development and investigation; and (5) Fundamental understanding has been achieved for the wear protection mechanism of ILs. (Qu)

- Massachusetts Institute of Technology (MIT) is identifying the best lubricant formulations for individual engine subsystems the best composite lubricant formulation for the overall engine system to demonstrate mechanical efficiency improvement for optimized lubricant formulations via engine testing towards the established goal of 10% improvement or better. In FY 2013 they: (1) Developed a detailed oil composition and rheology model that accounts for vaporization effects along the liner; (2) Successfully modified and fired a unique diesel test engine; (3) Mechanical efficiency improvements of over 5% were observed experimentally by operating a 16-hp diesel engine with separate multigrade oil formulations in the valve train and power cylinder subsystems; and (4) Friction reductions of over 10% were observed experimentally by varying shear thinning characteristics of a lubricant in a motored valve train. (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 FY 2013 they (1) formulated five new oils to improve friction and wear performance; (2) completed friction and wear evaluations on new oil formulations using a pin-on-disk machine, a high frequency reciprocating rig, and a block on ring machine; and (3) completed motored valvetrain friction tests on eight polyalkylene glycol formulations; all showed reduced friction over GF-5 5W-20 oil. (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 FY 2013 they: (1) Completed a set of simulation-based turbocharged spark ignition engine performance maps for a range of different knock-suppressing fuels, compression ratios, boost levels, and spark retard strategies; (2) Developed and validated a fundamentally based chemical kinetic methodology for predicting knock onset at close to peak cylinder conditions; (3) Used engine performance maps to explore and quantify through engine-in-vehicle simulations the significant fuel economy benefits that alcohol-based knock suppression can provide; and (4) Generated experimental boosted spark ignition engine efficiency data at higher compression ratios and boost levels for a range of gasoline-ethanol blends. (Heywood)

- Wisconsin Engine Research Consultants, LLC is optimizing dual-fuel Reactivity Controlled Compression Ignition (RCCI) combustion in both heavy-duty (HD) and light-duty (LD) on-highway diesel engines over the expected ranges of engine speed/load operation in vehicle applications. In FY 2013 they conducted initial experimental investigation of LD RCCI using gasoline+ethyl hexyl nitrate (EHN), conducted LD particulate characterization experiments using gasoline+EHN, created novel combustion bowl for RCCI that allows load extension, and analytically investigated several concept combustion systems for HD RCCI using gasoline+diesel. (Reitz)

**Fuel Property Effects on Advanced Combustion Regimes**

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

- ORNL is investigating the opportunities and challenges that advanced transportation fuels, including renewable fuels, have on advanced combustion regimes and emerging engine technologies. In FY 2013 they: (1) Characterized the potential of biofuels to enable and expand the operating range of RCCI combustion in a multi-cylinder engine; (2) Attained the 2013 technical target of demonstrating biodiesel blends allowed an improvement in RCCI operating range allowing for a simulated 65% coverage of the federal city and highway driving cycles; and (3) Completed initial comparisons of RCCI with conventional fuels and Partially Premixed Combustion (PPC) with a 70 Research Octane Number gasoline for efficiency, load expansion and controllability. (Curran)

- Sandia National Laboratories (SNL) is facilitating the introduction of renewable and/or unconventional fuels and advanced engine-combustion strategies for their utilization in a manner that optimally enhances domestic energy security, economic competitiveness, and environmental quality. In FY 2013 they: (1) Created and refined computational algorithms for comprehensive processing of data from parametric study of fuel effects on mixing-controlled combustion; (2) Completed initial analysis of the above data set and drafted a paper describing the results; and (3) Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council in developing second-generation surrogates with improved capabilities for matching market diesel fuels. (Mueller)

- NREL is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, emissions, and emission control systems. In FY 2013 they continued development of the 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 for fuel components and surrogate blends, and bridged fundamental ignition experiments to engine testing. (Zigler)

- SNL is researching how emerging alternative fuels impact the new highly-efficient direct-injection, spark-ignited light-duty engines being developed by industry, and how engine design and operation can be optimized to make the most efficient use of future fuels. In FY 2013: (1) Effects of gasoline-blend ratio, spark timing, and load on soot and oxides of nitrogen (NOx) emissions have been quantified, providing guidelines for achieving clean operation of these fuel-efficient spray-guided engines as the fuel composition changes; (2) The role of the in-cylinder flow field for highly stratified spark ignition operation has been clarified using a combination of particle image velocimetry measurements and performance testing; and (3) The dominant role of the spray-induced fuel/air-mixing and turbulence for the combustion rate of highly stratified spark ignition combustion has been demonstrated for 70% ethanol-30% gasoline fuel. (Sjoberg)

- ORNL is investigating the opportunities and challenges of gasoline boiling range non-petroleum-based fuels on advanced combustion regimes and emerging engine technologies. In FY 2013 they: (1) Mapped efficiency and emissions of spark ignition combustion and dilute spark ignition combustion for regular-grade gasoline, a blend of 24% iso-butanol with gasoline, and 30% ethanol with gasoline from 1,200 to 3,000 rpm and to the peak load at each speed in accordance with the experimental criteria applied in this study; (2) Mapped the efficiency and emissions of boosted Homogeneous Charge Compression (Szybist, ORNL)

Downspeed/downsize strategies investigated for E30 and 87 anti-knock index (AKI) gasoline at 15% EGR. (Szybist, ORNL)
Ignition (HCCI) combustion with the same three fuels at 1,600, 2,000, and 2,500 rpm to the peak load at each speed in accordance with the experimental criteria applied in this study; and (3) Mapped the efficiency and emissions of spark assisted-HCCI combustion with two of the three fuels at 1,600, 2,000, and 2,500 rpm to the peak load at each speed in accordance with the experimental criteria applied in this study. (Szybist)

- ORNL is investigating the potential of using ILs as lubricants and/or lubricant additives specifically for internal combustion engine applications. In FY 2013: (1) Working with a leading lubricant formulation company, the team successfully developed a prototype low-viscosity engine oil using a phosphonium-phosphate IL as an anti-wear additive; (2) Tribological bench tests of the IL-additized formulated oil showed 20-33% lower friction in mixed and elastohydrodynamic lubrication and 38-92% lower wear in boundary lubrication when compared with commercial Mobil 1™ and Mobil Clean™ 5W-30 engine oils; (3) High-temperature, high-load full-size multi-cylinder engine tests confirmed the excellent anti-wear performance for the IL-additized engine oil; (4) Sequence VID engine dynamometer tests demonstrated an improved fuel economy by >2% for this IL-additized engine oil benchmarked against the Mobil 1™ 5W-30 oil; and (5) In addition, accelerated catalyst aging tests suggest that the IL additive may potentially have less adverse impact on three-way catalysts compared to the conventional additive zinc dialkyl-dithiophosphate. (Qu)

- Ford Motor Company is identifying how fuel properties can be used to achieve controllable Extended Lift-Off Combustion with low NOx and particulate matter emissions. In FY 2013 they: (1) Conducted ignition delay tests on several test methods for cetane rating to better understand cetane rating variations; (2) Completed combustion spray vessel studies and evaluated six fuel blends; (3) Completed model development and validation using a grouped chemistry representation to model different cetane fuels; (4) Investigated various methods for modeling oxygenated and non-oxygenated fuels; and (5) Acquired high-pressure fuel system hardware with a nozzle suite based on computational fluid dynamics modeling. (Kurtz)

- ORNL is quantifying fuel and lubricant effects on particulate matter (PM) formation in gasoline direct injection (GDI) combustion, with an emphasis on component effects, and the importance of transient operation to overall GDI PM emissions, including start-stop operation. In FY 2013 they: (1) Optimized steady-state engine operation point to represent speed, load, PM output, and rich A/F during acceleration transients; (2) Collected and characterized PM samples for morphology, organic speciation, and size and number concentration for gasoline, gasoline-ethanol, and gasoline-isobutanol blends; and (3) Collected 36 gasoline particulate filter core samples for detailed oxidation studies. (Storey)

**Petroleum Displacement Fuels/Fuel Blending Components**

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

- NREL is assessing the impact of fuel metal impurities on the long-term durability of emission control systems found in modern diesel engines. In FY 2013 they: (1) Completed accelerated aging experiments with three separate exhaust aftertreatment systems; (2) Materials characterization of aged catalysts showed that increasing the rate of accelerated aging increases the amount of fuel-borne K captured by the diesel oxidation and selective catalytic reduction catalysts; and (3) Emissions characterization of the aged catalysts showed that the inlet portion of the most rapidly aged catalysts had significant changes in catalytic activity. (Williams)

- NREL is assessing the quality of biofuels to determine if quality is changing, particularly in response to changes in specifications. In FY 2013 they collected 73 samples, including gasoline, mid-level ethanol blends, and Flex Fuel, were collected from 20 stations, predominantly in the midwestern United States. All the Flex Fuel samples were on specification for ethanol content, with the exception of one, with extremely high ethanol content. Four of these samples failed to meet the required volatility. The example of station offering higher ethanol blends from the same hose as E10 (Alleman, NREL)
ethanol content of the mid-level ethanol samples was highly variably, between 3-10% different from the level on the pump label. Photographs of the sample pumps showed little standardization and consistency, potentially leading to confusion among consumers. (Alleman)

- **NREL** is developing a detailed understanding of issues that are preventing biodiesel blends from attaining drop-in fuel status. In FY 2013 they: (1) Revealed that some methods for measuring diesel cloud point (CP) may not accurately capture the CP of biodiesel blends; and that biodiesel blends containing saturated monoglycerides (SMG) are prone to polymorphic phase transformation; (2) Determined that monitoring of biodiesel blend Rancimat induction time is the most effect way to monitor blend stability during storage; (3) Showed that B5 and B20 blends can be stored for up to three years under clean storage conditions if the 100% biodiesel (B100) is of adequately high stability (B100 Rancimat induction time of 6 hr); (4) Demonstrated that engine emissions certification level has a dominant effect on transit bus NOx, with the kinetic intensity of the duty cycle being the secondary driving factor; and (5) Showed that selective catalytic reduction systems on the two 2010+ model year buses tested are effective at reducing NOx to near the detection limit on all duty cycles and fuels, including B100. (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, and identifying fuel properties and specific combustion products that may limit the implementation of biofuels and other alternative fuels. In FY 2013 they developed a thermal/pyrolysis method to analyze soot from gasoline direct injection combustion utilizing state-of-the-art thermal/pyrolysis gas chromatograph-mass spectrometry. (Lewis)

- **PNNL** is facilitating the successful introduction of future fuel feedstocks which will help reduce the U.S. dependence on foreign oil, while being compatible with future advanced combustion engines, and developing analytical approaches correlating fuel component molecular structure to fuel properties and fuel performance. In FY 2013 they: (1) Completed contributions to two Coordinating Research Council (CRC) Advanced Vehicle/Fuel/Lubricants Reports; (2) Continued development of new nuclear magnetic resonance (NMR) approaches for identifying structure-property relationships of diesel fuels; (3) Developed strategies for the separation of pyrolysis oil into aqueous and organic soluble components to allow NMR quantification of each component; and (4) Continued collaborative efforts with the CRC FACE Working Group, and the alternative and surrogate fuels subcommittees, through contributed NMR analyses of fuels and technical discussions. (Bays)

- **PNNL** is developing an agile decision-analysis tool to enable rapid exploration and analysis of a wide range of transportation fuel pathways and vehicle technologies. In FY 2013 they: (1) Updated estimates for biomass supply curves using results from the “billion-ton update” (DOE 2011) to improve biomass supply curves; (2) Calibrated the ATEAM model with reference to the Annual Energy Outlook 2013 model projections; (3) Extended modules for sensitivity and scenario analysis, to clarify which assumptions and uncertainties matter most to the results and why; (4) Developed a Web-based ATEAM user guide using direct links from the ATEAM model to corresponding webpages, and cross links within the guide for ease of access; (5) Applied ATEAM to analyze 10 key policy issues relating to the U.S. vehicle fleet and adoption of new fuels and technologies; and (6) Extended Megajoule.org, including improvements to the user interface and internal structure, and a set of new estimates and sources, probabilistic projections. (Bloyd)

- **NREL** is determining if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels for both diesel and gasoline applications. In FY 2013: (1) The effects of phenolic, carbonyl, and ether compounds derived from biomass on gasoline and diesel properties were quantified; (2) Diisoamyl ether and pentyl pentanoate were shown to be technically viable diesel blending components; and (3) Emission impacts of both residual and blending component oxygenates were measured. (McCormick)

- **ANL** is assessing the suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications. In FY 2013: (1) Operation on 10% ethanol in gasoline (E10) and 16% isobutene...
in gasoline (iB16) was found to result in a 15-30% reduction in total PM emissions due to a significant reduction in organic carbon emissions accompanied by a moderate increase in elemental carbon emissions; (2) A test over the full Environmental Protection Agency useful life of six recreational marine engines ranging from 10 to 200 HP indicates that hydrocarbon plus oxides of nitrogen (HC+NOx) emissions limits are met even after 350 hours of deterioration with E10 and iB16; (3) Over 100 hours of field testing of two vessels on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends comprised of 5 vol% ethanol, 8 vol% iso-butanol and 87 vol% gasoline were successfully completed; and (4) Scuffing load showed a near-linear decrease with increased amount of bio-derived fuel blend content up to 20-25% at 50% oil dilution. (Wallner)

I.3 SPECIAL HONORS/RECOGNITIONS

1. ORNL: 2013 DOE VTO R&D Award for PI, Scott Curran on RCCI research for “Leadership in transitioning RCCI combustion from single cylinder to a multi-cylinder engine using bio-renewable fuels.”


4. ORNL, Scott Curran: ASME Early Career Award – Awarded in part due to research in alternative fuels and the relation to high efficiency engines.


8. ANL: Oyelayo Ajayi received NMMA Environmental Achievement Award “for innovative research and outstanding contribution to the recreational boating industry.”

I.4 PATENTS ISSUED/PENDING


I.5 FUTURE ACTIVITIES

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

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

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 FY 2014 they will be working with Cummins
to investigate the impact of Na with the selective catalytic reduction catalyst after the diesel particulate filter. Particular focus will be on the migration of Na from the particulate filter to the downstream selective catalytic reduction catalyst. They will also investigate the impact of new lubricant additive formulations on catalytic activity of three-way catalyst, diesel oxidation catalyst, and selective catalytic reduction catalysis. (Toops)

- ORNL is quantifying EGR system performance when using non-petroleum-based fuels and identifying fuels or fuel properties that may reduce the effectiveness of the EGR system through problematic deposit formation. This project is complete. (Sluder)

- ANL is developing accurate and reliable correlations between benchtop tests used to evaluate friction and wear performance to engine tests that measure fuel economy, durability, and reliability of engine tests. In the coming year they plan to provide the ability to evaluate advanced technologies in terms of their performance and mechanisms before they progress to the next level of validation testing. (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 evaluate the thermal durability and limit of the tribochemical films with different structures, assess the impact of base fluid viscosity on the frictional performance and durability of various tribochemical surface films, and conduct tribological performance evaluation in terms of scuffing and wear under severe contact conditions for additives that produce low-friction tribochemical films. (Ajayi)

- ANL is seeking to develop lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in legacy vehicles. In the coming year they plan to: (1) Evaluate wear performance of candidate nano-additive systems under severe contact conditions using a four-ball test rig; (2) Evaluate the scuffing performance of potential nano-additive systems with standard block-on-ring test protocol; (3) Analyze the nano-structure of tribochemical films formed from nano-additive systems using transmission electron microscopy with focused ion beam; and (4) Measure nanoscale mechanical properties of the tribochemical films formed from nano-particle systems. (Ajayi)

- ANL is developing lubricants that would provide reduction in friction and wear and serve as a drop-in solution to existing systems. Even though significant progress with self-replenishing lubricant synthesis was made, they didn’t see the anticipated friction and wear reduction. Also, long-term stability has not been addressed. Furthermore, even with the use of organic surfactants that have both cationic and anionic tails, it has been difficult to avoid self-assembly in solution, which in turn prevents self-assembly during tribological interactions. This renders self-replenishment of a tribo-film not feasible at the moment. Therefore, a “no-go” decision has been made. (Demas)

- ORNL is developing oil-soluble ILs as engine oil additives to demonstrate 10% improvement in mechanical efficiency of internal combustion engines, and explore potential advantages and disadvantages of this new category of additives through systematic lab experiments, modeling, engine dynamometer tests, and field tests. In the coming year they plan to seek synergistic effects between the identified top two candidate ILs and zinc dialkyl-dithiophosphate as well as between different groups of ILs, further investigate and model the lubrication mechanisms of IL additives, complete standard additive evaluation for the top two candidate ILs, produce a formulated engine oil using the top-performing IL as an anti-wear additive, and conduct tribological bench tests and initial fired engine tests on the formulated IL-additized engine oil. (Qu)

- MIT is identifying the best lubricant formulations for individual engine subsystems the best composite lubricant formulation for the overall engine system to demonstrate mechanical efficiency improvement for optimized lubricant formulations via engine testing towards the established goal of 10% improvement or better. In the coming year they plan to experimentally verify results of modeling efforts by further quantifying benefits achievable from optimizing base oil formulations for particular engine subsystems, continue to develop advanced power cylinder friction models incorporating detailed effects of local oil composition changes and control, and experimentally investigate the effect of additive changes on valve train and power cylinder subsystem losses through parametric studies. (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 continue analyzing tribo-films formed on contacting surfaces to understand friction reduction mechanism(s), continue ASTM Sequence tests
to demonstrate fuel economy, anti-oxidation and wear protection capabilities, and initiate chassis roll
dynamometer tests for fuel economy and emission evaluations when oil is fresh and aged. (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) Experimentally determine knock-
onset limits of selected primary reference fuels and gasoline-methanol blends at higher loads: use this
data to further validate our knock onset model and compare methanol and ethanol; (2) Determine the
octane requirement of their turbocharged 2-liter engine at mid- and low-loads to explore the application
of onboard membrane-based fuel separation (prevaporation) to provide a higher octane (largely ethanol)
and a lower octane fuel streams; (3) Develop reference engine-in-vehicle drive-cycle simulation results
to enable knock-suppressed turbocharged-engine fuel economy data in the appropriate context; and (4)
Complete the data acquisition from the single-cylinder spark ignition engine tests (at Cummins) at higher
compression ratios and boost levels: process the data and compare with our simulation-based performance
maps. (Heywood)

- Wisconsin Engine Research Consultants, LLC is optimizing dual-fuel RCCI combustion in both HD
and LD on-highway diesel engines over the expected ranges of engine speed/load operation in vehicle
applications. In the coming year they plan to continue to develop novel combustion system and calibration
strategy for RCCI, continue to develop HD combustion system and calibration strategy for RCCI
combustion with focus on maximizing load capability and thermal efficiency, and finalize LD particulate
characterization and improve quantitative understanding of fuel and lube contribution to particulates.
(Reitz)

Fuel Property Effects on Advanced Combustion Regimes

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

- ORNL is investigating the opportunities and challenges that advanced transportation fuels, including
renewable fuels, have on advanced combustion regimes and emerging engine technologies. In the coming
year they plan to: (1) Conduct engine experiments for mapping RCCI with other renewable fuels to
determine how much of the light-duty drive cycle can be covered with RCCI as enabled by the unique
properties of renewable fuels; (2) Investigate the potential for alternative fuels to expand the drive-cycle
coverage of advanced combustion leading to higher potential fuel economy and lowered emissions; and
(3) Evaluate PPC as compared to RCCI on the same engine, with the same hardware over a variety of
gasoline-range fuels that seem well suited for PPC. (Curran)

- SNL is facilitating the introduction of renewable and/or unconventional fuels and advanced engine-
combustion strategies for their utilization in a manner that optimally enhances domestic energy security,
economic competitiveness, and environmental quality. In the coming year plan to: (1) Expand the
fuel-effects studies to include oxygenated/renewable fuels of interest and higher injection pressures
(≥2,400 bar); (2) Conduct engine tests on surrogate and real-world target fuels to more thoroughly
assess the success of the surrogate-fuel formulation methodology created previously and to assist in its
optimization; and (3) Develop and employ laser-induced incandescence and other diagnostics to better
understand and quantify the production, oxidation, and distribution of soot within the combustion
chamber. (Mueller)

- 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 continue expanding IQT™-based experimental and simulation research and collaborate with other
DOE and Canadian national laboratories, along with corporate industrial partners via the Coordinating
Research Council. (Zigler)

- SNL is researching how emerging alternative fuels impact the new highly-efficient direct-injection,
spark-ignited light-duty engines being developed by industry, and how engine design and operation can
be optimized to make the most efficient use of future fuels. In the coming year they plan to: (1) Continue
development of a conceptual model of stratified combustion that includes both highly-stratified operation
using “head ignition” for high-ethanol fuels, and less stratified operation using “tail ignition” for
acceptable soot with lower-ethanol fuels; (2) Examine further the role of the in-cylinder flow field for both
I. Introduction

the combustion rate and the ignition stability of selected gasoline/ethanol blends, with a focus on swirling flows measured in a horizontal plane; and (3) Broaden the range of combustion to also include other modes of lean or dilute spark ignition operation, examining fuel effects on well-mixed or partially stratified operation using either conventional spark or advanced ignition systems. (Sjoberg)

- ORNL is investigating the opportunities and challenges of gasoline boiling range non-petroleum-based fuels on advanced combustion regimes and emerging engine technologies. In the coming year they plan to: (1) Use experimental results from FY 2013 to feed vehicle-level models to determine volumetric fuel economy effects of fuel composition, advanced combustion, and the downsize/downspeed strategies that are enabled by certain fuels; and (2) Conduct an experimental campaign to determine the fuel-specific differences associated with a new advanced combustion concept being developed at ORNL: an in-cylinder non-catalytic fuel reforming strategy to enable highly dilute spark ignition combustion. (Szybist)

- ORNL is investigating the potential of using ILs as lubricants and/or lubricant additives specifically for internal combustion engine applications. This project was completed in 2013. (Qu)

- Ford Motor Company is identifying how fuel properties can be used to achieve controllable Extended Lift-Off Combustion with low NOx and particulate matter emissions. In the coming year they plan to: further investigate the influence of cetane number test methods; continue to improve and use models to guide fuel selection and boundary conditions; validate and use fuel and combustion models to understand the effect of fuel properties on Extended Lift-Off Combustion and identify combustion design changes needed to facilitate non-sooting diesel combustion; conduct optical engine experiments; complete the analysis of spray study results; and demonstrate non-sooting diesel combustion on an engine with modern power density requirements. (Kurtz)

- ORNL is quantifying fuel and lubricant effects on PM formation in GDI combustion, with an emphasis on component effects, and the importance of transient operation to overall GDI PM emissions, including start-stop operation. In the coming year they plan to: evaluate fuel effects on the oxidation kinetics of the PM collected on gasoline particulate filter cores; optimize PM collection method for start-stop engine operation; and quantify physical and chemical differences of PM emitted during start-stop operation. (Storey)

Petroleum Displacement Fuels/Fuel Blending Components

The focus of this portion of the Fuel & Lubricant Technologies program 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 assessing 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 evaluate the impact of fuel-borne metal impurities on the full-useful-life durability of a heavy-duty engine platform. Accelerated aging will simulate 435,000 miles of operation for a Cummins ISL engine. (Williams)

- NREL is assessing the quality of biofuels to determine if quality is changing, particularly in response to changes in specifications. In the coming year a survey of Flex Fuel will be completed. (Alleman)

- NREL is developing a detailed understanding of issues that are preventing biodiesel blends from attaining drop-in fuel status. In the coming year: (1) Factors affecting saturated monoglyceride precipitation, crystal growth, crystal shape, and ability to clog a fuel filter have not been fully explained and a more detailed explanation is likely to facilitate low-cost solutions to filter clogging problems; (2) Biodiesel blends as currently specified may not have adequate stability for modern, high-pressure common rail fuel injections systems, especially for situations where consumers do not rapidly consume the fuel; and (3) Additional data are needed to understand how fuels in general affect emissions of 2010+ model year heavy-duty vehicles during cold starts and low-speed, low-load operation when exhaust temperature may not be adequate for NOx reduction. (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, and identifying fuel properties and specific combustion products that may limit the implementation of biofuels and other alternative fuels. In the coming year they plan to perform analyses with capillary electrophoresis mass spectrometry of organic acid anions in exhaust condensates, and evaluate
I. Introduction

size-separated soot PM derived from engine combustion of non-petroleum-based fuel for determining unique soot chemistries for the different size ranges of soot particles. (Lewis)

- PNNL is facilitating the successful introduction of future fuel feedstocks which will help reduce the U.S. dependence on foreign oil, while being compatible with future advanced combustion engines, and developing analytical approaches correlating fuel component molecular structure to fuel properties and fuel performance. In the coming year they will 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 CanmetENERGY on analytical correlation of fuel properties and material compatibility investigations; and continue collaborative work with members of the CRC’s Working Group and the alternative and surrogate fuels subcommittees. (Bays)

- PNNL is developing an agile decision-analysis tool to enable rapid exploration and analysis of a wide range of transportation fuel pathways and vehicle technologies. In the coming year they plan to: (1) Update and expand the set of ATEAM model policy briefs to address additional policy issues of concern to the government and private sectors, including current and new policies and programs to promote electric vehicles, biofuels, and improved efficiency; and (2) Develop a simplified version of the ATEAM model to allow easier use and collaborative analysis for policy research and educational use. (Bloyd)

- NREL is determining if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels for both diesel and gasoline applications. In the coming year they plan to evaluate effects of these oxygenates on fuel storage stability and gum formation; apply solubility parameter theory to assess the compatibility of oxygenate blends with fuel system elastomers; complete several 300-hr engine durability tests with residual phenolic oxygenates; and conduct experiments to measure the impact of oxygenated aromatic compounds of particle number emissions from a spark-ignited, direct-injection engine. (McCormick)

- ANL is assessing the suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications. In the coming year they plan to perform end-of-season testing on recreational marine engines operated on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends; expand laboratory and field tests to include operation on mid-level blends with 5 wt% oxygen including 15 Vol% ethanol blends, 24 Vol% blend of iso-butanol in gasoline and a tri-fuel blend; and conduct cold-start, fuel system and fuel stability/long-term storage tests. (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
Vehicle Technologies Office
II. FUELS AND LUBRICANTS TO ENABLE HIGH EFFICIENCY ENGINE OPERATION
II.1 Compatibility of Emerging Fuels and Lubricants on Emissions Control Devices using Accelerated Aging Techniques

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DOE Technology Development Manager: Kevin Stork

Overall 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) 2013 Objectives

- Through collaboration with the National Renewable Energy Laboratory (NREL), evaluate the impact of the acceleration factor using K.
  - Evaluate materials properties and catalyst performance of emissions control system aged at 7x, 14x, and 28x the expected K content, but with the same overall dose.
- Establish the maximum acceleration factor for long-term heavy-duty engine evaluation.

FY 2013 Accomplishments

- Demonstrated that accelerating above 14x the exposure of the emissions control system to metal content leads to deactivation mechanisms that are not commensurate with normal aging.
  - Both 7x and 14x acceleration factors illustrated similar deactivation mechanisms.
- Established a stoichiometric gasoline aging system and evaluated compatibility of a novel lubricant additive with TWCs.
  - Demonstrated the novel additive affects the TWC similarly to the industry standard, zinc dialkyl-dithiophosphate (ZDDP).
- Published findings in *Topics in Catalysis* and SAE International technical papers and submitted additional manuscripts to *Catalysis Today* and SAE.
- Submitted a book chapter entitled “Fe-zeolite functionality, durability and deactivation mechanisms in the selective catalytic reduction (SCR) of oxides of nitrogen (NOx) with ammonia,” which has been accepted for publication by Springer for inclusion in *NH3-SCR Technology for deNOx Aftertreatment of Diesel Exhausts.*

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 DPF to the downstream SCR.
  - Goal is to determine if a new limitation for the biodiesel specification of less than 5 ppm is necessary.
- Investigate the impact of new lubricant additive formulations on the catalytic activity of TWC, diesel oxidation catalyst (DOC), and SCR catalysis.
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 develops and 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 full-useful-life (FUL) 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. Since 2010, diesel vehicles typically employ a DOC, a 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 standard 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 going forward, there is an increased emphasis on improving lubricant formulations to reduce the losses caused by friction. Thus, new additives are being studied such as the use of ionic liquids instead of the industry standard ZDDP. 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 or K in biodiesel—current specification is up to 5 ppm Na+K. Of particular concern is the deactivation of zeolite-based SCR catalysts, which has been recently reported [9-13]. 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 aging 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 continued a collaboration with NREL and Ford Motor Company to investigate the impact of the acceleration factor as it relates to K concentrations in biodiesel. The experimental details of this effort can be found elsewhere [13-14], 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) fuel containing no measureable metals, 20% biodiesel in diesel fuel (B20) containing 7x K, B20 containing 14x K, and B20 containing 28x K. Metals levels were selected to simulate the maximum allowable levels in 100% biodiesel (B100), i.e., 5 ppm, but the exposure time was adjusted to such that the total K dose was the same for each system. 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 ORNL, and detailed materials characterization of the aged DOCs and SCRs also at ORNL.

At ORNL, the catalysts received from NREL were removed from their metallic canisters, cored and sectioned. Intact cores were evaluated in the bench reactors 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 (SEM) with energy-dispersive X-ray spectroscopy for isolated or spot elemental analysis, and electron probe microanalysis (EPMA) for elemental concentration mapping.

Additionally, we established a stoichiometric gasoline aging system to evaluate the potential impact of a novel ionic liquid (IL) on TWC chemistry. The IL was added to the fuel and it underwent a combustion event before being exposed to the General Motors (GM)-provided TWCs. Bench-reactor evaluations were employed to evaluate the performance.

RESULTS

During the evaluation of the biodiesel-aged systems it was determined that the catalysts aged at 7x and 14x acceleration rates met each of the FTP-based emissions standards at the end of the test, but the 28x one failed
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The NOx emissions standard. Efforts commenced to understand if this evaluation with very high K levels created a deactivation mechanism that is not expected under typical field-use.

At the completion of catalyst aging and vehicle emissions testing the catalyst bricks were cored and sectioned for detailed post mortem analysis. The exhaust system consisted of two DOC and two SCR bricks mounted in series. Catalyst cores with approximately one inch diameter were taken down the length of each of these DOC and SCR bricks close to the radial center of each brick. Each catalyst core was then equally divided into four parts. From the inlet to outlet direction, the four parts were labeled as Inlet, Mid 1, Mid 2, and Outlet, respectively. Washcoat powders were scraped from each sample and ground into a fine powder for elemental analysis with the SEM-energy dispersive X-ray spectroscopy (EDAX).

Figure 1 shows the concentration of K that was measured in the washcoat of the aged DOCs. These data were collected by SEM-EDAX at eight separate locations down the length of the DOC bricks. In the case of each aged sample we see that the concentration of K is highest at the inlet to the DOC and decreases down the length of the catalyst. Also of note in Figure 1 is that the rate of accelerated aging has a large impact on the K concentration in the DOC washcoat. This is most pronounced at the inlet positions where the K concentration increases from 1.5% to 2.9% to 8.7% as the rate of accelerated aging is increased from a factor of 7x to 14x to 28x.

Figure 2 shows the concentrations of K that were measured in the washcoat of the aged SCR bricks. These data were collected by SEM-EDAX at eight separate locations down the length of the bricks. The relative location for each of these samples is illustrated in Figure 3. In comparing Figure 3 to Figure 4 one can see that there is significantly more K captured by the DOC than the SCR. For example, the inlet to the DOC aged at 28x acceleration rate contained 8.6% K, while the corresponding SCR sample only contained 0.8% K. As was the case for the DOC, the concentration of K is highest at the inlet to the SCR and decreases as you move further down the length of the catalyst. Also as was seen with the DOC, the rate of accelerated aging impacted the amount of K that was captured by the SCR. The K concentration measured at the inlet of the front brick increased from 0.5% to 0.6% to 0.8% as the rate of accelerated aging is increased from a factor of 7x to 14x to 28x. The K concentration in the washcoat was also measured for an un-aged SCR catalyst. It was found to be approximately 0.2%.

Measurement of the CO, hydrocarbon (HC) and NO oxidation activity of the DOC samples and the NO conversion of the SCR samples was conducted in a bench flow reactor. The temperature of the catalyst sample was ramped from 100ºC to 650ºC at a rate of 10ºC/min. Figure 3 shows the relative change in catalytic activity.
for each of these aged DOCs. Figure 3a shows the T90 light-off temperature for C\textsubscript{3}H\textsubscript{6}. These data illustrate the impact that rate of accelerated aging has on the catalyst deactivation. The light-off temperature for the inlet of the most rapidly aged catalyst was 77°C higher than the least rapidly aged catalyst. This is consistent with the nearly 6-fold increase in K found in the washcoat of this catalyst. The light-off for the catalyst aged at a 14x rate of acceleration is only 8°C higher than that of the catalyst aged at a 7x rate of acceleration. Also note that the impact of accelerated aging rate on HC light-off was isolated to the inlet of the catalyst, with no differences seen at the outlet of the DOCs.

Figure 3b shows the T90 light-off temperatures for CO. This data shows a similar trend in performance with the most rapidly aged catalyst having a 79°C higher light-off temperature than the least rapidly aged catalyst. As with the HC light-off performance this change in performance between the catalyst aged at a 14x rate of acceleration and a 7x rate of acceleration was minimal. There was also little impact of accelerated aging rate on the performance at the outlet of the DOCs.

Figure 3c illustrates the performance for NO oxidation of the aged catalysts. This figure shows the temperature at which 20% of the total NO\textsubscript{x} is NO\textsubscript{2}. Compared to the HC and CO light-off, NO oxidation appears to be the most sensitive to rate of accelerated aging. T20 for the most rapidly aged catalyst was 140°C higher than T20 of the least rapidly aged catalyst. Unlike the HC and CO light-off performance, the catalyst aged at a 14x rate of acceleration is even different than the catalyst aged at a 7x rate of acceleration. Again this impact of accelerated aging rate is primarily isolated to the inlet of the front brick with the outlet performance being very similar.

Figure 4 illustrates the emissions performance for these SCR catalysts aged at the different rates of acceleration. This plot shows the percent NO conversion, measured in a bench flow reactor, over a range of temperatures. This performance was measured for the inlet of the front SCR brick. As seen in the plot, the un-aged catalyst and the catalyst aged at a 7x rate of acceleration have similar performance. The catalyst aged at a 14x rate of acceleration has similar performance above about 250°C, but slightly reduced performance below 250°C. The catalyst aged at a 28x rate of acceleration has decreased performance throughout the entire temperature range. Illustrating the impact on low-temperature operation, the NO conversion for 200°C drops from 88%, to 82%, to 77% as the rate of accelerated aging was increased from 7x, to 14x, to 28x.

Additionally, ORNL researchers set up an accelerated aging system to compare the effects of an advanced IL and a commercial secondary ZDDP on TWCs. About 35 g of the IL or ZDDP was used in each test to simulate the maximum lifetime anti-wear additive consumption in a modern automotive engine. The lifetime anti-wear additive consumption was estimated based on the oil consumption data from both vehicle
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Toops – Oak Ridge National Laboratory and engine dynamometer tests and assumes 1% additive concentration in the lubricant.

With 950°C max temperature and 900°C target temperature at the mid-catalyst point, it was not possible to operate the TWC under precise stoichiometric operation as would be typical in a vehicle. This is because the genset operates fuel-rich with up to 7-8% CO in the exhaust and at stoichiometric conditions the exhaust temperature will reach well above 1,000°C due to the combustion of all of the reductants. Instead, tests were conducted by altering the genset operation between lean and rich in such a way that the total time on rich matches that on lean. The switch between rich and lean was achieved through changing the flow rate of makeup air. For the engine aging experiments, 7.5 gallons of gasoline was consumed in a time period of more than 20 hours.

A close-coupled TWC was provided by GM that had been thermally aged to 150,000 miles, or the equivalent of FUL. These catalysts were employed in this study as they would be significantly more sensitive to the potential effects caused by the anti-wear additives. Large catalyst cores were extracted from the TWCs for the genset (42 mm outside diameter and 155 mm in length) and smaller cores were extracted for the bench reactor tests (11 x 11 x 50 mm).

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The bench flow reactor was used to evaluate the TWCs. Reaction conditions were 0.1% C3H6, 1.8% CO, 0.12% NO, 1.59% O2, 0.6% H2, 5% H2O, 5% CO2, and balance N2. Temperature ramped from 100 to 550°C at 2°C/min. The light-off temperatures for 90% conversion of NO, C3H6, and CO for the FUL-TWC were ~230°C before additional aging on the genset.

In order to investigate the impact of IL exposure on the performance of TWC activity, small cores from the

| FIGURE 3. Temperature for 90% or 20% conversion, T90 or T20, respectively, for (a) CO, (b) C3H6 and (c) NO to NO2 for the K-aged DOCs. |
| FIGURE 4. NOx conversion for aged front brick inlet SCR samples. |
FUL-TWCs were evaluated in a bench core reactor before and after IL exposure. A typical metric for the evaluation of TWC is based on the measurement of a temperature for a given conversion of either NOx, CO, or HCs. This is reported as T50, T80, or T90 for the temperature of 50%, 80%, or 90% conversion, respectively. The performances of the FUL-TWC aged on the genset but without anti-wear additive showed an increase in light-off temperatures of about 20°C—T90 was 249, 249, and 248°C, for NOx, HCs or CO respectively (Figure 5). After exposure to the IL in the genset, the T90 increased to 302, 290, and 291°C, respectively (Figure 6). Thus, the T90 increased about 50°C when exposed to the IL. Similarly, the ZDDP-aged samples saw an increase in T90 to 276°C and 279°C for HC and CO, but the NOx was not able to exceed 70% conversion. Thus, although the IL does illustrate some additional deactivation compared to the no anti-wear additive case; its impact on the TWC performance is similar or even better than the industry standard, ZDDP.

**CONCLUSIONS**

- Accelerating the exposure of the emissions control system to metal content that is above 14x leads to deactivation mechanisms that are not commiserate with normal aging.
  - Both 7x and 14x acceleration factors illustrated similar deactivation mechanisms.
  - 28-ppm K is too high to use in the long-term heavy-duty engine study.

**FIGURE 5.** (a) NO, CO, and C3H6 light-off curves and (b) temperatures of T50, T80, and T90 for FUL-TWC aged without anti-wear additive. Temperature ramp: 2°C/min under stoichiometric conditions.

**FIGURE 6.** (a) NO, CO, and C3H6 light-off curves and (b) temperatures of T50, T80, and T90 for FUL-TWC aged by gasoline + 1% IL. Temperature ramp: 2°C/min under stoichiometric conditions.
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- Accelerating with 14-ppm K has minimal additional impact over 7-ppm K.
- Impact of dosing concentration decreases along the length of the exhaust pipe.

- Using a newly developed stoichiometric gasoline aging system for TWC, demonstrated the novel additive effects the TWC similarly to the industry standard, ZDDP.

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

Overall 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) 2013 Objectives

Identify underlying causes for cooler fouling to lead to effectiveness stabilization in some cases and to cooler plugging in other cases.

FY 2013 Accomplishments

- Resolved an important modeling issue by showing that effectiveness “stabilization” does not necessarily require that the deposition rate reaches zero.
- Showed that the prevailing conditions during deposition determine the fouling outcome (either stabilization or plugging) by their influence on the deposit layer temperature and density.
- Provided recommendations for avoiding plugging through minimizing hydrocarbon deposition during low-temperature cooler conditions.

Future Directions

Project concluding this year.

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 hydrocarbons (HCs) and, in some cases, acids derived from sulfur present in the fuel and nitrogen dioxide (NO_2) produced during combustion. 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 Environmental Protection Agency emissions control durability requirements 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 pressures 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.
fuels. Examination of the deposits can provide insights into the fouling processes with these fuels and possible strategies to mitigate the problem. These experimental efforts are coupled to modeling through collaboration with other groups involved in EGR cooler fouling research.

RESULTS

Efforts this year have focused on analysis of multiple datasets with differing boundary conditions from this project as a means of discerning overall fouling trends and to gain a broader perspective on the process. The boundary conditions for this aggregate analysis include variable levels of hydrocarbon content, gas temperature, gas velocity, and coolant temperature. The objective of the analysis was to examine differences in end-state of the surrogate heat exchanger tubes in order to lend further understanding to the outcomes of “stabilization” of effectiveness and plugging. Differentiating between the conditions that cause these differing outcomes remains a critical need in terms of inclusion of physical mechanisms in models of the fouling process.

Data from several experimental efforts at different fouling conditions were combined to analyze the thermal resistance posed by the deposit layer. Figure 1 shows the relationship between deposit thermal resistance and the non-volatile deposit mass. Both scales have been divided by the tube heat transfer area, allowing the relationship to be generalized to coolers of different geometry. The results shown in Figure 1 are represented well by the linear fit, indicating that the thermal resistance increases at a constant rate with deposit mass as the deposit develops. The constant (or nearly constant) relationships between deposit mass and both the deposit thickness and deposit thermal resistance suggests that the characteristic thermal conductivity of the deposit is also nearly constant. Performing a regression of deposit thickness to deposit thermal resistance over the entire tube area produces a best-fit line, with the slope of the line being the deposit thermal conductivity in W/m*K. This regression is shown in Figure 2, which shows that a linear relationship fits the data well. The slope of the line, 0.033W/m*K is the effective thermal conductivity of the deposit, measured in situ. The result agrees well with previously published results that utilized a combination of ex situ measurements to characterize the deposit thermal conductivity [1]. For comparison, the thermal conductivities of many insulating materials fall within the range of 0.026–0.091 W/m*K [2].

The dominant mechanism in soot accumulation as a deposit in the EGR cooler is accepted to be thermophoresis [3]. Thus, the rate of non-volatile mass accumulation is strongly coupled to the temperature gradient that exists in the cooler. This gradient is defined by the gas temperature and the temperature at the gas/surface interface. Initially the gas/surface interface is at the tube wall, but occurs at the deposit surface as the deposit builds. As shown in Figure 2, the thermal resistance posed by the deposit layer increases linearly with its thickness (or non-volatile mass), and so the temperature at the gas/deposit interface is a function of the deposit thermal conductivity, deposit thickness, and the heat transfer rate through the deposit. The thermophoretic velocity also depends on other factors, including the particle concentration, thermal conductivity of the particles and gas, and gas viscosity. However, for a given operational condition, it is linearly proportional to the prevailing temperature gradient [3]. As the deposit builds and the surface gets hotter, the thermophoretic velocity and consequently the rate of deposit growth must slow.
In order to understand why thermal effectiveness appears to stabilize, it is necessary to understand the relationship between effectiveness and the overall heat transfer coefficient. Newton’s Law of Cooling governs the relationship between inlet and outlet temperatures and the overall heat transfer coefficient, and can be expressed as in Equation 1 [2]:

$$\Delta T_i = \exp\left(-\frac{P^i - P}{m + C_p^i} \cdot U\right)$$  \hspace{1cm} (1)

$\Delta T_i$ and $\Delta T_o$ are the temperature differences between coolant and gas at the tube inlet and outlet, respectively. $P$ is the inner perimeter and $L$ the length of the tube. $U$ is the overall heat transfer coefficient, $C_p$ is the specific heat of the gas, and $m$ is the mass flow rate. Making the simplifying assumption that the coolant is essentially isothermal, the denominator of the effectiveness expression can also be written as $-\Delta T_i$. Similarly, the numerator of the effectiveness expression can be shortened to $\Delta T_i$, the change in temperature of the gas through the cooler. Making these changes in notation, substituting the effectiveness expression for $\Delta T_i$ in the previous expression for Newton’s Law of Cooling, and solving for effectiveness one obtains Equation 2:

$$
\varepsilon = -\frac{\Delta T_o}{\Delta T_i} \cdot \exp\left(-\frac{P^i - P}{m + C_p} \cdot U\right) \hspace{1cm} (2)
$$

In this expression, $\Delta T_o$ is the change in the temperature of the gas between the tube inlet and outlet and $\Delta T_i$ is the difference in the gas and coolant temperatures at the tube outlet. As shown previously, the deposit non-volatile mass has a linear relationship with thermal resistance, meaning that it decreases the overall heat transfer coefficient linearly as mass is deposited in the tube. The expression above shows that effectiveness is related non-linearly to the overall heat transfer coefficient. This non-linearity is a consequence of the exponential decay of temperature difference between gas and coolant along the cooler.

Because $\ln(x) < x$, the change in effectiveness for an incremental change in thermal resistance declines as the thermal resistance increases. Hence, as the deposit develops, measurements of effectiveness become less sensitive to incremental changes in the deposit thickness (or mass). In one example case, the data show that at the onset of fouling the effectiveness drops by about 2.6% for every 0.0005 m K/W increase in thermal resistance. By the end of the experiment, the same increase in thermal resistance causes the effectiveness to drop by only about 1.4%, representing nearly a 50% loss in the sensitivity of the effectiveness measurement to increasing thermal resistance.

For deposits that experience stabilization, the non-volatile portion of the deposit is most important in terms of the deposit properties. However, in discussing plugging, the volatile portion of the deposit and its deposition mechanism becomes much more important. The volatile species of interest include HCs, water, and other species including organic acids and anhydrides that derive from partial combustion of fuel-related hydrocarbons. These species are driven towards the gas/surface interface by diffusion rather than by thermophoresis. If the surface has enough capacity to adsorb or condense significant amounts of the volatile species, then a concentration gradient is formed which causes more of these species to diffuse toward the surface. Carbon has long been used as a sorbent species, and soot also exhibits the tendency to adsorb gaseous species. If one considers the deposit structure as an adsorption medium, then the capacity for adsorption of volatile species in the layer is influenced by a number of factors, including temperature. For a given sorbent, the capacity to adsorb gaseous species is known to decrease as the temperature of the sorbent increases. This decrease in sorption capacity occurs because of increasing kinetic energies of the gaseous species. As a consequence, the deposit layer has a decreasing capacity to adsorb volatile species as it increases in temperature. Once the temperature of the surface (whether it is the tube wall or the gas/deposit interface) exceeds the dew point of the volatile species present, deposition of volatiles will shift from condensation to adsorption, decreasing the rate of deposition. As deposit build up continues, the deposit will saturate with volatile species as dictated by its local temperature and the partial pressure of the relevant gaseous species. It is possible for the volatile species to continue to diffuse through the porous deposit to the tube wall. Since the intermediate layers of the deposit have already been saturated by volatiles at their local temperature they may not participate significantly in adsorption once they are subsumed by deposit growth. Thus, the thickening deposit causes diffusion to become slower by increasing the distance through a porous layer for the volatile species to diffuse to the cold tube wall. This moderating effect may contribute, along with the higher surface temperature, to higher concentrations of volatile species at the deposit surface.

Diffusion across the boundary layer flow is driven by a concentration gradient, and so the rising concentration of volatiles at the deposit surface causes the migration of these species to slow. This condition is analogous to the higher temperature of the deposit surface causing thermophoretic deposition to slow. This process plays out when the deposit increases in temperature. If one considers a deposit that does not increase in temperature, however, this mechanism limiting volatile deposition no longer applies.

In order for the deposit to exhibit a very low rise in temperature and for the deposition of volatile species to remain significant, two possibilities exist. The first is that
very little heat transfer through the deposit takes place, thus causing the temperature rise through the deposit to be very low even if the thermal conductivity is also very low. The second is that the deposit thermal resistance must be much lower than has been shown previously in this paper.

If the deposit thermal conductivity is comparable to the results previously discussed in this report, then low deposit surface temperatures can only be achieved through very low heat transfer rates. As the deposit grows, the conditions under which the deposit can remain conducive to volatile species deposition become less likely to be sustained for long periods of time. Deposits dominated by the fractal structure formed from soot have very large void spaces. The combination of these factors suggests that “filling” of the voids in an established low-thermal conductivity deposit by condensation of volatiles is unlikely to lead to plugging. A more likely pathway to cooler plugging is one in which the formation of large void spaces is avoided, or that these void spaces are filled as rapidly as they form.

It is possible for high-density, low-thermal resistance deposits to form given certain conditions at the inception of fouling of a clean tube. To cause this situation, it is necessary for the initial deposition rate of volatile species to outpace that of non-volatile soot. In this case, the rate of coverage of the metal surface can be very rapid. For example, consider a very realistic volatile deposition rate of 4 mg/hr. This rate of deposition can form a fluid film approximately 30 nm in thickness in less than 5 minutes for the tube areas used in this study. Microscopic examination of the coverage of the tube surface with soot showed that complete coverage with soot deposits did not occur within 30 minutes, even with relatively high soot deposition rates. Hence, if the initial volatile deposition is high enough to create a film that is thicker than the characteristic diameter of a soot particle, the particles will deposit into a liquid film layer, rather than on the metal surface or on other soot particles. The thermal conductivity for many hydrocarbons is approximately 0.12 W/m*K, approximately a factor of 4 higher than the thermal conductivity measured herein and in a previous study for soot deposits [1,4,5]. The carbon included in the film may increase the thermal conductivity further, as the thermal conductivity value for solid amorphous carbon is 1.6 W/m*K [2]. Because of the difference in thermal conductivity, a deposit that is essentially a slurry of soot particles contained within a hydrocarbon film matrix can grow in thickness with much less surface temperature rise than soot-dominated deposits. The lack of a substantial rise in temperature means that the deposition mechanisms for both soot and volatiles are not self-limiting, as was the case for the fractal deposits discussed previously. Additionally, the inclusion of soot particles within the fluid layer may serve to allow the layer to become thicker than would otherwise be possible through increasing its viscosity.

An experiment was conducted to examine low-temperature deposit layers. In this experiment tubes were fouled for 8 hours using low gas mass flow rates (0.006 kg/min and 0.018 kg/min) in the presence of elevated HC concentrations (~150 PPM as C) and relatively high PM (Filter Smoke Number = 1.5). The inlet gas temperature was held at just over 200°C. The low mass gas flow rates represent either a leaky EGR valve condition or a situation in which the cooler is larger than is needed for a given condition. The coolant temperature was held at 40°C. Assessments of the deposit densities were conducted. The tubes fouled with flow rates of 0.018 kg/min exhibited densities of approximately 0.411 g/cm³ with the volatile species present and 0.295 g/cm³ with the volatile species removed. These density values, like the thickness values, differ by approximately an order of magnitude from the high-temperature deposits. The void space contained in these deposits is on the order of 5 times the volume occupied by solids, about a factor of 15 decrease from the high-temperature deposits. The measured thicknesses and densities for the low-temperature deposits show that the characteristic density of the non-volatile portion of the deposit is much higher than for the high-temperature deposits. Thus, the results support the concept of deposition of soot into a liquid film, which allowed the fractal soot aggregates to achieve a higher packing efficiency and reducing the formation of large void spaces within the deposit. The layer retains this characteristically high density even when the liquid film is subsequently removed.

**CONCLUSIONS**

- The fouling process in EGR coolers typically leads to either “stabilization” of effectiveness and plug failure of the cooler. The difference in these two outcomes is the characteristic thermal state of the deposit, as defined by the dominant deposition conditions for the engine system.
- “Stabilization” of effectiveness has been shown to require that the marginal growth rate of the deposit be small, but perhaps non-zero. This finding means that thermophoretic deposition can be ongoing, but slow. Thermophoretic deposition does not need to stop for effectiveness to appear stabilized. This outcome will occur when the duty cycle for the engine system results in relatively high-temperature, high-flow rate conditions in the EGR cooler.
- Plugging results from deposits that have a much lower thermal resistance, on the order of 5 times lower than the fractal, insulative deposits that
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are characteristic of “stabilized” effectiveness. Low thermal resistance deposits result from a predominance of relatively low-temperature conditions in the cooler, which result in very high levels of deposition of volatile species. The increased deposition of volatile species leads to lower formation of void spaces within the deposit, which is the characteristic that leads to reduced thermal resistance.

REFERENCES


FY 2013 PUBLICATIONS/PRESENTATIONS


SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

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

INTRODUCTION

Bench screening tests are not representative of real-world operation, and correlation between laboratory screening tests to real-world engine tests (such as automobile fleet trials) is a challenging task. This project deals with the development of accurate and reliable correlations between tribological data obtained from laboratory tests and actual engine data.

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 complex nature 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. 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 that the technology will function on real-world materials. These tests can be performed with fully formulated lubricants or pure base stock fluids. The rig tests are followed by single-cylinder tests using fired engines, multi-cylinder engine tests, and eventually with vehicle and fleet studies. As the technology progresses from one stage of test complexity to the next, the results are more and more representative of real-world conditions, however, the costs of the tests increase dramatically.

APPROACH

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 (Figure 1) utilize test protocols that are representative of vehicle conditions so that the tests can accurately screen technologies in the early stages of development, thus avoid testing technologies that will fail in full-scale tests. Laboratory tests such as the High-Frequency Reciprocating Rig (HFRR) are rapid, cost-effective, repeatable, and can provide information on the behavior of a system operating under certain conditions. Using
prototypical components, we are trying to determine the relevance of benchtop tests to real world conditions.

RESULTS

A test method for conducting friction tests of piston ring and cylinder liner materials under lubricated conditions was identified and reviewed. This test method (ASTM G181-11) covered 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 was to provide a means for preliminary, cost-effective screening or evaluation of candidate ring and liner materials. A reciprocating sliding arrangement was 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 was paid to specimen alignment, running in, and lubrication condition.

We performed tests that consisted of an initial ramp-up, then a 1-hour test at a constant speed, followed by a second speed “ramp” at the end at a specified load. The speed/time profile is shown in Figure 2. This speed profile allowed for the construction of a Stribeck curve which was used to categorize friction regimes for sliding of lubricated surfaces as shown in Figure 3. The variation of friction between two liquid-lubricated surfaces can be studied as a function of a dimensionless lubrication parameter $\eta N/P$, where $\eta$ is the dynamic viscosity, $N$ the speed, and $P$ the load projected on to the geometrical surface (pressure).

Figure 4 shows the frictional response for the two liner surfaces—a typical “plateau-honed” surface used on engine liners, and a smoother “slide-honed” surface. The smoother slide-honed surface minimizes metal-to-metal contact between surface asperities during midstroke of the piston and thus exhibits lower friction. The “cusps” of the waveforms are characteristic of a contact operating in the mixed or hydrodynamic regime which means that part of the contact is supported by metal asperities and part or the entire contact is supported by an oil film. From this figure it is evident that slide honing enables faster transition from boundary to mixed lubrication with respect to sliding speed.

The experimental results were compared with simulated results obtained from a model developed by Mahle Metal Leve S.A, Virtual Tribology Laboratory.
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Various lubricant formulations were also studied. Additives affect the frictional behavior of a lubricant. Figure 6 shows friction coefficient waveforms captured during the rubbing together of two steel surfaces (a 52100 steel ball against a 52100 steel flat) under reciprocating conditions (hence the positive and negative values). The surfaces were protected using three different oils. The waveforms are “square” in nature which means that the contact between the samples is in the boundary lubrication regime—a severe asperity interaction. It can be seen that a fully-formulated oil (FF) results in a significantly lower friction coefficient compared to a semi-formulated oil (SF), which is much like the FF without any friction modifiers and a base oil (BF) that contains only base stock with no additives.

Experimental friction tests were carried out with twin land oil control rings against the cylinder liner segments obtained from different slide-honing processes (baseline, diamond, and ceramic). Topography characterization was performed for slide-honed liner segments using three-dimensional white light interferometry measurements. The main bearing ratio parameters (i.e., Rpk, Rk, and Rvk) representing the statistical distribution of the roughness heights were practically similar, indicating the slide-honing features of such topographies. Only the percentage of folded metal distinguished the different honing processes. Profilometric measurements and topographical parameters are shown in Figure 7 and Table 1, respectively.

direction for the experimental data matches the positive predicted in the slide- and fine-honing plots but not the plateau-honed. The reason for this might be because more accurate inputs (Patir & Cheng’s model and Massachusetts Institute of Technology’s deterministic model) are needed in the code.

which used the Greenwood-Tripp asperity contact model and Swift-Steiber (Reynolds) cavitation model to predict the performance of a cylinder liner and piston ring under reciprocating conditions. The results are shown in Figure 5. Each test had a positive and negative direction because of the reciprocating nature of the tests; however, the labels positive and negative were arbitrary. There seems to be good correlation between the positive direction for both the experimental data and the simulated data for all three liners. However, the negative direction for the simulated data is high. The negative
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The influence of different lubricant oils (PAO10, commercial fully synthetic 10W-30) at 25°C and 100°C was investigated. The cycle average coefficient of friction was plotted as a function of speed for the three liners. In general, the boundary friction for the 10W-30 was lower than the base PAO10, possibly due to the friction modifiers present in the FF acting at the asperity level, as seen in Figure 8. No significant influence was observed on the friction losses of twin land oil control rings for liners with different honing processes. Similar results were observed in previous tests that used top compression rings. The results are shown in Figure 9.

During this project we investigated the effect of various nanoparticles on friction and wear behavior. Oxides and carbon-based additive were studied. Typical tests were performed under laboratory test conditions using a reciprocating test rig and two test configurations (a ball-on-flat and ring-on-liner) at speeds up to 5 Hz. Tests were performed over a range of temperatures up to 160°C using different oils. These oils were BF, SF, and FF. It was found that the addition of most nanoparticles reduced the coefficient of friction of base stock oil. However, a positive effect was not observed when nanoparticles were added to fully-formulated oil. In some cases, the formation of a non-conductive boundary film separating the sliding surfaces was evident. Examination of the rubbed surfaces showed the pronounced formation of a thick tribofilm, while mild polishing on the surface

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
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<tbody>
<tr>
<td>Sa [µm]</td>
<td>0.47 ± 0.10</td>
<td>0.34 ± 0.04</td>
</tr>
<tr>
<td>Sq [µm]</td>
<td>0.66 ± 0.10</td>
<td>0.48 ± 0.06</td>
</tr>
<tr>
<td>Sk [-]</td>
<td>-1.70 ± 0.40</td>
<td>-1.60 ± 0.20</td>
</tr>
<tr>
<td>Sku [-]</td>
<td>6.67 ± 2.29</td>
<td>7.30 ± 1.53</td>
</tr>
<tr>
<td>Spk [µm]</td>
<td>0.32 ± 0.03</td>
<td>0.35 ± 0.01</td>
</tr>
<tr>
<td>Sk [µm]</td>
<td>0.99 ± 0.20</td>
<td>0.81 ± 0.06</td>
</tr>
<tr>
<td>Svk [µm]</td>
<td>1.42 ± 0.13</td>
<td>1.02 ± 0.13</td>
</tr>
<tr>
<td>Folded Metal [%]</td>
<td>-</td>
<td>1.59 - 2.26</td>
</tr>
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</table>

FIGURE 7. Profilometric measurements for three liners: (a) baseline, (b) diamond-honed and (c) ceramic-honed.

FIGURE 8. Effect of honing processes using twin land oil control rings for (a) PAO10 and (b) 10W-30 at 25°C.

FIGURE 9. Effect of honing processes using top compression rings for (a) 10W-30 at 25°C and (b) 100°C.
was also observed in some cases. Our discussions with industry are continuing, and through a cooperative research and development agreement, we are trying to understand why there is friction performance improvement when using a carbon-based additive.

CONCLUSIONS

- Using the test protocol developed in this work, it is possible to distinguish between different types of honing.
- Improvements are needed to the Virtual Tribology Laboratory program to more accurately simulate the results from the reciprocating test rig.
- Depending on the synergistic role of the various additives and the amounts (i.e., wt% concentration) of fully-formulated oil used, oils from different manufacturers may result in different boundary friction.

- Temperature has a pronounced effect. Tribochemical reactions are often driven by or accelerated by temperature changes. Therefore, the boundary friction observed for the same lubricant at low temperatures might be different than at higher temperatures.
- Due to the formation of a tribofilm, tribochemical film or other means (such as physical mechanisms that might be responsible for friction reduction, i.e., layered low-shear strength particles) the boundary friction can also vary significantly.
- The addition of nanoparticles can reduce the coefficient of friction of base stock oil and improve wear in most cases. However, the positive effect is not observed when nanoparticles are added to semi-formulated or fully-formulated oil.
II.4 Advanced Lubrication Additives for Improved Fuel Efficiency

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Overall 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
- Determine durability limits and interaction of tribochemical films with basestock oil
- Validate performance in both bench-top testing and engine environments

Fiscal Year (FY) 2013 Objectives

- Explore, develop, and optimize techniques for the production of films with the same or similar structure as the tribochemical films from appropriate lubrication additives.
- Measure nano-mechanical properties of tribochemical films with different structures. This will enable the establishment of correlation between the structure and properties of the film and ultimately the frictional properties.
- Determine the mechanical durability of tribochemical surface films with different structures.

FY 2013 Accomplishments

- Measured the nano-mechanical properties of hardness and elastic modulus for films with different structures. Results need further studies to better elucidate the observed behaviors.

Future Directions

- Evaluate the thermal durability and limit of the tribochemical films with different structures.
- Assess the impact of base fluid viscosity on the frictional performance and durability of various tribochemical surface films.
- Conduct tribological performance evaluation in terms of scuffing and wear under severe contact conditions for additives that produce low-friction tribochemical films.

INTRODUCTION

Most critical components in engines and transportation vehicle sub-systems are lubricated by oil. 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 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. 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 to attain 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 the low-friction tribochemical surface layer, better understanding of the nature, the composition, and 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 advance the in situ-generated surface layer film with low friction to the point of commercialization. This will involve development of a controlled method of production, characterization of tribological properties, and performance optimization for a variety of pertinent components. Detailed modeling and validation studies (bench-top and engine tests) will also be performed.

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

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

**RESULTS**

In FY 2012, we determined the effect of temperature on the frictional behavior of tribofilms formed from both model and commercial lubricants [1]. A complex dependence of friction on temperature was observed. Analysis of the structure of the films with various frictional attributes was consistent with our previous observation that crystalline films exhibit relatively high friction, while films containing a significant amount of amorphous phase tend to exhibit low friction. Based on these observations and the role of temperature, a method was developed via temperature ramp with appropriate additives to produce desirable frictional properties for the tribofilm. Figure 1 shows the frictional variation in a reciprocating sliding line contact of a 52100 steel roller sliding against a 52100 steel flat as an illustration of the friction behavior during the formation of a low-friction and a high-friction tribofilm. The film formed from lubricant 1 has an amorphous crystalline phase and is the low-friction variation, as indicated by a near steady friction of 0.05 during its formation. The film formed from lubricant 2 is the high-friction variant with crystalline phase structure. This is indicated by the steady friction of 0.11 during its formation.

**Mechanical Durability**

The mechanical durability of various types of tribofilm was also evaluated by determining the load-carrying capacity of the films under dry reciprocating sliding. The tests were conducted by sliding a 52100 steel roller on various tribofilms using a step-load increase protocol. Starting with an initial value of 50 N, the contact load was increased by 25 N every minute until failure occurred, as indicated by a sudden large permanent increase in friction coefficient or the maximum load limit of the test rig, which is 800 N. The maximum load a film can sustain without failure is defined as its “load-carrying capacity.” Figure 2 shows an example of typical variation of friction coefficient with increasing contact load during the durability test for a film that did not fail and one that failed at about 300 N.

Tests of load-carrying capacity were also conducted with uncoated 52100 steel flat and flats that were coated with two variants of state-of-the-art diamond-like carbon (DLC), as well as two variants of low-friction tribofilms. As shown in Figure 3, the uncoated steel has a load-carrying capacity of only 50–75 N, as indicated by the permanent and large increase in friction. The two DLC coatings were able to sustain the maximum load of 800 N.
II. Fuels and Lubricants to Enable High Efficiency Engine Operation

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Films that are a mixture of amorphous and crystalline phases possess low friction and high load-carrying capacity. Thus, in terms of optimal tribological performance with regard to friction and durability, tribofilms containing amorphous and crystalline phase mixtures are desirable.

Nano-Mechanical Properties

The nano-mechanical properties of the tribofilms with different structures were also studied. The measurements were conducted with a Hysitron TriboIndenter® system using a Berkovich indenter. The surfaces of the tribofilms were first scanned to determine areas and locations suitable for nano-indentations. Tests were conducted in the displacement control mode. This involves indenting to a predetermined depth ranging from 20 nm to 100 nm. The procedure enables the measurement of the tribofilm hardness and elastic modulus at different depths. Figure 4a plots the hardness measurements for several tribofilms with different structures. In the figure, “A” stands for amorphous structure; “A/M” for mostly amorphous with a small amount of nano-crystalline phase; “M” for a mixture of amorphous and crystalline phases; and “C” for all-crystalline films.

Based on the study of numerous tribofilms with different structures, in general, we have observed that the films that are all amorphous have low friction but also low load-carrying capacity. Films that are a mixture of amorphous and crystalline phases possess low friction and high load-carrying capacity. Thus, in terms of optimal tribological performance with regard to friction and durability, tribofilms containing amorphous and crystalline phase mixtures are desirable.

**Figure 2.** Friction coefficient variation during a load-carrying capacity test for (a) film that did not fail and (b) film that failed at 300 N.

**Figure 3.** Load-carrying capacity of two low-friction tribofilms, two DLC coatings, and an uncoated steel surface.

The hardness of all tribofilms, regardless of the structure, is much lower than the hardness of the steel substrate material at all depths between 20 nm and 100 nm. The procedure enables the measurement of the tribofilm hardness and elastic modulus at different depths. Figure 4a plots the hardness measurements for several tribofilms with different structures. In the figure, “A” stands for amorphous structure; “A/M” for mostly amorphous with a small amount of nano-crystalline phase; “M” for a mixture of amorphous and crystalline phases; and “C” for all-crystalline films.

The hardness of all tribofilms, regardless of the structure, is much lower than the hardness of the steel substrate material at all depths between 20 nm and 100 nm. The average steel substrate hardness was about 13 GPa while that of the hardest tribofilms was...
CONCLUSIONS

Based on the firm connection established between the frictional behavior and the structure of tribochemical surface films in the previous year in this project, the focus of the project during this reporting period is development of methods to produce tribofilms with a structure that can produce desirable tribological attributes. A thermally based method was developed to produce tribofilms with low friction. Under dry sliding contact, the films produced by the new method exhibit friction coefficients significantly lower than state-of-art DLC coatings. A patent was filed and is pending for this invention. The mechanical durability of the tribofilms was also evaluated during the reporting period. Although films with all-amorphous structure have low-friction properties, they have relatively poor durability. By contrast, films with amorphous and nano-crystalline structure exhibit both low friction and very good load-carrying capacity. Finally, the nano-mechanical properties in terms of hardness and elastic modulus were measured for several tribochemical surface films with different structures. The measured hardinesses of all the tribofilms studied were lower than those of the steel substrate. Films with an amorphous structure have higher hardness than the films with crystalline structure. The observation was rather surprising given that amorphous films exhibit lower frictional properties. More work is needed to elucidate the mechanical properties and mechanical behavior of the tribochemical surface films.

REFERENCES


FY 2013 PUBLICATIONS/PRESENTATIONS


SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

II.5 Fuel Efficient Lubricants for Legacy Vehicles

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Overall Objectives

- Design and develop a novel lubricant additive package that can provide sustainable friction reduction while ensuring reliability and durability of legacy vehicles.
- Conduct a comprehensive tribological performance evaluation in terms of friction, wear, and scuffing for the new lubricant additive system(s).
- Develop a mechanistic understanding of how the new additives function in lubricated interface.
- 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) 2013 Objectives

- Establish tribological performance benchmark in terms of friction and wear properties for the new nano-based additive systems.
- Evaluate the impact of the encapsulating system on tribological performance and time sensitivity of the nano-additive.
- Assess the impact of concentration on tribological performance of different viable nano-additive systems.
- Initiate preliminary characterization of surfaces lubricated by nano-additive systems for mechanistic understanding and eventual additive system optimization.

FY 2013 Accomplishments

- Established friction and wear benchmark for nano-additive systems. Based on evaluation of five advanced engine oils and one gear oil, the boundary friction was observed to be in the range of 0.07 to 0.13.
- Evaluated and identified several nano-particulate additive systems with frictional and wear performance equivalent to or superior to the benchmark.
- Assessed the impact of encapsulation for time release attributes, as well as the effect of temperature and concentration on the tribological performance of many additive systems.

Future Directions

- Evaluate wear performance of candidate nano-additive systems under severe contact conditions using a four-ball test rig.
- Evaluate the scuffing performance of potential nano-additive systems with standard block-on-ring test protocol.
- Analyze the nano-structure of tribo-chemical films formed from nano-additive systems using transmission electron microscopy (TEM) with focused ion beam.
- Measure nanoscale mechanical properties of the tribo-chemical films formed from nano-particulate systems.

INTRODUCTION

Significant petroleum fuel savings and the consequent reduction in emissions can be achieved by improving fuel efficiency and using non-petroleum-based fuels in legacy vehicles currently on U.S. roads. At present, there are an estimated 250 million vehicles on U.S. roads and less than 10 million of them are flex-fueled models. About 95% of fuels for these vehicles comes 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 ongoing 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 from now), these programs will reduce petroleum use 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 a lubricant that can reduce engine friction compared to the currently available ones. Also, the use of higher levels (greater than the current 10%) of ethanol bio-based fuel in the current legacy gasoline engines will require an engine lubricant that can protect the engine components from expected accelerated wear. Thus, substantial reduction of petroleum can be achieved in the near term with legacy vehicles by developing 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. The current proposed project seeks to develop lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in legacy vehicles.

**APPROACH**

The main goal of this effort is to develop and deploy novel lubricant additive packages that can provide sustainable friction reduction in legacy vehicle engines over an extended duration. The additive 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, nano-particles will be specifically designed and functionalized 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 release manner, similar to the time release of pharmaceutical agents. Layered nano-particles with a friction-reducing core and pressure-sensitive shell will be designed and synthesized. Under high contact pressure in the boundary lubrication regime, wherein friction is high, the particle shell will decompose, making available the friction-reducing core. In the vehicle application, 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 can also act to dissipate frictional heat generated at the sliding contact interface. Additives that can increase heat removal from the tribological contact interface, especially under severe contact conditions, will enhance the reliability and durability of the surface. Such additives exhibit an extreme pressure action. Layer nano-particles will be designed and synthesized to increase dissipation of heat from tribological contact interface.

**RESULTS**

During the first year of the project, preliminary evaluation of tribological performance for several nano-particulate systems showed that friction and wear reduction can be achieved by the above approach [1]. Encapsulation as a means to achieve time-release attributes was also demonstrated. During FY 2013, efforts were devoted to the establishment of tribological performance benchmarks for the project by means of tribological testing of state-of-the-art commercially available oils. For the new lubricant additive formulation to be acceptable, its performance in terms of friction reduction, wear, and scuffing prevention must be at least equal, and preferably superior to, those for current advanced lubricants.

Figure 1 shows the average friction coefficient of steel-on-steel sliding contact pairs when lubricated by five engine oils (E1 through E5) and one gear oil (G1) under unidirectional (Figure 1a) and reciprocating sliding (Figure 1b). The range of friction coefficients for the current lubricants is shown on both graphs (dark horizontal lines). This represents the frictional benchmarks for the project. Similar benchmarks were also established for wear attributes.

Figure 2 shows the frictional behavior of candidate nano-additive systems during unidirectional sliding of contact involving a steel ball on steel flat. All the tests were conducted at 100°C, and the nano-additives were blended into 5W40 synthetic basestock fluid. Normal load was 10 N, and sliding velocity was 10 mm/s, which ensures that the contact operates under the boundary lubrication regime and that the additives will have an effect on friction behavior. Included in the figure are the results of the effects of nano-additive concentration (ranging from 0.01 to 2%) and encapsulation for different nano-particulate additives.

For some additives, the optimum concentration was very low, e.g., 0.05% for TiO$_2$ with average boundary friction coefficient of 0.07. With encapsulation of the TiO$_2$ additive, a very low boundary friction coefficient of 0.04 was observed, but the additive concentration had to be increased to 2%. For other additives (e.g., CaCO$_3$), significant boundary friction redirection was observed at concentrations as low as 0.05%, with no further reduction in friction with increased concentration. With still other additives (e.g., SiO$_2$), an increase in concentration results in an increase in friction coefficients. In general, many of the tested additive systems exhibited frictional properties
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(a) Unidirectional Sliding – Coefficient of Friction
All Tested with Fully Formulated Engine and Gear Oil

(b) Reciprocating Sliding – Coefficient of Friction: Final 2 min.
All Tested with Fully Formulated Engine and Gear Oil

**Figure 1.** Average friction coefficient in boundary lubrication regime for advanced commercially available engine and gear oils in (a) unidirectional sliding at 100°C and (b) reciprocating sliding at 100°C and 130°C.
**Figure 2.** Average friction coefficient for nano-particulate additive in synthetic base oil under unidirectional sliding at 100°C, including effect of concentration and encapsulation. Horizontal solid lines show benchmark for five engine oils and one gear oil.
equivalent to, or superior to, the frictional properties of current advanced lubricants. Results of the initial assessment of the nano-particulate additive concentration and the encapsulation showed a plausible pathway to even better performance.

In addition to friction, the nano-particulate additive systems also showed improved wear performance compared to the current advanced lubricants. Figure 3 shows the wear of the flat specimens at the conclusion of the tests. The benchmarks for the wear properties of advanced, commercially available lubricants are also indicated on the figure. Several of the systems showed significant reduction in wear. Indeed in many systems, negative wear via buildup of a layer on the surface was observed, as noted by an asterisk above the bar. More work is underway to further elucidate the negative wear phenomenon.

The friction behavior of various nano-additive systems for a reciprocating sliding steel ball on steel flat under the boundary lubrication regime is summarized in Figure 4. The bar graphs show the effects of encapsulation system, additive concentration, and operating temperature (100°C and 130°C). For additives such as CaCO₃, there is a critical concentration of about 0.1% for sustainable friction reduction. Higher concentration did not produce further reduction in friction. The average boundary friction of about 0.06 with this additive is comparable to the best available commercial lubricant today. Furthermore, the friction appears to be independent of the temperature (at least for the two temperatures tested). Another system with significant boundary friction reduction is the encapsulated Cu; here again, the friction is independent of temperature. By contrast, other systems are very temperature sensitive, such as encapsulated SiO₂. Overall, except for a few cases, the friction behavior of most systems tested is within the performance range of the current state-of-the-art advanced lubricants. The wear behavior in reciprocating sliding for various additives was similar to that in the unidirectional sliding, with many systems showing negative wear.

Preliminary characterization of the near surface layer and tribo-films formed from one of the promising additive (CaCO₃) showed the formation of a relatively uniform layer of about 20-nm thickness (Figure 5). The film consisted of an amorphous and nano-crystalline mixture. Films with such structure are known to exhibit relatively low friction and wear resistance. This observation is in agreement with the present friction and wear results.

CONCLUSIONS

A tribological performance benchmark was established for the evaluation and functional assessment of the nano-particulate additive technology being developed in this project. To that end, the friction and wear performance was determined under different lubrication regimes of the best state-of-the-art commercial engine and gear oils. Several nano-particulate systems with and without encapsulation were observed to meet or exceed the performance benchmark. Optimal additive concentration was also determined for several candidate systems. In some systems, the concentration had no effect on friction and wear performance. Similarly, some systems were sensitive to temperature, while others were not. Initial nano-structural analysis by focused ion beam/TEM of surface films formed from nano-additive system showed that the layer is similar to the ones formed from advanced lubricant via tribo-chemical reaction.

REFERENCES


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Figure 3. Wear volume in the flat specimen in the unidirectional sliding test at 100°C. Horizontal solid lines show benchmark for five engine oils and one gear oil.
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**Figure 4.** Average friction coefficient for nano-particulate additive in synthetic base oil under reciprocating sliding at 100°C and 130°C, including effect of concentration and encapsulation. Horizontal solid lines show benchmark for five engine oils and one gear oil.
FIGURE 5. TEM micrograph of tribo-film formed from CaCO₃ nanoparticulate additives.
II.6 Self-Replenishing Smart Lubricants

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Overall Objectives

Develop lubricants that would provide reduction in friction and wear and serve as a drop-in solution to existing systems

Fiscal Year (FY) 2013 Objectives

Develop, characterize, and optimize self-replenishing lubricants that would provide reduction in friction and wear and remain in suspension

FY 2013 Accomplishments

- Organic-coated polyoxometalates (O-POMs) were synthesized by reacting silicotungstic acid (H$_4$SiW$_{12}$O$_{40}$) with or without ammonium chloride (NH$_4$Cl) and then modified with a surfactant
- It was determined that O-POMs tend to self-assemble into a variety of structures with the morphology dependent on concentration and type of the surfactant used
- The most beneficial additives reduced the average coefficient of friction by almost 20% but wear remained high
- The highest performing additives were ones that produced a conductive or semi-conductive tribo-film for the length of the reciprocation test

Future Directions

Even though significant progress with O-POM synthesis was made, we didn't see the anticipated friction and wear reduction. Also, long-term stability has not been addressed. Furthermore, even with the use of organic surfactants that have both cationic and anionic tails, it has been difficult to avoid self-assembly in solution, which in turn prevents self-assembly during tribological interactions. This renders self-replenishment of a tribo-film not feasible at the moment. Therefore, a “no-go” decision has been made.

INTRODUCTION

Current challenges for improved wear, friction and performance require 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, offering higher efficiencies, and extending the life of components. Nanolubricants (dispersion of nano-sized materials [10-100 nm] in liquid lubricant) are emerging concepts in lubrication, some of which have demonstrated reduction in friction and wear of moving parts.

This work aims to develop, characterize, and optimize self-replenishing lubricants that would provide reduction in friction and wear comparable to the effects of low-friction, solid-lubricant coatings in cost-effective form of drop-in solution, applicable to any existing system. Dispersed into the liquid, new low-friction additives will provide higher efficiencies than direct nanoparticle dispersions, improved heat dissipation, superior stability in solution, and will also represent environmentally friendly alternatives to 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. Approximately 10 to 15% of all fuel consumed in transportation is lost to parasitic friction in engines and transmissions. A 10% reduction in engine friction will result in a 1% improvement in fuel economy and save over 100,000 bbl of petroleum per day.

It has been established that parasitic friction in vehicle engines results in a 10% loss of the total energy input. To improve performance, lubricant additives can be used to reduce boundary friction and increase fuel economy. Researchers have shown that nanoparticles can significantly improve tribology properties of a lubricant. Specifically, the anti-wear properties, friction properties, and load-carrying capacity of various lubricants are improved. The factors that determine lubricant effectiveness are viscosity, dispersion quality, applied load, temperature, and sliding velocity. Because friction generates large amounts of heat, thermally stable, non-oxidizing and nonvolatile lubricants are preferred. Inorganic nanoparticles as lubricant additives have been previously studied. It was shown that their tribological performance depends on the size, shape,
and concentration of nanoparticles, and that layered nanomaterials, such as graphite and MoS₂, provide highest improvements in friction and wear reduction. However, nanomaterial usage is limited by poor dispersion stability in base lubricant oils due to their dissimilar nature. To resolve this issue, and improve suspension stability of inorganic nanoparticles in organic oils, surfactants with long hydrocarbon chains are utilized.

Although several friction and wear reduction mechanisms have been proposed, nanoparticle effects in tribological improvements are often attributed to tribo-film formation. At elevated temperatures, tribo-active elements (P, S, W, N, etc.) can react with the surface and form a layered protective tribo-film, significantly limiting asperity contact.

The prospective additive studied in this work is O-POMs. POMs are inorganic metal oxide macromolecular clusters formed by transition metals (Figure 1).

The clusters are notable for their thermal and oxidative stability, distinct size and shape, and self-assembly into layered structures. POM’s potential for applications in material science and other fields has been extensively researched. However, little has been done to test their effectiveness as nanoscale lubricant additives. In order to achieve a stable dispersion of inorganic POM clusters in organic polyalphaolefin (PAO) oils, modification of the POM with organic compounds is required. The ability of POMs to self-assemble into layered structures, as well as, the presence of hydrocarbon chains may allow for the chain to fill the peaks and valleys of the friction surfaces, reducing shear stress (Figure 2 and Figure 3).

Moreover, POMs are composed of tribo-active elements, which may lead to effective film formation and ultimately to tribological improvements. In this research effort, \((\text{NH}_4)_4\text{SiW}_{12}\text{O}_{40}\) was synthesized and modified with various types of surfactants. The resulting hybrid POMs were characterized with scanning electron microscope (SEM), dispersed in synthetic oil PAO10, and their tribological properties were evaluated against pure PAO10 oil.

**APPROACH**

The novel approach to lubricant additives we propose to develop 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
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In a minority of the syntheses, NH\textsubscript{4}Cl was also used. NH\textsubscript{4}Cl crystals were synthesized and purified in the lab after a reaction of ammonium hydroxide (NH\textsubscript{4}OH) and hydrochloric acid (HCl). The modified (NH\textsubscript{4})\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40}POMs were prepared by adding a weighted amount of H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40} to a flask and then dissolving the powder with deionized water. In the syntheses that utilized NH\textsubscript{4}Cl, NH\textsubscript{4}Cl crystals were added to a beaker in a molar ratio of 4 NH\textsubscript{4}Cl: 1 H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40}, dissolved in a minimal amount of de-ionized H\textsubscript{2}O, and heated to 60°C. The syntheses with DODA and DODAPS were done with and without NH\textsubscript{4}Cl. In a

RESULTS

The chemicals used in each synthesis were H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40} and surfactant. Our initial approach of using oleic acid did not result in a true solution. Instead, nanoparticles formed and then settled. Therefore, a surfactant that could produce a true solution had to be identified. Five surfactants were tried. The basis for selecting them was that they had to be organic and cationic in nature so that they could react with the inorganic anionic POM, but also be miscible in PAO. These were: cetyl trimethyl ammonium bromide (CTAB), benzethonium chloride (BZT), benzalkonium chloride (BAC), dimethyldioctadecylammonium chloride (DODA), and N-Dodecyl-N, N-dimethyl-3-ammonio-1-propanesulfonate (DODAPS) (Figure 4). The procedure was based on the methods of Sun, et al [1].

Each surfactant, as well as, H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40}, was chemically pure and obtained from Sigma Aldrich. In a majority of the syntheses, NH\textsubscript{4}Cl was also used. NH\textsubscript{4}Cl crystals were synthesized and purified in the lab after a reaction of ammonium hydroxide (NH\textsubscript{4}OH) and hydrochloric acid (HCl).

The modified (NH\textsubscript{4})\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40} POMs were prepared by adding a weighted amount of H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40} to a flask and then dissolving the powder with deionized water. In the syntheses that utilized NH\textsubscript{4}Cl, NH\textsubscript{4}Cl crystals were added to a beaker in a molar ratio of 4 NH\textsubscript{4}Cl: 1 H\textsubscript{4}SiW\textsubscript{12}O\textsubscript{40}, dissolved in a minimal amount of de-ionized H\textsubscript{2}O, and heated to 60°C. The syntheses with DODA and DODAPS were done with and without NH\textsubscript{4}Cl. In a
separate beaker, a surfactant was added according to a 4 surfactant: 1 H₄SiW₁₂O₄₀ molar ratio and dissolved in absolute ethanol or DI H₂O. The contents of the second beaker were heated to 60°C with stirring. In the case of CTAB, a synthesis with a 10 CTAB: 1 H₄SiW₁₂O₄₀ molar ratio was also performed. When NH₄Cl was used, the surfactant solution was added to the ammonium chloride solution. The combined surfactant and NH₄Cl solutions were transferred to an Erlenmeyer flask and maintained at ~60°C. Next, the H₄SiW₁₂O₄₀ solution was added drop-wise to the Erlenmeyer flask with vigorous stirring and periodic ultra-sonication. In most cases, a white precipitate formed upon addition. After the complete addition of H₄SiW₁₂O₄₀, the reaction flask was maintained at 60°C with vigorous stirring and periodic ultra-sonication for one hour. A thermocouple was used to monitor all solution temperatures. After the hour, the contents of the reaction flask were transferred to centrifuge tubes, and centrifuged at 6,000 RPM. After centrifugation, for all samples, except DODAPS, there were clearly two products observed. There was a solid product at the side of the vial and a liquid product at the bottom of the vial, which was a heavier fraction than water or ethanol. The centrifuge tubes were decanted, and the solid and liquid phases were separated and purified with absolute ethanol. This process was repeated twice. In some cases, both the solid and liquid products were tested tribologically, but for most compositions only the solid fraction was tested. After obtaining a pure solid, it was dried under vacuum. When DODAPS was used as the surfactant, a white solid was not produced upon addition of H₄SiW₁₂O₄₀. In this case, excess water was evaporated until a clear, glass-like solid was obtained.

The morphology of O-POMs was established via scanning electron microscopy. SEM images have been obtained for the CTAB, BAC, BZT and DODA modified POMs (Figure 5). Due to the liquid state of the DODAPS-modified POMs, SEM imaging was not performed. SEM images of the synthesized O-POMs reveal that the surfactant-modified POM clusters self-assembled into a variety of layered structures. Specifically, spherical (Figure 5, Row D), disk-shaped (Figure 5, Row E, Column 2), sheet-like (Figure 5, Row B, Column 3), amorphous (Figure 5, Row B, Column 1), and tube-shaped self-assemblies (Figure 5, Row C, Column 1) are present. Some of the factors that influence morphology might be the type of surfactant, concentration of surfactant, and solvent system.

The average size of an individual O-POM self-assembly in PAO10 dispersion was determined using dynamic laser scattering and found to be 50 nm. The size was not significantly affected by the type of surfactant used to modify the POM. However, the concentration of surfactant to POM had an effect. The sheet-like and amorphous self-assemblies of the CTAB modified POMs at 10 CTAB: 1 H₄SiW₁₂O₄₀ molar ratio (Figure 5, Row B) were over 10 microns long. However, this was in a dried sample and size can vary in PAO dispersion. Currently, the dispersion quality of the O-POMs in PAO10 has been established qualitatively. For most additives, the solid O-POMs separated from PAO10 within 15 hours and the 0.1 wt% samples maintained dispersion for a longer period than the 1.0 wt% samples. In contrast, the DODAPS modified POMs, synthesized with and without NH₄Cl, maintained dispersion for at least 60 hours. Because commercial applications rely on dispersion ability, the quality of O-POMs’ dispersion in PAO10 needs to be improved.

The tribological properties of the O-POMs as lubricant additives were characterized using a ball-on-flat test configuration. Based on our tests it was evident that the tribological performance is dependent on the type of O-POM used as the additive in PAO10. Because the inorganic core, H₄SiW₁₂O₄₀, was always present, the surfactant must be a key reason for the variance of tribological improvements between differing O-POMs.
A reason for this may be found in the morphology of the resulting O-POM self-assemblies. The shape of the additive has minimal effect on the tribology properties of the additive [2]. Another reason may be the composition of the surfactant used to modify the POM. As seen in Figure 4, the surfactants share certain characteristics, but they also have chemical differences. All are quaternary ammonium cations, but DODAPS also has a negative charge present. CTAB, DODA, and DODAPS each have a long hydrocarbon side chain. Unlike CTAB and DODAPS, DODA has two long hydrocarbon side chains. The long side chain of BZT is the most complex; it is composed of an ethoxy, phenox, and other branching hydrocarbon functional groups. The DODA modified POM performed the poorest compared to the rest of the O-POMs. This demonstrates that the presence of a second long hydrocarbon chain does not improve the quality of tribological performance. The BZT-POM additive also performed poorly. It was determined that presence of oxygen and a benzene ring in the long side chain did not have significant beneficial effects on the tribological properties of PAO10. The BAC, CTAB, and DODAPS modified POMs each improved the friction properties of PAO10 by at least 10%. Even so, there was a difference between the BAC modified POM and the CTAB and DODAPS modified POMs. This was the occurrence of a semi-conductive tribo-film during reciprocation, which was maintained for an extended period of time for the CTAB and DODAPS modified POMs. For DODAPS-POM, the conductive properties of the tribo-film most likely result from the presence of its negative charge.

The reciprocation was done on a high frequency reciprocation rig for one hour at 120°C with a 15.6 N applied load at varying rpm. A ½” Grade 25 steel ball was reciprocated against a mirror-polished 52100 steel flat. The reciprocation was done on a high frequency reciprocation rig for one hour at 120°C with a 15.6 N applied load. The O-POM additive was dispersed in PAO10 through ultra-sonication. Most additives were tested at 0.1 wt% and 1.0 wt% concentration in PAO10, while some compositions were only tested at 1.0 wt%. The friction test results of the best performing additives are shown in Figure 6. A reduction in friction was observed over PAO10.

Following reciprocation, the wear scars were imaged. Figure 7 shows microscope images of the balls and flats tested with the best performing additives. It was found that each additive improved the friction properties of PAO10. This effect is most likely due to the formation of an O-POM tribo-film on the sample surface during reciprocation. The highest performing additives were ones that produced a semi-conductive tribo-film for the length of the reciprocation test. Additionally, surfactants with one long hydrocarbon tail performed better than a surfactant with two long hydrocarbon tails. Furthermore, an O-POM synthesized in the absence of NH4Cl improved the tribology properties of PAO10 more than the same O-POM synthesized with NH4Cl.

The concentration of a surfactant used during the synthesis was increased because it was thought that better coating of the inorganic POM clusters would occur, improving dispersion stability.

An increased concentration of surfactant to H2SiW12O40 did affect the morphology of the resulting O-POM, in fact, the degree of the self-assembly increased dramatically. In addition to morphology, the tribological properties of the additive were also affected. Specifically, the performance of the 1.0 wt% CTAB-POM additive decreased by almost 10% when using the additive with a 10 CTAB: 1 H2SiW12O40 molar ratio. Although both additives resulted in tribo-film formation, the CTAB-POM, synthesized with an increased surfactant concentration, lacked coverage when compared to the other CTAB-POM additive. The ball and flat had a large fraction of exposed metal. This bare metal exposure results from a tribo-film being rubbed off faster than it can be applied during reciprocation, limiting tribological improvements. Additionally, it was noticeable that the 4 CTAB: 1 H2SiW12O40 molar ratio CTAB-POM maintained a conductive film for a longer period of time.

After examining the synthesis procedure, it was evident that the ammonium cation and the positively charged surfactant may be competing to react with the [SiW12O40]4- inorganic core. In order to study this, the syntheses of the DODA and DODAPS modified POMs were completed with and without ammonium chloride. The wear scars of the flat have similar
morphology dependent on concentration and type of the surfactant used. The majority of the O-POMs dispersed in PAO10 had an average self-assembly size of 50 nm.

After characterization, the tribological properties of the O-POM additives in PAO10 were studied. The data shows that each additive reduced the average coefficient of friction of PAO10. The most beneficial additives reduced the average coefficient of friction by almost 20% which at the moment cannot be considered significant since commercial fully formulated oils offer improvements in the order of 60% or more. The highest performing additives were ones that produced a semi-conductive tribo-film formed from reactions of the O-POMs with the metal surfaces of the ball and flat for the length of the reciprocation test. Additionally, surfactants with one long hydrocarbon tail performed better than a surfactant with two long hydrocarbon tails. Furthermore, an O-POM synthesized in the absence of NH$_4$Cl improved the tribology properties of PAO10 more than the same O-POM synthesized with NH$_4$Cl.

**CONCLUSIONS**

O-POMs were synthesized by reacting H$_4$SiW$_{12}$O$_{40}$ with or without NH$_4$Cl and then modified with a surfactant. In total, five surfactants were used and eight distinct additives were synthesized. The surfactants were BAC, BZT, CTAB, DODA, and DODAPS. After each synthesis, the morphology of the O-POMs was evaluated with SEM imaging. It was determined that O-POMs tend to self-assemble into variety of structures with the morphology dependent on concentration and type of the surfactant used. The majority of the O-POMs dispersed in PAO10 had an average self-assembly size of 50 nm. After characterization, the tribological properties of the O-POM additives in PAO10 were studied. The data shows that each additive reduced the average coefficient of friction of PAO10. The most beneficial additives reduced the average coefficient of friction by almost 20% which at the moment cannot be considered significant since commercial fully formulated oils offer improvements in the order of 60% or more. The highest performing additives were ones that produced a semi-conductive tribo-film formed from reactions of the O-POMs with the metal surfaces of the ball and flat for the length of the reciprocation test. Additionally, surfactants with one long hydrocarbon tail performed better than a surfactant with two long hydrocarbon tails. Furthermore, an O-POM synthesized in the absence of NH$_4$Cl improved the tribology properties of PAO10 more than the same O-POM synthesized with NH$_4$Cl.

**REFERENCES**


FIGURE 7. Wear images of PAO10 and the three best performing additives. Top row shows the balls after test. Bottom row shows the wear tracks on the flats.
II.7 ORNL-Shell: Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency

Overall Objectives

- Develop oil-soluble ionic liquids (ILs) as engine oil additives.
- Demonstrate 10% improvement in mechanical efficiency of internal combustion 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) 2013 Objectives

- Design, synthesis, and characterization of a series of oil-soluble ILs with various molecular structures.
- Tribological bench tests to evaluate the anti-wear (AW) performance of the ILs.
- Investigation of lubrication mechanism of IL additives.
- Identification of the top candidate ILs.

FY 2013 Accomplishments

- Multiple groups of quaternary structured ILs have been designed and synthesized.
- Oil solubility, corrosion behavior, thermal stability, and compatibility with other oil additives were used to screen candidate ILs.

- Tribological bench tests have demonstrated up to 96% wear reduction in boundary lubrication and up to 50% friction reduction in mixed lubrication when adding ILs into a gas-to-liquid (GTL) base oil (at a phosphorus content of 800 ppm).
- Top two candidate ILs have been identified for further development and investigation.
- Fundamental understanding has been achieved for the wear protection mechanism of ILs.
- Results were presented at the Vehicle Technologies Office (VTO) Annual Merit Review and the Society of Tribologists and Lubrication Engineers Annual Meeting in May 2013.

Future Directions

- Seek synergistic effects between the identified top two candidate ILs and zinc dialkyl-dithiophosphate (ZDDP) as well as between different groups of ILs.
- Further investigate and model the lubrication mechanisms of IL additives.
- Complete standard additive evaluation for the top two candidate ILs.
- Produce a formulated engine oil using the top-performing IL as an AW additive.
- Conduct tribological bench tests and initial fired engine tests on the formulated IL-additized engine oil.

INTRODUCTION

For an internal combustion 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. This project proposes to develop ILs as a new class of lubricant additives to improve the engine mechanical efficiency, under a joint effort between ORNL and Shell, a world-leading lubricant supplier.
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.

Results

Several groups of ILs with three-dimensional quaternary structures have been designed and synthesized at ORNL, as illustrated in Figure 1. Table 1 lists the ILs synthesized in this study and the screening test results of corrosion behavior on grey cast iron in an ambient environment, thermal stability by thermal gravimetric analysis in air, and solubility in the GTL base oil and a semi-formulated oil without AW additives.

Table 1. List of synthesized ILs and screening test results of corrosion behavior, thermal stability, and oil-solubility.

<table>
<thead>
<tr>
<th>Ionic liquid</th>
<th>Corrosive to iron at room temperature?</th>
<th>Onset decomposition temperature (°C)</th>
<th>GTL 4 cSt base oil</th>
<th>GTL + GF-5 additive package w/o AW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphonium-phosphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P66614][DEHP] (IL-A)</td>
<td>No</td>
<td>~290</td>
<td>&gt;50%</td>
<td>&gt;10%</td>
</tr>
<tr>
<td>[P66614][DEHP] (IL-C)</td>
<td></td>
<td>~310</td>
<td>&gt;50%</td>
<td>&gt;10%</td>
</tr>
<tr>
<td>[P44414][DEHP] (IL-F)</td>
<td></td>
<td>~310</td>
<td>&gt;1%, &lt;2%</td>
<td></td>
</tr>
<tr>
<td>[P44414][DEHP] (IL-I)</td>
<td></td>
<td>~290</td>
<td>&lt;1%</td>
<td></td>
</tr>
<tr>
<td>Phosphonium-phosphinate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P66614][BTMPP] (IL-B)</td>
<td>No</td>
<td>~300</td>
<td>&gt;10%</td>
<td>&gt;10%, but causes viscosity fluctuation</td>
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<tr>
<td>Phosphonium-thiophosphate</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[P66614][BTMPTP]</td>
<td>Yes</td>
<td>Not measured</td>
<td>10%</td>
<td>Not measured</td>
</tr>
<tr>
<td>Aprotic amine-phosphate</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[Nxxxx][DEHP] (x=2,4,6)</td>
<td>No</td>
<td>&lt;200</td>
<td>&lt;1%</td>
<td>&lt;1%</td>
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<tr>
<td>[Nxxxx][DEHP] (IL-G)</td>
<td></td>
<td>~220</td>
<td>&lt;1%</td>
<td>Not measured</td>
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<tr>
<td>[Nxxxx][DEHP] (IL-H)</td>
<td></td>
<td>~220</td>
<td>&gt;3%, &lt;5%</td>
<td></td>
</tr>
<tr>
<td>Protic amine-phosphate</td>
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<td>[Nxxxx][DEHP] (x=2,4,6)</td>
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<td>&lt;200</td>
<td>&lt;1%</td>
<td>&lt;5%</td>
</tr>
<tr>
<td>[Nxxxx][DEHP] (IL-D)</td>
<td></td>
<td>~220</td>
<td>&gt;50%</td>
<td>&gt;50%</td>
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<tr>
<td>Protic amine-phosphinate</td>
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<td></td>
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<tr>
<td>[Nxxxx][BTMPP] (x=2,3,6)</td>
<td>No</td>
<td>&lt;200</td>
<td>&gt;10%</td>
<td>Not measured</td>
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<tr>
<td>[Nxxxx][BTMPP] (IL-E)</td>
<td></td>
<td>~210</td>
<td>&gt;10%</td>
<td>&gt;2%, but causes viscosity fluctuation</td>
</tr>
</tbody>
</table>

DEHP - bis(2-ethylhexyl)phosphate; BTMPP - bis(2,4,4-trimethylpentyl)phosphinate; BTMPTP - bis(2,4,4-trimethylpentyl)thiophosphinate
II. Fuels and lubricants to enable high efficiency engine operation

Qu – Oak Ridge National Laboratory

Distribution. X-ray photoelectron spectroscopy chemical analysis confirmed the film thickness and suggested major compounds of the tribofilm to be iron oxides and iron phosphates, as shown in Figure 3.

To investigate the friction behavior in elastohydrodynamic and mixed lubrication (ML), ball-on-disc unidirectional rolling-sliding tests were conducted at Shell. ILs were added to the semi-formulated engine oil w/o ZDDP at the treat rates specified in Table 1. As shown in Figure 4, three oil-IL blends containing ILs (IL-A, IL-B, and IL-C) exhibited significantly lower friction (by up to 50%) than the engine oil with ZDDP in mixed lubrication and the early stage of boundary lubrication (BL). This suggests that, unlike the ZDDP tribo film known to have high friction, some IL tribo films may possess low-friction characteristics.

Conclusions

In FY 2013, the ORNL-Shell team designed and synthesized six groups of oil-soluble ILs as potential lubricants additives. The oil solubility, corrosion behavior, thermal stability, and compatibility with a GF-5 additive package were used to screen candidate ILs. Tribological bench tests have demonstrated up to 96% wear reduction in boundary lubrication and up to 50% friction reduction in mixed lubrication when adding ILs into a GTL base oil. The IL wear protection mechanism was investigated via tribofilm characterization. Two candidate ILs have been identified for further development and investigation.

Nine ILs (A through I, as noted in Table 1) were selected to evaluate their AW performance in boundary lubrication. A ball-on-flat reciprocating sliding bench test was used under a constant 100 N load and a 10 Hz oscillation frequency with a 10 mm stroke. An American Iron and Steel Institute 52100 steel ball was rubbing against a CL35 grey cast iron flat at 100°C for a sliding distance of 1,000 m. Each IL was blended into the Shell GTL 4 cSt base oil at a phosphorous content of near but not exceeding 800 ppm to meet the specifications of International Lubricants Standardization and Approval Committee GF-5. Table 2 summarizes the wear results. All nine ILs showed effective AW capability with the wear rate reduced by >80%, and six ILs (A, B, C, D, F, and H) performed similar to or better than a commercial secondary ZDDP. The two phosphinate ILs (B and E) were, however, found to be incompatible in the semi-formulated engine oil, inducing viscosity fluctuation of the oil-IL blends in storage and dark purple precipitates in wear testing. The best candidates in wear protection have been identified to be IL-C and IL-D.

The tribofilm formed on the cast iron surface lubricated by the IL-C additized GTL oil was characterized to understand the wear protection mechanism. Aided by the focused-ion-beam technique, cross-sectional transmission electron microscopy examination clearly revealed an amorphous tribofilm in a thickness up to 200 nm, as shown in Figure 2. Elemental mapping by energy-dispersive X-ray spectroscopy in Figure 2 indicates this tribofilm composed of iron, oxygen, and phosphorus with relative homogeneous distribution. X-ray photoelectron spectroscopy chemical analysis confirmed the film thickness and suggested major compounds of the tribofilm to be iron oxides and iron phosphates, as shown in Figure 3.

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In FY 2013, the ORNL-Shell team designed and synthesized six groups of oil-soluble ILs as potential lubricants additives. The oil solubility, corrosion behavior, thermal stability, and compatibility with a GF-5 additive package were used to screen candidate ILs. Tribological bench tests have demonstrated up to 96% wear reduction in boundary lubrication and up to 50% friction reduction in mixed lubrication when adding ILs into a GTL base oil. The IL wear protection mechanism was investigated via tribofilm characterization. Two candidate ILs have been identified for further development and investigation.

Table 2. Summary of bench test wear results. ILs, when added into the GTL base oil, reducing wear by up to 96% and outperforming ZDDP by up to 76%.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>AW treat rate (wt%)</th>
<th>Wear volume (mm³)</th>
<th>Wear reduction to GTL base</th>
<th>Wear reduction to GTL+ZDDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>GTL 4 cSt base oil</td>
<td>--</td>
<td>1.128</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>GTL+ZDDP</td>
<td>1.0</td>
<td>0.183</td>
<td>83.8%</td>
<td>--</td>
</tr>
<tr>
<td>GTL+[P_{666}][DEHP] (IL-A)</td>
<td>1.03</td>
<td>0.179</td>
<td>84.1%</td>
<td>2.2%</td>
</tr>
<tr>
<td>GTL+[P_{666}][DEHP] (IL-C)</td>
<td>1.03</td>
<td>0.105</td>
<td>90.7%</td>
<td>42.4%</td>
</tr>
<tr>
<td>GTL+[P_{666}][DEHP] (IL-F)</td>
<td>0.93</td>
<td>0.131</td>
<td>88.4%</td>
<td>28.3%</td>
</tr>
<tr>
<td>GTL+[P_{666}][DEHP] (IL-I)</td>
<td>0.75*</td>
<td>0.190</td>
<td>83.1%</td>
<td>-4.0%</td>
</tr>
<tr>
<td>GTL+[P_{666}][BTMPP] (IL-B)</td>
<td>0.99</td>
<td>0.098</td>
<td>91.4%</td>
<td>46.7%</td>
</tr>
<tr>
<td>GTL+[N_{8888}][DEHP] (IL-G)</td>
<td>2.03*</td>
<td>0.201</td>
<td>82.2%</td>
<td>-9.7%</td>
</tr>
<tr>
<td>GTL+[N_{8888}][DEHP] (IL-H)</td>
<td>1.78*</td>
<td>0.102</td>
<td>91.0%</td>
<td>44.5%</td>
</tr>
<tr>
<td>GTL+[N_{8888}][DEHP] (IL-D)</td>
<td>1.74</td>
<td>0.043</td>
<td>96.2%</td>
<td>76.7%</td>
</tr>
<tr>
<td>GTL+[N_{8888}][BTMPP] (IL-E)</td>
<td>1.66</td>
<td>0.210</td>
<td>81.4%</td>
<td>-14.6%</td>
</tr>
</tbody>
</table>

* Treat rate higher than the solubility and tested at an emulsion condition.
FIGURE 2. Cross-sectional transmission electron microscopy images and energy-dispersive X-ray spectroscopy elemental maps of the tribofilm formed on the cast iron surface lubricated by the IL-C additized GTL oil.

FY 2013 PUBLICATIONS/PRESENTATIONS


SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

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Figure 3. X-ray photoelectron spectroscopy composition-depth profile and binding energy spectra of the IL-C induced tribofilm.

Figure 4. Stribeck curves suggesting up to 50% reduced friction when using IL-A, IL-B, or IL-C to replace ZDDP in an engine oil.
II.8 Lubricant Formulations to Enhance Engine Efficiency in Modern Internal Combustion Engines

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DOE Technology Development Manager: Steven Przesmitzki
NETL Project Manager: Nicholas D’Amico

Overall Objectives

• Identify the best lubricant formulations for individual engine subsystems.
• Identifying the best composite lubricant formulation for the overall engine system.
• Develop in situ oil composition model and apply results to explore further opportunities for friction reduction in engine and subsystems.
• Demonstrate mechanical efficiency improvement for optimized lubricant formulations via engine testing towards the established goal of 10% improvement or better.

Fiscal Year (FY) 2013 Objectives

• Identify opportunities for optimizing lubricant base oil formulation by modeling the effects of lubricant parameters on friction and wear for subsystems.
• Identify optimal lubricant formulations for subsystems by developing and conducting experiments on a diesel engine with the assistance of lubricant and engine industry partners.

FY 2013 Accomplishments

• Successfully modified and fired a unique diesel test engine. The engine includes custom instrumentation for valve train friction torque measurement and a modified lubrication system capable of providing different lubricants to major subsystems.
• Mechanical efficiency improvements of over 5% were observed experimentally by operating a 16-hp diesel engine with separate multigrade oil formulations in the valve train and power cylinder subsystems.
• Friction reductions of over 10% were observed experimentally by varying shear thinning characteristics of a lubricant in a motored valve train.

Future Directions

• Experimentally verify results of modeling efforts by further quantifying benefits achievable from optimizing base oil formulations for particular engine subsystems.
• Continue to develop advanced power cylinder friction models incorporating detailed effects of local oil composition changes and control.
• Experimentally investigate the effect of additive changes on valve train and power cylinder subsystem losses through parametric studies.

INTRODUCTION

It is estimated that up to 15% of fuel energy is lost to friction in modern diesel engines [1]. Of this, half of the losses are attributed to friction in the power cylinder subsystem, consisting of the main bearings and piston, rings, and rods. The remaining losses are due to friction in the valve train and auxiliary losses from operating of pumps and other components necessary for engine operation. Engine lubricants play a key role in controlling friction and wear. The environment in which the lubricant operates in an engine varies substantially in space (location in the engine) and time (warm-up and degradation). Temperatures, mechanical loads, shear rates vary widely in an engine, from region to region, and therefore so does the degradation rate. The extent to which a lubricant/additive package can tailor to the local conditions in the engine determines the further gains that can be achieved, in terms of friction, wear, and emissions.
APPROACH

The Fuel & Lubricant Technologies subprogram supports fuels and lubricants R&D to provide vehicle users with cost-competitive options that enable high fuel economy with low emissions, and contribute to petroleum displacement [2]. Significant R&D has already been done in recent years (in industry) for advanced chemistries for base oils, viscosity modifiers, and friction modifiers (anti-wear; low sulphated ash, phosphorus, sulphur; or ashless agents; etc.) of various types. However, their effectiveness depends strongly on the local environments (thermal, mechanical, shear, contamination, oxidation/ degradation, depletion, replenishment, etc.) internal to the engine in which the lubricant/additives operate, which we still do not fully understand and on which we lack data and analyses. Therefore the overall approach in this study focuses on the critical issue: “What the lubricant/additives face in the detailed local operating environments in the engine, and what the lubricant/ additives need for best performance.” This is being investigated using advanced computer modeling and practical engine laboratory tests. A diesel engine was modified to investigate friction and lubricant changes in particular subsystems, particularly the cylinder head/valve train subsystem and the power cylinder subsystem. With an advanced understanding of friction and composition changes in various parts of the engine, and actual engine data, the proper lubricant base oil and additive technologies will be selected and methods proposed for optimizing the lubricant/additive package. Final testing will be demonstrated using the advanced lubricant formulations. These data and technologies developed will be available to the lubricant and engine industries at large (multiple beneficiaries) for further technology fine-tuning, and competitive production and commercialization, as appropriate.

RESULTS

Modeling previously developed at the authors’ institution [3,4] was adapted to predict top ring and skirt friction response and estimate the potential for increase or decrease in wear resulting from different lubricant formulations. In particular, performance due to base oil temperature and shear thinning dependence was evaluated. Local hydrodynamic and boundary friction, as well as oil film thickness, were characterized for the top ring and piston skirt along the cylinder liner. Results are shown for an 11.0-liter heavy-duty diesel engine at the A100 operating condition of the 13-Mode Steady State dynamometer test.

Shear thinning effects were incorporated into the models to allow for investigation of viscosity modifier impacts. Detailed viscosity vs. shear rate data was gathered with industry partners for the oils investigated. The results were consistent with those predicted by the Cross and Carreau equations, which are described in several works including Sorab, et al. [5], in characterizing the shear response of the motor oils under investigation. Average viscosity reductions for a cycle are typically over 10% due to shear thinning alone.

Piston skirts may contribute to over half of the overall friction experienced by the piston skirt and ring system. Figure 1 shows the instantaneous friction loss for the top ring and skirt plotted with respect to the liner temperature. The results indicate that wear effects tend to occur in regions of higher temperature, while hydrodynamic friction is confined to the lower temperatures along the liner. The results suggest how oil properties in this temperature range should be targeted for fuel economy improvement.

Figure 2 was developed to characterize the temperature viscosity curve as it relates to the engine under investigation. A transition temperature is defined, above which the majority of boundary friction, and therefore wear, is expected to occur. Modeling results indicate that increasing viscosity above this temperature will reduce wear with a limited impact on overall friction. Lowering viscosity at temperatures below the transition temperature will reduce overall friction losses significantly. These results, along with a detailed review of the findings, will be published in peer reviewed literature in the near future.
The modeling efforts were extended beyond traditional friction characterization to capture local lubricant composition effects. Previous liner vaporization models, also developed at the authors' institution [6], were coupled to a top ring friction model through incorporation of modern rheological property correlations developed in literature and using data obtained with industry partners. The results offer unique insight into the effect of composition changes on friction and wear. Rheological properties change along the liner due to the change in composition, as shown in Figure 3, as lighter hydrocarbons are lost due to the combined effects of oil transport due to ring movement and vaporization. Significant changes in molecular weight and viscosity were estimated for the upper portions of the liner which experience relatively low film thicknesses.

The MIT team developed a unique engine test platform for investigation of subsystem friction in a diesel engine; Figure 4 shows the engine test stand. A 16-hp twin cylinder diesel was instrumented for the measurement of indicated mean effective pressure from both cylinders, as well as valve train and crankshaft torque. The configuration allows for detailed characterization of valve train and power cylinder friction. In addition, the lubrication system was divided to allow different oils in the cylinder head and block. As a result, parametric studies were started to characterize optimal lubricants for each subsystem in an actual engine environment. A separate cylinder head, identical to that on the subject engine, was also mounted for motoring to allow for detailed tear down tests with and without fuel supply. Initial results for the cylinder head bench tests are shown in Figure 5. They indicate friction response for the valve train resulting from the use of different multi-grade oils formulated with the same additive package.

**FIGURE 2.** Relative viscosity temperature dependence as it relates to power cylinder friction. Significant hydrodynamic friction losses from 100°C-150°C suggest reducing the mean viscosity over this range will have the greatest impact on fuel economy.

**FIGURE 3.** Lubricant viscosity estimates along the region of the liner where the piston comes to top-dead center. Results assuming constant composition (“No Vap”) and vaporization changes (“Vap”) are shown. Viscosity differences of over 50% were estimated when accounting for vaporization.

**FIGURE 4.** A Kohler 16-hp twin-cylinder diesel engine on a dynamometer test bed.
II. Fuels and Lubricants to Enable High Efficiency Engine Operation

Cheng – Massachusetts Institute of Technology

Viscosity multi-grade oil may be preferable to reduce friction.

Conclusions

In the power cylinder subsystem, losses are predominantly due to hydrodynamic friction, indicating reduction in viscosity at temperatures below those of the mid liner can have a significant impact on friction reduction. Base oil formulation strategies for fuel economy could focus in this area. Accordingly, effects of various base oil and viscosity modifier combinations were analyzed and tested to optimize the preferred viscosity versus temperature characteristics.

Increasing lubricant viscosity near top-dead center, through temperature or composition control, may have a significant impact on reducing top ring wear in the power cylinder subsystem. A low-volatility organic additive could change the thickness and viscosity of any residual oil film near the top of the liner, thus extending the low viscosity limit of practical oils, further improving fuel economy.
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Fuel & Lubricant Technologies FY 2013 Annual Progress Report


REFERENCES


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

Overall Objectives

- Formulate new modified polyalkylene glycol (PAG)-based engine oils
- Evaluate 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 antiwear 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) 2013 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 motored friction evaluations in a valvetrain using a direct acting mechanical bucket design and piston ring friction using a single-cylinder engine
- Initiate cam and tappet wear measurements using a motored single cam and direct acting mechanical bucket valvetrain rig
- Initiate motored engine friction evaluation
- Continue friction evaluation in ASTM International (ASTM) Sequence VID tests and wear evaluations in Sequence IIIG and Sequence IVA tests.

FY 2013 Accomplishments

- Dow Chemical Company (Dow) formulated five new oils by adjusting the high temperature, high shear viscosity at 150°C for a given base oil chemistry to understand its effect on friction, and additive packages to improve friction and wear performances.
- Argonne National Laboratory (ANL) completed friction and wear evaluations on new oil formulations using a pin-on-disk machine, a high frequency reciprocating rig, and a block on ring machine. One of the PAG formulations, 201202403-17-1, showed a 25% lower friction coefficient and 53% lower wear volume than GF-5 5W-20 oil at 100°C in pin-on-disk tests. The same PAG oil showed a 35% improved load carrying capability in block-on-ring scuffing test.

The wear surfaces of GF-5 5W-20 and three PAG oils including 201202403-17-1 were examined using X-ray photo electron spectroscopy to gain an understanding of the formation of additive-derived films. The results showed the presence of sulfur, phosphorus in the form of pyrophosphate and sulfides and zinc in the form of ZnO/ZnS and iron oxides. The base PAG oil, XZ97011.00, however showed only the presence of iron oxide.

- Ford Motor Company completed motored valvetrain friction tests on eight PAG formulations; all showed reduced friction over GF-5 5W-20 oil. Two formulations with the same high-temperature, high-shear (HTHS) viscosity as the GF-5 oil showed about a 50% friction reduction at 100°C and camshaft speed range below 1,000 RPM. The friction reduction is primarily due to PAG base oil chemistry. All PAG oils showed reduced piston ring friction force compared to GF-5 5W-30 oil using the motored single-cylinder friction tests. One of the oils, with the same HTHS viscosity as the GF-5 oil, showed 10-38% friction reduction over GF-5 5W-30 oil at 100°C oil temperature. One of the PAG oil formulations, with the same HTHS viscosity as the GF-5 5W-20 oil, showed about a 9% friction reduction in motored engine tests at 93°C oil temperature. Two PAG oils showed encouraging fuel economy improvement in Sequence VID tests.
Future Directions

- Upon receipt of a Nuclear Regulatory Commission license, initiate valvetrain wear measurements
- Continue analyzing tribo-films formed on contacting surfaces to understand friction reduction mechanism(s)
- Continue ASTM Sequence tests to demonstrate fuel economy, anti-oxidation, and wear protection capabilities
- Initiate chassis roll dynamometer tests for fuel economy and emission evaluations when oil is fresh and when aged

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 Ford Motor Company, Dow Chemical Company, and Argonne National Laboratory. The project is led by Arup Gangopadhyay (Ford), 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. Ford 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 fuel economy 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 modified additive package to improve friction and wear performances. The test results have and will continue to be used throughout this program to improve oil friction reduction capabilities.

Friction and Wear Evaluations

Figure 1 shows friction and wear results obtained from pin-on-disk tests under boundary lubrication condition at 100°C. The results for some of the PAG oils are compared against fully formulated factory fill GF-5 oil. PAG oil 201202403-17-1 showed a lower friction coefficient and lower wear than GF-5 5W-20 oil.

Figure 2 compares block-on-ring load carrying capability of various oil formulations. The load carrying capability is determined by the load at which the friction coefficient jumped abruptly indicating scuffing. Although some of the PAG formulations had lower load carrying capability than GF-5 oil, PAG oil 201202403-17-1 outperformed GF-5 oil.

Engine Component Friction Testing

Motored valvetrain friction tests were conducted with PAG and GF-5 oils at 40°C, 80°C, and 100°C oil temperatures at varied camshaft speeds from 300 RPM to 2,500 RPM. At least two tests were conducted at each temperature with very good repeatability. Figure 3 shows a typical result at 100°C. Generally, the friction torque decreased with increasing camshaft speed as the
lubrication regime changed from boundary to mixed. PAG formulations showed lower friction than GF-5 5W-20 oil at all speeds. Among the PAG formulations, 15-4 oil showed the lowest friction torque. Since PAG oils were formulated to different viscosity levels, it was not possible to separate the effects of viscosity and PAG base oil chemistry. Figure 4 shows friction torque of selected PAG formulations at the same viscosity level. Clearly showing friction reduction is primarily due to PAG base oil chemistry.

The friction force at the interface between cylinder liner and piston rings and skirt was measured as a function of crankshaft speed at 40°C, 60°C, 80°C, 100°C, and 120°C oil temperatures. Figure 5 shows a typical plot at 100°C. All PAG formulations showed lower friction force than GF-5 5W-30. Analysis of all friction force data at a constant viscosity revealed friction reduction was due to PAG base oil chemistry and not due to lower viscosity.

Motored engine friction tests were also conducted at 49°C, 79°C, and 93°C oil temperatures. Figure 6 shows motored engine friction torque as a function of engine speed at 93°C oil temperature. PAG oils showed friction reduction at lower temperature consistent with previous results.

**FIGURE 1.** Pin-On-Disk Friction and Wear Results at 100°C

**FIGURE 2.** Load Carrying Capability of PAG Oils
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CONCLUSIONS

- Reformulation of PAG oils with a modified additive package showed 25% lower friction coefficient, 53% lower wear volume, and 35% improved wear carrying capability over GF-5 5W-20 oil under boundary lubrication conditions.

- Motored valvetrain results showed PAG oils reduced friction by about 50% over GF-5 5W-20 oil at low cam shaft speeds. Piston ring friction was also reduced by 10-38%. The friction reduction is primarily due to PAG oil chemistry and not due to lower viscosity.

- Motored engine tests showed PAG oil reduced friction by about 9% over GF-5 5W-20 oil at low speed range.
II.10 High Compression Ratio Turbo Gasoline Engine Operation Using Alcohol Enhancement

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NETL Project Manager: Nicholas D’Amico

Subcontractor:
Cummins, Inc., Columbus, IN

Overall 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 the 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) 2013 Objectives

- Complete and validate initial set of performance maps of a turbocharged spark-ignited (SI) engine with different blends of gasoline with ethanol, through experiments and computer simulation, with knock onset limits.
- Develop and evaluate empirical and chemical-kinetic-based approaches that define knock onset and peak pressure limits on these performance maps as a function of spark retard at the higher loads.
- Develop expanded performance maps with higher compression ratios and boost levels, with knock onset lines for gasoline and gasoline-ethanol blends, incorporating spark retard and gasoline and ethanol-blend fuel consumption.
- Develop and implement a framework for doing engine-in-vehicle simulations using the code Autonomie to assess the fuel economy benefits and ethanol usage as a function of compression ratio, boost level, and extent of engine downsizing, i.e., commence evaluating the benefits of using alcohols, when needed, to suppress knock in gasoline engines.
- Develop an extended experimental engine performance data set, over a range of compression ratios, boost levels, and spark sweeps for methodology validation (Cummins, Inc.).

FY 2013 Accomplishments

- Completed a set of simulation-based turbocharged SI engine performance maps for a range of different knock-suppressing fuels, compression ratios, boost levels, and spark retard strategies.
- Developed and validated a fundamentally based chemical kinetic methodology for predicting knock onset at close to peak cylinder conditions.
- Used our engine performance maps to explore and quantify through engine-in-vehicle simulations, using Autonomie, the significant fuel economy benefits that alcohol-based knock suppression can provide.
- Generated experimental boosted SI engine efficiency data at higher compression ratios and boost levels for a range of gasoline-ethanol blends.

Future Directions

- Experimentally determine knock-onset limits of selected primary reference fuels and gasoline-methanol blends at higher loads and use this data to further validate our knock onset model and compare methanol and ethanol.
- Determine the octane requirement of our turbocharged 2-liter engine at mid- and low-loads to explore the application of onboard membrane-based fuel separation (prevaporation) to provide higher octane (largely ethanol) and a lower octane fuel streams.
• Develop reference engine-in-vehicle drive-cycle simulation results to enable knock-suppressed turbocharged-engine fuel economy data in the appropriate context.

• Complete the data acquisition from the single-cylinder SI engine tests (at Cummins) at higher compression ratios and boost levels; process the data and compare it with our simulation-based performance maps.

INTRODUCTION

The objectives of this project are to quantify the potential for improving the performance and efficiency of gasoline engine technology through 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, and significant 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 auto-ignition modeling. These performance maps will be used in engine-in-vehicle simulations (Autonomie) 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 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.

Engine fuel conversion efficiencies and the knock onset limits for different fuel blends have been determined, using direct fuel injection. Fuel conversion efficiencies at different load conditions and speeds, for 85% ethanol and 15% gasoline (E85), and Research Octane Number (RON) 96 and RON 91 gasolines, and 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” below the knock onset limit for each of these fuels.

Figure 1 shows an example of a simulation-based brake mean effective pressure (BMEP) versus engine speed performance map for a 2-liter direct injection turbocharged spark-ignition engine. Knock onset lines are shown for 91 RON gasoline, E10, E25, and E50, all with maximum brake torque (MBT) spark timing. The impact of spark retard from MBT has been quantified (e.g., a 5-degree crank angle retard raises each knock onset line by about 500 kPa), and an algorithm for the effect of spark retard on the amount of knock-suppressing alcohol fuel developed.

Work on modeling knock onset with a given fuel (gasoline and gasoline-ethanol blends) has progressed well. A number of questions have been explored and clarified as our chemical kinetic modeling using CHEMKIN progressed: the point in the engine cycle where knock onset occurs; the initial unburned mixture temperature at intake valve closing; the engine component temperatures; non-uniformities in composition and temperature in the end-gas. These have been plausibly explained in a quantitative manner.

A set of engine-in-vehicle simulations using the code Autonomie has been completed for several engines with different compression ratios (9.2, 11.5, 13.5) and boost levels. The vehicle parameters used corresponded to a mid-sized U.S. passenger car. Constant vehicle performance was approximated by holding wide-open-throttle torque constant and adjusting engine displaced volume appropriately. Figure 2 shows the average engine brake fuel conversion efficiency during the U.S. Urban Driving Cycle as maximum boost levels (in BMEP) are increased and the engine is downsized. The average engine efficiency is about 20% with the 2.5-liter (standard) naturally-aspirated gasoline engine (corresponding to about 25 miles per gallon fuel economy for this urban drive cycle). Boosting to 3,000 kPa maximum BMEP and downsizing to approximately...
II. Fuels and lubricants to enable high efficiency engine operation

Figure 1. Performance map (BMEP vs. speed) of a highly-boosted turbocharged gasoline engine with constant brake fuel conversion efficiency contours; knock onset lines for RON 91 gasoline, (E0), E10, E25, and E50; compression ratio 11.5; and maximum-brake-torque spark timing.

Figure 2. Average engine brake fuel conversion efficiency from the U.S. Federal Urban Driving Cycle from engine-in-vehicle computer simulation code Autonomie, as a function of engine displaced volume as boost level is increased (to 3.5 bar) with naturally-aspirated engine displacement at 2.75 liters. Spark retard up to 10 degrees was employed prior to the use of knock-suppressing fuel at higher loads where knock would occur with 90 RON gasoline. Simulations were at constant vehicle performance level.

Figure 3. Ethanol fraction of total fuel used (mostly gasoline) as a function of boost level and thus engine displaced volume, from engine-in-vehicle simulation through U.S. Urban Drive Cycle. Details are the same as in Figure 2.
1-liter engine displacement increases average drive-cycle engine efficiency to about 29%, and urban drive-cycle fuel economy to 36 miles per gallon gasoline equivalent. These increases are both close to 45%. Note in the example results shown, when knock would occur with gasoline, as much spark retard as was needed to shift out of knock was utilized to a maximum of 10 degrees retard.

The impact of spark retard under high-load conditions to initially avoid knock, prior to use of the knock suppressing fuel, on engine efficiency and vehicle fuel economy was modest. The most significant impact was the reduction in amount of knock-suppressing fuel required. Figure 3 shows the fraction of ethanol required to suppress knock as compression ratio is varied and as the engine's size is decreased and maximum boost (and BMEP) is increased. For the 1-liter displacement turbocharged engine with the performance map of Figure 1, the ethanol fraction is 3.5% of the gasoline used. (This fraction increases as compression ratio is raised; it also decreases sharply as boost level is decreased at a displaced volume of 1.5 liters.)

CONCLUSIONS

- **Engine performance maps (BMEP vs. speed)** can be satisfactorily generated through high level engine simulation codes (such as GT-POWER). Turbocharger configuration and size scaling are a complex additional challenge for such turbocharged engines, as are the effects of spark retard at the higher loads on knock onset, maximum pressure level, and performance and efficiency.

- Blends of gasoline with increasing amounts of ethanol, and continuing with E85-water mixtures, substantially increase the knock-suppressing impact of the high-octane fuel, as does spark retard.

- Chemical-kinetic-based knock onset prediction modeling in the SI engine end gas can reliably predict autoignition. Empirical induction-time integral models can be calibrated to match experimental data, also.

- Engine-in-vehicle simulations of various drive cycles in a mid-size car show that knock suppression with alcohol fuels allows a significant increase in compression ratio and boost level, and thus engine downsizing, and offers substantially higher average engine efficiency and vehicle fuel economy.

- The amount of knock-suppressing fuel required can be significantly reduced with the use of spark retard down into the 1% to 10% range relative to the (mostly) gasoline consumed.

FY 2013 PUBLICATIONS/PRESENTATIONS


II.11 Demonstration/Development of Reactivity Controlled Compression Ignition (RCCI) Combustion for High Efficiency, Low Emissions Vehicle Applications

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Subcontractors:
• Oak Ridge National Laboratory (ORNL), Knoxville, TN
• University of Wisconsin-Madison, Engine Research Center (UW-ERC), Madison, WI

Overall Objectives
• Optimize dual-fuel RCCI combustion in both heavy-duty (HD) and light-duty (LD) on-highway diesel engines over the expected ranges of engine speed/load operation in vehicle applications.
• Quantify the effects of gasoline/diesel fuel blending strategies and the role of lubricants on engine-out particulate.
• Develop and test optimized combustion systems and calibration strategy to maximize RCCI efficiency benefits and operating range.

Fiscal Year (FY) 2013 Objectives
• LD gasoline+cetane improver RCCI experimental/analytical development.
• LD gasoline+cetane improver particulate matter (PM) characterization.
• Complete HD C15 single-cylinder engine install and break-in.
• HD gasoline+diesel RCCI demonstration.
• HD gasoline+diesel RCCI analytical combustion system development.

FY 2013 Accomplishments
• HD engine installed December 28, 2012, and operated with RCCI combustion.
• Initial experimental investigation of LD RCCI using gasoline+ethyl hexyl nitrate (EHN).
• LD particulate characterization experiments using gasoline+EHN.
• Created novel combustion bowl for RCCI that allows load extension.
• Analytically investigated several concept combustion systems for HD RCCI using gasoline+diesel.

Future Directions
• Continue to develop a novel combustion system and calibration strategy for RCCI.
• Continue to develop an HD combustion system and calibration strategy for RCCI combustion with focus on maximizing load capability and thermal efficiency.
• Finalize LD particulate characterization and improve the quantitative understanding of fuel and lube contribution to particulates.

INTRODUCTION
RCCI is a dual-fuel engine combustion technology that was developed at the UW-ERC laboratories. RCCI is a variant of Homogeneous Charge Compression Ignition that provides more control over the combustion process and has the potential to dramatically lower fuel use and emissions [1]. A highly efficient, low-emissions combustion technology that is strongly dependent on fuel properties is in alignment with DOE project objectives. A combined analytical/experimental approach such as employed in the present work is considered optimal as it allows for robust model development (validation), deeper physical understanding of engine processes, and proof of concept of analytically supported/driven findings.
II. Fuels and Lubricants to Enable High Efficiency Engine Operation

Reitz – Wisconsin Engine Research Consultants, LLC.

APPRAOCHE

For FY 2013, the LD engine experimental work was conducted at ORNL, while the HD engine testing was done at UW-ERC in collaboration with Caterpillar. The HD work included installation of a new CAT® C15 single-cylinder test engine, as well as initial demonstration of RCCI. The LD work was carried out on a GM 1.9-L multi-cylinder diesel engine and included RCCI demonstration with gasoline and various mixtures of gasoline+EHN, as well as experimental data generation for particulate characterization.

WERC used advanced computational fluid dynamics (CFD) modeling tools to explore combustion system design and engine calibration with the focus on extending the useful operating range with maximum efficiency. For the HD engine, this included high-load investigation of several combustion bowl designs as well as comparing port fuel injection (PFI) and direct injection (DI) of gasoline. The LD analysis effort was focused on combustion system development at part-load operation considering gasoline+EHN.

RESULTS

HD RCCI load extension was investigated analytically. One of the main challenges for RCCI combustion is maintaining control over the rate of heat release and the combustion phasing as the load is increased. Mixture stratification is known to help control the rate of heat release for premixed compression ignition combustion [2]. With DI of both fuels one can strategically control mixture formation and optimize mixture stratification, therefore DI gasoline and diesel was considered and compared to baseline PFI gasoline and DI diesel [3]. Baseline model validation can be seen in Figure 1.

Parametric studies were conducted to explore directions for improved engine performance. For example, diesel start of injection (SOI) timing sweeps were performed and the results were compared to the base RCCI data, as well as for premixed gasoline with a single late diesel injection using the modified boundary conditions.

Figure 2 shows the maximum rate of pressure rise (RoPR) vs. gross indicated specific fuel consumption (GISFC). This plot summarizes one of the key trade-offs for RCCI load extension, since measures taken to reduce the peak RoPR tend to reduce the combustion efficiency, which increases the GISFC. The single late diesel injection strategy with the modified boundary conditions was successful in lowering the peak RoPR compared to the base RCCI point.

When compared at the same diesel SOI timing, the re-entrant Case 4 piston bowl/nozzle has a lower maximum RoPR compared to the other cases; however, its combustion efficiency was generally lower also, resulting in an inferior RoPR vs. GISFC trade-off. The results demonstrate that the piston bowl geometry has an effect on RCCI combustion when using DI of both fuels. The RCCI piston with premixed gasoline and modified boundary conditions had the most stable combustion across the diesel SOI sweep and was able to achieve all targets.

The effort at UW-ERC has focused on commissioning the C15 engine. The engine has been
II. Fuels and lubricants to enable high efficiency engine operation

At 5% EHN is presented in Figure 5. Characterization of the particulates to reveal the contribution of the lube oil to RCCI PM is also in progress. Figure 6 shows particulate size distributions over a DI SOI sweep with 5% EHN at 2,300 rev/min, 4.2 bar. In this sweep, the highest brake thermal efficiency was obtained at the -40° after top-dead-center (ATDC) DI timing, which also produced the lowest particulate number count and the smallest particle mean diameters. This point had a combustion phasing of -1.4° ATDC with oxides of nitrogen (NOx) of over 350 ppm. The lower NOx points of -70, -60 and -50 -40° ATDC had very similar particulate size distributions, with a small shift in particle mean diameter for the -60 -40° ATDC cases. Additional operating points have been studied, including detailed hydrocarbon speciation.

CONCLUSIONS

- Code validation studies were performed and indicate that the CFD modeling satisfactorily reproduces experimental engine data.
- The CFD models have been used to propose novel piston designs that significantly reduce pressure rise rates and allow load extension of RCCI.
- Experimental data on the LD engine shows that cetane improvers are effective to provide the high reactivity fuel stream and the influence on the PM size distributions has been quantified.
- LD PM characterization still ongoing, but currently there is no evidence of lube oil impact on PM.
II. Fuels and Lubricants to Enable High Efficiency Engine Operation

Reitz – Wisconsin Engine Research Consultants, LLC.

Initial validation data has been obtained on the HD engine.

REFERENCES

III. FUEL PROPERTY EFFECTS ON ADVANCED COMBUSTION REGIMES
III.1 Advanced Fuels Enabling Advanced Combustion on Multi-Cylinder Engines

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Kevin Stork

Overall Objectives

- Investigate the opportunities and challenges that advanced transportation fuels, including renewable fuels, have 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) 2013 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 (second quarter Joule Milestone).
- Conduct apples-to-apples comparison of dual-fuel RCCI and single-fuel Partially Premixed Combustion (PPC) with a range of fuels.

FY 2013 Accomplishments

- Characterized the potential of biofuels to enable and expand the operating range of RCCI combustion in a multi-cylinder engine.
- Attained the 2013 technical target of demonstrating biodiesel blends allowed an improvement in RCCI operating range allowing for a simulated 65% coverage of the federal city and highway driving cycles.
- Completed initial comparisons of RCCI with conventional fuels and PPC with a 70 Research Octane Number (RON) gasoline for efficiency, load expansion and controllability.
- Presented initial findings of RCCI-PPC comparison to International Energy Agency task leaders.

Future Directions

- Conduct engine experiments for mapping RCCI with other renewable fuels to determine how much of the light-duty drive cycle can be covered with RCCI as enabled by the unique properties of renewable fuels.
- Investigate the potential for alternative fuels to expand the drive-cycle coverage of advanced combustion leading to higher potential fuel economy and lowered emissions.
- Evaluate PPC as compared to RCCI on the same engine, with the same hardware over a variety of gasoline-range fuels that seem well suited for PPC.
- Other potential advanced combustion approaches will continue to be evaluated on multi-cylinder engines with a focus on fuel and lubricant effects.
- Identify other alternative fuels that may have high enabling potential for advanced combustion.

INTRODUCTION

Many renewable and other advanced fuels have unique properties which enable expanded operation of advanced combustion methods and improve performance as compared to conventional fuels. For dual-fuel approaches, in-cylinder blending of two fuels with different fuel reactivity (octane/cetane) allows increased control over combustion (compared to single fuel advanced combustion techniques). Initial research from ORNL has demonstrated RCCI sensitivity to diesel cetane number especially with low-load performance. For single-fuel approaches, the unique properties of certain renewable fuels can have a benefit as well.

In-cylinder blending of gasoline-like fuels and diesel-like fuels to achieve RCCI has been shown to reduce oxides of nitrogen (NOx) and particulate matter (PM) emissions while maintaining or improving brake thermal efficiency as compared to conventional diesel combustion. The RCCI concept has an advantage over many advanced combustion strategies in that by varying both the percent of premixed gasoline and exhaust gas recirculation rate, stable combustion can be extended over more of the light-duty drive cycle load range. Increasing the drive-cycle load range is expected to allow improvements in fuel economy and lowered drive-cycle emissions. The prototype nature of advanced combustion...
means that approaches such as using vehicle systems simulations with experimental engine maps may be needed to investigate this potential. Other single-fuel advanced combustion modes such as PPC with gasoline range fuels also have shown potential to improve fuel efficiency and lower NOx and PM emissions.

**APPROACH**

For these activities, a state-of-the-art light-duty multi-cylinder engine (MCE) laboratory is in operation based on a 2007 model year General Motors 1.9-L common-rail turbocharged diesel in both the stock configuration and with pistons modified for RCCI operation. Previous multi-cylinder experimental work with advanced combustion and many alternative fuels puts ORNL in a unique position to evaluate real-world benefits and challenges associated with advanced combustion and fuel effects. The conceptual diagrams for RCCI and PPC are shown in Figure 1. How this approach compares to RCCI on the same engine hardware is not clearly understood.

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 highly premixed RCCI operation. A schematic of the MCE advanced combustion platform capable of RCCI or PPC is shown in Figure 2. A flexible microprocessor based control system allowed for control over both fueling systems and complete authority over engine operating parameters allowing operation of both single-fuel and dual-fuel advanced combustion modes. The stock high-pressure exhaust gas recirculation system was used for these experiments. Vehicle systems simulations to evaluate light-duty drive-cycle coverage are conducted in the MATLAB®/Simulink®-based Autonomie suite using engine maps from experimental data for fuel consumption, engine performance, and emissions.

**RESULTS**

The unique properties of renewable fuels such as ethanol and biodiesel have previously been shown to increase the load range of RCCI compared to conventional gasoline and diesel operation [1]. This investigation aimed to estimate the drive-cycle coverage improvements through vehicle systems simulations using an experimental RCCI engine map created using certification gasoline and 20% biodiesel, 80% diesel fuel (B20). B20 was found to advance combustion phasing without significantly increasing pressure rise rate.

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**FIGURE 1. Conceptual Diagram for RCCI and PPC**

**FIGURE 2. Multi-Cylinder Advanced Combustion Engine Schematic for RCCI or PPC**
Other partially premixed, low-temperature combustion strategies are also in development and show promise in increasing fuel economy and lowering engine-out NOx and PM emissions. Single-fuel PPC-like combustion strategies with gasoline range fuels were compared to dual-fuel RCCI on the aforementioned engine setup. Initial results, shown in Figure 3 with a 70 RON fuel using an injection hardware limited injection strategy allowing a pilot injection of up to -108° after top-dead center, showed comparable NOx emissions at 2,000 rpm, 4.0 bar brake mean effective pressure to RCCI using gasoline injected through the port fuel injection system and B20 injected through the direct injection system. Both RCCI and PPC-like combustion were shown to achieve higher than diesel brake thermal efficiency at the 2,000 rpm, 4.0 bar brake mean effective pressure with significantly increased CO and hydrocarbon emissions compared to diesel combustion.

![Figure 3: PPC and RCCI Combustion at 2,000 RPM, 4.0 bar Brake Mean Effective Pressure](image-url)
CONCLUSIONS

The role of alternative fuels to enable advanced combustion operation has been demonstrated. The ability of the unique properties of renewable fuels to improve drive-cycle coverage for RCCI combustion leading to higher potential fuel economy has been shown through vehicle systems simulations using experimental engine operating maps. Initial comparisons between RCCI and PPC-like combustion are underway and have both been shown to have higher than diesel brake thermal efficiency with similar hydrocarbon and CO emissions increases. Further investigations on injection strategy are underway to allow a comparison of RCCI and PPC on the same engine with the same production-viable hardware.

REFERENCES


Fy 2013 Publications/Presentations


SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

1. 2013 DOE VTO R&D Award for PI, Scott Curran on RCCI research for “Leadership in transitioning RCCI combustion from single cylinder to a multi-cylinder engine using bio-renewable fuels”.

2. Best Presentation Award for 2012 ASME ICEF Conference – RCCI Paper


4. ASME Early Career Award – Awarded in part due to research in alternative fuels and the relation to high efficiency engines
Overall Objectives

Facilitate the introduction of renewable and/or unconventional fuels and advanced engine-combustion strategies for their utilization in a manner that optimally 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 chemically and physically well-characterized reference fuels made from commercial blending stocks as well as pure compounds.
- High-quality experimental data for model development to facilitate rapid and cost-effective computational engine optimization for evolving fuels.
- Unbiased guidance to stakeholders on which emerging fuel and combustion strategies are most promising.

Fiscal Year (FY) 2013 Objectives

- Develop computational algorithms to summarize and organize data from a large parametric study of fuel effects on mixing-controlled combustion.
- Begin analyzing and communicating the results from the parametric study of fuel effects.
- Continue to advance the state-of-the-art of diesel surrogate fuels.

FY 2013 Accomplishments

- Created and refined computational algorithms for comprehensive processing of data from parametric study of fuel effects on mixing-controlled combustion, specifically data from over 25,000 replicates including high-speed imaging of chemiluminescence and natural luminosity from combustion, as well as elastic scattering from liquid fuel; engine-out emissions of oxides of nitrogen (NOx), unburned hydrocarbons (HCs), CO, CO\textsubscript{2}, O\textsubscript{2}, and smoke; exhaust laser-induced incandescence; cylinder pressure; and injection rate and quantity measurements.
- Completed initial analysis of the above data set and drafted a paper describing the results.
- Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council in developing second-generation surrogates with improved capabilities for matching market diesel fuels.

Future Directions

- Expand the fuel-effects studies described in the following to include oxygenated/renewable fuels of interest and higher injection pressures (≥2,400 bar).
- Conduct engine tests on surrogate and real-world target fuels to further assess the success of the surrogate-fuel formulation methodology created previously and to assist in its optimization.
- Develop and employ laser-induced incandescence and other diagnostics to better understand and quantify the production, oxidation, and distribution of soot within the combustion chamber.

INTRODUCTION

The purpose of this project is to obtain an improved understanding of the effects of emerging bio-derived, unconventional, and conventional fuels on mixing and combustion processes within modern compression-ignition (CI) engines. This information can be used to identify cost-effective fuels that provide maximum efficiency and performance, minimal emissions, and improved U.S. energy security for use in current and future transportation systems and machines.

A robust, general methodology for quantitatively assessing fuel effects on engine performance is urgently needed for identifying optimal fuel properties, but such a methodology has been elusive for a number of reasons. First, results obtained from different engines are often different. This can be due to different engines being calibrated to operate in different combustion modes (e.g., premixed vs. mixing-controlled) across the speed/load map. It can also be due to differences in: fuel-jet/piston-
bowl interactions, jet-jet interactions, fuel-injection strategies, and engine hardware in general. Due to their proprietary nature, such critical calibration and hardware details are seldom provided for production engines. A second challenge in studies of fuel effects is that often only some of the critical engine operating parameters are reported, while others are not. For example, a research group might report exceptionally low indicated specific nitrogen oxides (ISNOx) emissions for a given fuel, but not talk about its combustion efficiency or cyclic variability in load. A final challenge lies in the variability and complexity of the fuel itself. It is difficult to systematically study fuel-property effects because it is effectively impossible to change only one fuel property at a time. Market diesel fuels can exhibit wide variability in composition and hence properties, and this variability can have a pronounced effect on engine emissions, efficiency, and performance. Analytical techniques to accurately determine diesel-fuel composition in detail are only now becoming available. These techniques show that modern diesel fuels are incredibly complex, typically containing hundreds or thousands of distinct chemical compounds, and the impacts of these compounds on engine performance are not yet understood.

**APPROACH**

Effort on this project during FY 2013 has been focused on developing the needed robust, general methodology discussed above for quantitatively comparing fuels, and applying it to evaluate CI-engine fuels with wide composition and property variations. To address the calibration and hardware differences noted above, a common engine configuration has been selected for which all key details of the calibration and hardware are available. A 2-hole injector tip and simplified piston-bowl geometry are used to make the results more globally applicable by preventing jet-jet interactions and mitigating other hardware-dependent effects. The work is focused on mixing-controlled combustion modes because these modes are well-suited to high-load operation, an increasingly important range for future engines that are likely to be downsized and boosted. To address the problem with critical operating parameters not being reported, a great deal of effort has been focused on quantifying every important engine input and output parameter, including using optical diagnostics to measure in-cylinder parameters believed to have strong effects on emissions and efficiency. To address the problem with unknown fuel composition, only fuels for which detailed composition and property data are available have been studied.

The experiments were performed in the 1.72-liter single-cylinder heavy-duty optical CI engine described in [1] and [2]. A large parametric study was conducted to evaluate the differences among five chemically and physically well-characterized reference diesel fuels. The fuels included a #2 ultra-low sulfur emissions-certification diesel fuel (CF) and four of the Coordinating Research Council Fuels for Advanced Combustion Engines diesel fuels (F1, F2, F6, and F8) developed to have a wide range of cetane number (CN, 30 to 55), aromatic content (20 to 45 vol%), and 90 vol% distillation temperature (T90, 270 to 340°C). Selected general fuel properties are provided in Table 1. Detailed fuel compositional characteristics can be found in [3] and [4]. The engine operating conditions are shown in Table 2. Further details about the experimental setup and diagnostics can be found in [2].

**TABLE 1. General fuel properties.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>ASTM Method</th>
<th>CF</th>
<th>F1</th>
<th>F2</th>
<th>F6</th>
<th>F8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity [g/ml]</td>
<td>D4052</td>
<td>0.848</td>
<td>0.8084</td>
<td>0.8037</td>
<td>0.8411</td>
<td>0.8688</td>
</tr>
<tr>
<td>Cetane number</td>
<td>D613</td>
<td>43.3</td>
<td>30.3</td>
<td>28.4</td>
<td>53.7</td>
<td>49.5</td>
</tr>
<tr>
<td>Distillation temperature [°C]</td>
<td>D86</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T10 = 10 vol% recovered</td>
<td></td>
<td>211</td>
<td>184</td>
<td>181</td>
<td>223</td>
<td>248</td>
</tr>
<tr>
<td>T50 = 50 vol% recovered</td>
<td></td>
<td>253</td>
<td>200</td>
<td>193</td>
<td>275</td>
<td>273</td>
</tr>
<tr>
<td>T90 = 90 vol% recovered</td>
<td></td>
<td>310</td>
<td>284</td>
<td>346</td>
<td>339</td>
<td>342</td>
</tr>
<tr>
<td>Carbon [mass %]</td>
<td>D5291</td>
<td>87.04</td>
<td>85.74</td>
<td>85.71</td>
<td>86.25</td>
<td>87.40</td>
</tr>
<tr>
<td>Hydrogen [mass %]</td>
<td>D5291</td>
<td>13.03</td>
<td>13.82</td>
<td>13.94</td>
<td>13.62</td>
<td>12.42</td>
</tr>
<tr>
<td>Molar carbon-to-hydrogen ratio</td>
<td></td>
<td>0.561</td>
<td>0.521</td>
<td>0.516</td>
<td>0.532</td>
<td>0.591</td>
</tr>
<tr>
<td>Sulfur [ppm]</td>
<td>D5453</td>
<td>14.4</td>
<td>1.8</td>
<td>0.4</td>
<td>8.2</td>
<td>1.7</td>
</tr>
<tr>
<td>Aromatics (by SFC)</td>
<td>D5186</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-ring [wt%]</td>
<td></td>
<td>20.7</td>
<td>24.6</td>
<td>22</td>
<td>17.1</td>
<td>21.8</td>
</tr>
<tr>
<td>2 or more rings [wt%]</td>
<td></td>
<td>9.0</td>
<td>2</td>
<td>1.3</td>
<td>4.4</td>
<td>22.6</td>
</tr>
<tr>
<td>Total [wt%]</td>
<td></td>
<td>29.7</td>
<td>26.6</td>
<td>23.3</td>
<td>21.5</td>
<td>44.4</td>
</tr>
<tr>
<td>Net heat of combustion [MJ/kg]</td>
<td>D240</td>
<td>42.9</td>
<td>42.8</td>
<td>43.2</td>
<td>42.8</td>
<td>42.2</td>
</tr>
<tr>
<td>Kinematic viscosity @ 40°C [cSt]</td>
<td>D445</td>
<td>2.3</td>
<td>1.7</td>
<td>1.8</td>
<td>3.1</td>
<td>3.2</td>
</tr>
</tbody>
</table>
TABLE 2. Engine operating conditions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine speed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>Intake-manifold pressure</td>
<td>2.50 bar (abs.)</td>
</tr>
<tr>
<td>Intake-manifold O₂ mole fractions</td>
<td>21, 18, and 16%</td>
</tr>
<tr>
<td>Intake-manifold temperature</td>
<td>95.0 °C</td>
</tr>
<tr>
<td>Coolant temperature</td>
<td>95 °C</td>
</tr>
<tr>
<td>Injection pressures</td>
<td>80 and 180 MPa</td>
</tr>
<tr>
<td>Start-of-combustion timing</td>
<td>-5.0° ATDC compr.</td>
</tr>
<tr>
<td>Indicated duration of injection</td>
<td>3640 µs</td>
</tr>
</tbody>
</table>

RESULTS

Selected emissions results are shown in Figure 1. Significant differences among the fuels are evident. Figures 1a and 1b show that the high-CN fuels F6 and F8 have lower ISNOₓ emissions than the low-CN fuels F1 and F2. The high-aromatic F8 has higher ISNOₓ than the low-aromatic F6 at all dilution levels. Because the combustion phasings of F8 and F6 are effectively identical (see Figure 3), this indicates that a factor other than dilution level and phasing is affecting ISNOₓ emissions.

Figures 1c and 1d indicate that although ISNOₓ emissions generally increase with decreasing CN, smoke emissions generally decrease. Smoke reductions by more than an order of magnitude are possible by switching from CF to a low-CN, low-aromatic fuel like F2. Perhaps not surprisingly, the smoke emissions from the high-aromatic F8 are substantially higher than those from the low-aromatic F6. Figures 1e and 1f show that high-CN fuels have lower indicated-specific hydrocarbon (ISHC) emissions than the low-CN fuels F1 and F2. Similar trends are evident for indicated-specific carbon monoxide (ISCO) emissions (not shown). The high-aromatic F8 exhibits lower ISHC and ISCO emissions than F6. This result is surprising because aromatics typically have lower reactivities than other fuel constituents, and it suggests that compositional differences between F8 and F6 other than aromatic content may be responsible for the lower ISHC and ISCO emissions.

The higher ISHC and ISCO emissions of the low-CN fuels would be expected to lead to lower combustion efficiencies for these fuels, and Figure 2a shows that this is indeed the case. One might further expect the lower combustion efficiencies of the low-CN fuels to lead to low fuel-conversion efficiencies, but Figure 2b shows that...
Conclusions

Fuel-property changes can lead to profound changes in emissions and efficiencies. Some of the trends are as expected, and others are not. Changes in CN, aromatic content, and T90 of the fuel are insufficient to fully explain the observed changes. Quantification of in-cylinder processes such as the flame lift-off length as well as detailed fuel composition also appear to be required. Strong correlations between emissions/efficiency parameters and the flame lift-off length are observed and warrant further study; this analysis is ongoing.

References

III. Fuel Property Effects on Advanced Combustion Regimes


FY 2013 PUBLICATIONS


FY 2013 PRESENTATIONS


AWARD


PATENT PENDING

III.3 Advanced Combustion and Fuels Research at NREL

Overall Objectives

- 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 R&D program for high-efficiency engines with cost-effective emission controls.

Fiscal Year (FY) 2013 Objectives

- Develop experimental and simulation tools to characterize fuel ignition behavior in support of advanced combustion engine development, especially for low-temperature combustion (LTC).
- 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.

FY 2013 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 for fuel components and surrogate blends.
  - Bridged fundamental ignition experiments to engine testing.

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 mechanism 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 Coordinating Research Council to:
    - Expand fuels research to develop surrogate fuel blends with kinetic mechanisms.
    - Characterize advanced alternative and renewable fuel streams to address the paucity of data relevant to the engine research community.

INTRODUCTION

Development of more energy-efficient and environmentally friendly transportation vehicles demand simultaneous increases in powertrain efficiency and reductions 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 drives 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 Office’s Fuel & Lubricant Technologies program 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 mechanisms.
- Using engine-based studies to correlate data for experimental and simulation efforts.

AC&F’s team members closely collaborate with relevant industry stakeholders (primarily through the Coordinating Research Council), 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 Office’s Advanced Combustion Engine R&D program. 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 2013 with a joint appointment for Prof. Greg Bogin at CSM and NREL, in addition to sponsoring Ph.D. dissertation research for Eric Osecky (Ph.D., Chemical Engineering, 2013).

**RESULTS**

**Ignition Kinetics Research**

During FY 2013, NREL’s AC&F activity 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 such as Homogeneous Charge Compression Ignition (HCCI). 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 [2,3].

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 [4]. This technique was applied to the nine fuels comprising the Fuels for Advanced Combustion Engines diesel research fuel set [5-6], 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 [2-3,7-8]. 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, Red Rock, and beginning in 2013, the new Peregrine system [3,8].
III. Fuel property effects on advanced combustion regimes

NREL's focus on larger compounds expanded to larger n-alkanes, including decane \((\text{C}_{10}\text{H}_{22})\), dodecane \((\text{C}_{12}\text{H}_{26}, \text{a jet fuel surrogate})\), and hexadecane \((\text{C}_{16}\text{H}_{34}, \text{a diesel surrogate})\). Conducted in collaboration with CSM, Lawrence Livermore National Laboratory, and University of California, Berkeley, this research provides critical feedback for development of both full and reduced mechanisms. Validation of a 237-species skeletal reduced mechanism for hexadecane (developed by J.Y. Chen at UC-Berkeley) using NREL’s Red Mesa supercomputing cluster generated significant new knowledge. Hexadecane defines the cetane number value of 100, and hexadecane is included in a new diesel surrogate blend developed project under Coordinating Research Council project AVFL-18 [13].

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 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. Much of the FY 2013 research focused on longer chain compounds that are important surrogates, but for which few experimental ignition data had previously existed to support accurate kinetic mechanisms.

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™.

FIGURE 2. IQT™-based experimental ignition delay data for \(\text{C}_7\) isomers.
III. Fuel Property Effects on Advanced Combustion Regimes

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1. Introduction
2. Expanding the Experimental Capabilities of the Ignition Quality Tester for Autoigniting Fuels
3. Experimental Investigation of n-Heptane Autoignition in the Ignition Quality Tester (IQT)
4. Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber
5. Chemical and Physical Properties of the Fuels for Advanced Combustion Engines (FACE) Research Diesel Fuels
6. The Autoignition of Iso-Cetane at High to Moderate Temperatures and Elevated Pressures: Shock Tube Experiments and Kinetic Modeling
7. Using the Ignition Quality Tester (IQT) as a Tool for Mechanism Validation and Improvement

References


11. Osecky, G. Bogin, S. Villano, M. Ratcliff, J. Luecke, B. Zigler, and A. Dean, “Using the Ignition Quality Tester (IQT) as a Tool for Mechanism Validation and Improvement”.

Figure 3. Experimental data (symbols) and updated model (lines) predictions for HMN at 10 bar (blue) and 15 bar (black); \( \Phi = 0.9-1.1 \). Global equivalence ratio model predictions (solid lines) and double global equivalence ratio (dash lines) are shown for comparison [11].
III. Fuel Property Effects on Advanced Combustion Regimes

2013 Fall Technical Meeting, Western States Sections of The Combustion Institute, Colorado State University, Fort Collins, CO, October 7–8, 2013.


FY 2013 PUBLICATIONS/PRESENTATIONS


5. E. Osecky, G. Bogin, S. Villano, M. Rattcliff, J. Luecke, B. Zigler, and A. Dean, “Using the Ignition Quality Tester (IQT) as a Tool for Mechanism Validation and Improvement”, 2013 Fall Technical Meeting, Western States Sections of The Combustion Institute, Colorado State University, Fort Collins, CO, October 7–8, 2013.
III.4 Alternative Fuels DISI Engine Research

Overall Objectives

Provide the science-base needed by industry to understand:

- How emerging alternative fuels impact the new highly-efficient direct-injection, spark-ignited (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) 2013 Objectives

- Start developing a conceptual model of stratified SI combustion that incorporates the effects of fuel on combustion rate, ignition stability and exhaust emissions formation.
- Develop injection- and spark-timing guidelines that enable clean and stable stratified operation regardless of the blend ratio of gasoline and ethanol.

FY 2013 Accomplishments

- Effects of gasoline-blend ratio, spark timing, and load on soot and oxides of nitrogen (NOx) emissions have been quantified, providing guidelines for achieving clean operation of these fuel-efficient spray-guided engines as the fuel composition changes. This addresses one of the barriers identified by Vehicle Technologies Office: inadequate data for fuel property effects on combustion and engine efficiency optimization.
- The role of the in-cylinder flow field for highly stratified SI operation has been clarified using a combination of particle image velocimetry (PIV) measurements and performance testing.
- The dominant role of the spray-induced fuel/air-mixing and turbulence for the combustion rate of highly stratified SI combustion has been demonstrated for 70% ethanol-30% gasoline (E70) fuel.

Future Directions

- Continue development of a conceptual model of stratified combustion that includes both highly-stratified operation using “head ignition” for high ethanol fuels, and less stratified operation using “tail ignition” for acceptable soot with lower-ethanol fuels.
- Examine further the role of the in-cylinder flow field for both the combustion rate and the ignition stability of selected gasoline/ethanol blends, with a focus on swirling flows measured in a horizontal plane.
- Broaden the range of combustion to also include other modes of lean or dilute SI operation, examining fuel effects on well-mixed or partially stratified operation using either conventional spark or advanced ignition systems.

INTRODUCTION

In light of constrained petroleum supply and anthropogenic climate change, increased engine efficiency and alternative fuels are of interest. This project aims at providing the science-base needed by industry to develop highly efficient stratified-charge DISI engines that also beneficially exploit the different properties of alternative fuels. For lean and stratified operation, low engine-out NOx and soot emissions must be achieved to avoid expensive aftertreatment technology in markets with stringent exhaust legislation. Previous results from this project demonstrate the potential of 85% ethanol-15% gasoline (E85) fuel to enable clean and efficient stratified combustion [1]. The low smoke is mostly attributed to the high oxygen content of the E85 fuel. The low NO emissions are attributed to E85’s ability to accept an injection near top-dead center that is combined with an early spark, giving rise to highly stratified combustion that is phased relatively late [2].

Because of these beneficial soot- and NO-reducing effects of ethanol, it is of interest to study how soot and NOx emissions are affected by other fuel blends. This is particularly important for flex-fuel engines as the fuel properties change widely depending on the exact mix of gasoline and E85 being present in the fuel tank. This project aims to address knowledge barriers facing industry regarding fuel effects on these highly efficient stratified-charge engines.
APPRAOCH

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. Computer modeling provides knowledge of governing combustion fundamentals. The combination of performance testing, exhaust-emissions measurements, optical diagnostics, and modeling allows building a comprehensive science-base.

RESULTS

As mentioned previously, E85 allows clean operation with highly stratified combustion. This was accomplished using “head ignition” whereby the spark ignition coincides with the beginning of the fuel-injection event. Figure 1 shows the engine-out smoke level as a function of engine load for five fuels using this head-ignition strategy. An engine speed of 1,000 rpm was used and start of injection (SOI) was fixed at -23° crank angle (CA) for all data points. The spark timing was -22° CA. This spark timing corresponds to when the two fuel sprays that straddle the spark plug electrode have penetrated to the location of the spark gap. It can be observed that the smoke level is highly dependent on both fuel type and engine load when this head-ignition strategy is used. For all fuels, smoke increases with load. This trend was examined optically for E85 and attributed primarily to increasing amounts of bulk-gas soot in combination with slow soot burn-out [3]. It is important to note that the load range with acceptable smoke is highly dependent on the fuel type. A smoke level of 0.1 Filter Smoke Number is commonly used as a limit for acceptable exhaust soot. With this limit, Figure 1 shows that for E35 the engine can only be operated at very low loads when head ignition is employed. In contrast, neat ethanol (E100), can reach a gross indicated mean effective pressure (IMEP) of 470 kPa before the smoke becomes unacceptable. For load/fuel combinations that are above the smoke limit using head ignition, a different ignition strategy needs to be employed to abate soot formation. This is explained in Figure 2.

Figure 2 plots exhaust smoke against the spark timing relative to the time when fuel sprays arrive at the spark plug gap. Data for gasoline and E85 are plotted, and the particular data points for head ignition at 0° CA correspond to the two circled data points in Figure 1. Consistent between Figures 1 and 2, operation with head ignition at this load results in very high smoke for gasoline. To avoid this “soot disaster,” the spark timing must be retarded to allow more time for fuel and air to mix prior to combustion. Without sufficient time for mixing, fuels like gasoline form ultra-rich mixtures near the spark plug [2]. This in combination with an aromatics content of 25% results in formation of large amounts of in-cylinder soot.

In the following, Figures 3–6 exemplify recent research aimed at determining both what factors govern the combustion rate for stratified operation with head ignition and the role of the in-cylinder flow field generated by the intake and compression strokes. Here, E70 fuel is used, but trends are expected to be very similar for E85 and E100. The strength of the in-cylinder flow field was altered by changing the engine speed in the 1,000 to 2,000 rpm range. Figure 3a shows the heat-release traces for stratified operation. The data are plotted as absolute heat-release rate in kW against real

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**FIGURE 1.** Engine-out smoke level as a function of load for gasoline, ethanol (E100), and three blends thereof (E35, E70, E85); 1,000 rpm.

**FIGURE 2.** Exhaust smoke as a function of spark timing relative to the arrival of fuel sprays at the spark plug for gasoline and E85; IMEP = 320 kPa, SOI = -23°CA, [O2] = 19%.
time in ms. It can be seen that, on average, the stronger in-cylinder air flow at higher speed does not affect the stratified combustion much. In strong contrast, for traditional well-mixed stoichiometric operation, the peak heat release scales proportionally with engine speed, as Figure 3b shows. This increase of apparent heat release rate (AHRR) in kW for well-mixed operation is well understood to be caused by higher flame speeds as a result of increased turbulence [4]. The very different response to engine speed for the stratified operation shows that its combustion rate is not controlled by turbulence generated by the intake and compression strokes. Based on this, a hypothesis is formulated; the combustion rate of stratified operation is controlled by mixing rates and turbulence level in fuel-containing regions, and that these mixing rates are governed by the fuel-injection process.

To illustrate cycle-to-cycle variations, each of Figures 4a and 4b plots 250 individual heat-release traces for stratified operation at 1,000 and 2,000 rpm, respectively. They show that the higher speed exhibits much larger variations in the magnitude of the AHRR. This leads to the formulation of a second hypothesis: the observed increase of combustion variability at higher speeds should be attributed to random in-cylinder flow variations that become sufficiently strong at 2,000 rpm to influence fuel/air-mixing, ignition, and combustion. Both of these hypotheses are tested and ultimately strengthened in two recent paper submissions [5,6]. Some of the key observations are presented in the following.

Figure 5a provides two examples of spray imaging via the piston-bowl window. The differences between the two images exemplify that the in-cylinder flow field becomes sufficiently strong at 2,000 rpm that it is able to perturb the liquid portion of the fuel jets. In Figure 5b, this is quantified in terms of liquid spray-tip penetration. A very low engine speed of 333 rpm serves as a reference case with very weak in-cylinder gas flows. The lower portion of Figure 5b shows that the average tip penetration for the 1:00-fuel spray is similar for the two engine speeds. Vaporization causes a quasi-steady liquid length to be established 0.20 ms after SOI. (The measured length in this horizontal projection is less than the actual axial penetration because the injector-tip configuration aims the fuel sprays downwards towards the camera.) The upper portion of Figure 5b shows that the standard deviation of the spray-tip penetration becomes substantially elevated 0.20 ms after SOI for the 2,000 rpm case. This quantifies the observations of substantial interaction between the liquid fuel sprays and the stochastic in-cylinder flow at 2,000 rpm.

Figure 6a shows an example of PIV measurements of the in-cylinder flow in a central portion of the combustion chamber. It can be seen that, on average, the stronger in-cylinder air flow at higher speed does not affect the stratified combustion much. In strong contrast, for traditional well-mixed operation, the peak heat release scales proportionally with engine speed, as Figure 3b shows. This increase of apparent heat release rate (AHRR) in kW for well-mixed operation is well understood to be caused by higher flame speeds as a result of increased turbulence [4]. The very different response to engine speed for the stratified operation shows that its combustion rate is not controlled by turbulence generated by the intake and compression strokes. Based on this, a hypothesis is formulated; the combustion rate of stratified operation is controlled by mixing rates and turbulence level in fuel-containing regions, and that these mixing rates are governed by the fuel-injection process.

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Figure 6a shows an example of PIV measurements of the in-cylinder flow in a central portion of the combustion chamber.
III. Fuel Property Effects on Advanced Combustion Regimes

because the strength of the in-cylinder flow generated by the intake and compression strokes is comparable to that of the spray-induced flow. Overall, these observations combined with other observations in Refs. [5,6] support the second hypothesis that in-cylinder flow variations become sufficiently strong at 2,000 rpm to influence fuel/air-mixing, ignition, and combustion, thereby causing the larger heat-release variations shown in Figure 4b.

CONCLUSIONS

• Substantial progress has been made towards a conceptual model of highly stratified SI combustion.
• The combustion rate for highly stratified SI operation with closely coupled injection and combustion is primarily governed by fuel/air mixing and turbulence associated with the fuel-injection process.
• The primary role of the in-cylinder flow field generated by the intake and compression strokes is to cause stochastic variations of the fuel-jet mixing,
resulting in elevated cycle-to-cycle variations of the spray-guided stratified combustion.

- The gasoline/ethanol blend ratio of the fuel strongly influences how a spray-guided stratified-charge engine should be operated for low exhaust emissions of soot.
- For E85 and E100, highly stratified combustion using head-ignition can be used over relatively large load ranges.
- For gasoline and low-ethanol blends, more fuel/air mixing is required prior to combustion to avoid excessive smoke, and this can be accomplished by retarding the spark relative to the injection event.

ACKNOWLEDGEMENTS

The work was performed at the Combustion Research Facility, Sandia National Laboratories, Livermore, CA. Financial support was provided by the U.S. Department of Energy, Office of Vehicle Technologies. Sandia is a multiprogram laboratory operated by the Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy’s National Nuclear Security Administration under contract DE-AC04-94AL85000.

REFERENCES

Overall 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) 2013 Objective

Map the efficiency and emissions of four different combustion modes: spark-ignited (SI), exhaust gas recirculation (EGR) dilute SI; boosted Homogeneous Charge Compression Ignition (HCCI); and spark-assisted HCCI (SA-HCCI); using three different fuels in a common engine platform.

FY 2013 Accomplishments

- Mapped efficiency and emissions of SI combustion and dilute SI combustion for regular-grade gasoline, a blend of 24% iso-butanol with gasoline, and 30% ethanol with gasoline from 1,200 to 3,000 rpm and to the peak load at each speed in accordance with the experimental criteria applied in this study.

- Mapped the efficiency and emissions of boosted HCCI combustion with the same three fuels at 1,600, 2,000, and 2,500 rpm to the peak load at each speed in accordance with the experimental criteria applied in this study.

- Mapped the efficiency and emissions of SA-HCCI combustion with two of the three fuels at 1,600, 2,000, and 2,500 rpm to the peak load at each speed in accordance with the experimental criteria applied in this study.

Future Directions

- Use experimental results from FY 2013 to feed vehicle-level models to determine volumetric fuel economy effects of fuel composition, advanced combustion, and the downsize/downspeed strategies that are enabled by certain fuels.

- Conduct an experimental campaign to determine the fuel-specific differences associated with a new advanced combustion concept being developed at ORNL: an in-cylinder non-catalytic fuel reforming strategy to enable highly dilute SI combustion.

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 engine platforms as a means to increase fuel efficiency and/or reduce engine emissions. Additionally, the calibration of conventional combustion strategies is becoming more aggressive and demanding more from the fuel. Non-petroleum fuels, such as ethanol and butanol are largely compatible with SI engines optimized for gasoline. However, there is a need to investigate whether these fuels offer potential advantages in SI operating modes through hardware and/or calibration changes, and to determine their impact on advanced combustion strategies where there is less direct control over the start of combustion.

This project focuses on alternative fuels that are capable of displacing large volumes of petroleum, namely ethanol and iso-butanol. The research strategy employed in FY 2013 was to use the same single-cylinder research engine to provide a common basis for comparison between the three fuels and the four combustion strategies investigated.

APPROACH

In FY 2013, the approach was to map the efficiency and emissions across the applicable speed/load operating map using three common fuels with four different operating conditions. This was done on a common SI research engine platform that has been highly modified from its original configuration to make it a more versatile research platform. The research engine is based
on a 2.0-L General Motors Ecotec engine with direct fuel injection and modifications include conversion to single-cylinder operation, a fully flexible hydraulically actuated valve train, and multiple pistons to change the compression ratio. The FY 2013 studies were conducted with a compression ratio of 11.85:1 with the exception of a baseline map with that was done at the stock compression ratio of 9.2:1. The engine platform is also equipped with a laboratory air handling system capable of delivering boost and external EGR. The three fuels that were investigated are 1) regular-grade gasoline (87 anti-knock index, AKI), 2) 24 vol% iso-butanol blended with gasoline (IB24), and 3) 30 vol% ethanol blended with gasoline (E30).

The four combustion modes were 1) conventional SI under stoichiometric conditions, 2) 15% EGR dilute SI under stoichiometric conditions, 3) boosted lean HCCI, and 4) stoichiometric SA-HCCI. The limitations on engine operation were the peak cylinder pressure of 100 bar, a maximum exhaust temperature of 800°C, and crank angle at which 50% of the combustion heat release has occurred (CA50) combustion phasing of 25 degrees after firing top dead center (aTDCf). Mapping for the first two combustion modes was conducted at 1,200, 1,600, 2,000, 2,500, and 3,000 rpm. A subset of these speeds were mapped for the boosted HCCI so that additional parametric investigations could be conducted (1,600, 2,000, and 2,500 rpm). For SA-HCCI, parametric investigations were conducted at 1,600, 2,000, and 2,500 rpm with 87-AKI gasoline and E30, however, it was concluded that this is an inherently unstable mode of combustion, and thus the results are not shown here.

RESULTS

For the conventional and EGR diluted modes of combustion, the engine was operated in the same manner up to the maximum operation load for each fuel, as measured by the gross indicated mean effective pressure (IMEPg). The CA50 combustion phasing is maintained at 8 CA aTDCf (approximately maximum brake torque phasing) until knock is encountered, at which point combustion phasing becomes knock-limited. Once-knock limited, combustion phasing is retarded to mitigate knock until one of the criteria is met that limit IMEPg. All tests are run under stoichiometric conditions, thus power enrichment to extend the peak torque is not considered.

The operable speed/load range with and without EGR is show for each fuel in Figure 1. For all fuels, the use of EGR allows the peak IMEPg to be increased by 100-200 kPa, which can be attributed to a combination of reduced exhaust temperature and enhanced resistance to knock. Compared to 87-AKI fuel, IB24's enhanced resistance to knock allows the IMEPg to be increased by about 20%, and E30’s resistance to knock allows the IMEP to be roughly doubled. It is noteworthy that a severe limitation on the maximum IMEPg for 87-AKI gasoline is imposed by the high compression ratio configuration used in this study. Figure 2 illustrates that when the engine is operated at its stock compression ratio of 9.2:1, the IMEPg for 87-AKI fuel increases substantially, but this comes at a reduced thermal efficiency because of the lower compression ratio. In addition, the maximum IMEPg for 87-AKI fuel at the 9.2:1 compression ratio remains lower than for E30 at the higher compression ratio.

The doubling of the maximum IMEPg for E30 is attributed to superior anti-knock properties of the fuel, but this is not purely related to the knock onset. Figure 3 shows the CA50 combustion phasing as a function of load for each fuel, with and without EGR. As load increases, combustion phasing has to be retarded to mitigate knock. However, the slope of the combustion phasing retard is less severe for E30, indicating that combustion phasing retard has more authority to mitigate knock for E30 than for the regular grade gasoline. This behavior is essential to enhanced power density relative to 87-AKI gasoline and can be attributed to a combination of ethanol's high latent heat of vaporization and high octane number sensitivity.

FIGURE 1. Operable speed/load range for each fuel for conventional SI combustion (solid) and SI combustion diluted with 15% EGR (hashed).
While there are measurable thermal efficiency differences between fuels, the most significant implication of the increased load for the E30 is it being an enabler of downsizing and downspeeding, which is a system-level approach for increasing vehicle fuel economy. Figure 4 shows efficiency contour plots for 87-AKI gasoline and E30 and considers four different ways to produce 16 kW: (a) 2.0-L engine at 2,500 rpm, (b) downspeeding to 1,600 rpm, (c) downsizing to a 1.2-L displacement, and (d) downsizing and downspeeding. While there are many design considerations that are not included in this simplified analysis, it is illustrative of the efficiency advantages that are the basis of downsizing and downspeeding, and the complete analysis is included in publication 6 listed at the end of this report. The primary result is that at a steady-cruise condition, the downsizing and downspeeding enabled by the E30 fuel, could produce an increase in efficiency sufficient to make up for the energy density penalty, resulting in a better volumetric fuel economy for E30 compared to 87-AKI gasoline. Complete details of the SI and dilute SI studies can be found in publications 6, 7, and 12.

The lean-burn boosted HCCI combustion used in this project was based on the strategy used in an earlier study on this same engine platform [1]. The operable speed/load regime for each fuel is shown in Figure 5. In contrast to the SI and dilute SI combustion strategies, all of the fuels can be operated to the same maximum load. This was accomplished with only minor variations in operating conditions, namely earlier fuel injection timing and/or a longer negative overlap for the less reactive fuels. The minor changes required in the negative valve overlap and fuel injection strategy are shown in Figure 6. The gross thermal efficiency for the boosted HCCI combustion was high, including several points above 45%. However, the air handling requirements for such a combustion strategy will likely drive up the pumping losses, making it unclear if there will be a brake efficiency advantage of the boosted HCCI combustion. Complete combustion and air handling details of the boosted HCCI study are presented in publication 14.

**CONCLUSIONS**

Experimental efforts in FY 2013 focused on mapping efficiency and emissions for 87-AKI gasoline, IB24, and E30 over the operable speed/load range for four different combustion strategies. The primary findings are as follows:
E30 has superior anti-knock properties compared to 87-AKI gasoline, enabling a doubling of the maximum IMEPg under a high compression ratio configuration.

The higher maximum IMEPg of E30 is an enabler to downsizing/downspeeding strategies without having to sacrifice efficiency with a reduced compression ratio.

In contrast to conventional SI combustion, the fuel-specific differences under boosted HCCI conditions can be readily compensated for with minor changes to engine controls.

REFERENCES


FY 2013 PUBLICATIONS/PRESENTATIONS

II. Fuel Property Effects on Advanced Combustion Regimes


SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

III.6 Ionic Liquids as Novel Lubricants and/or Lubricant Additives

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DOE Technology Development Manager:
Steve Przesmitzki

Overall Objectives

• Investigate the potential of using ionic liquids (ILs) as lubricants and/or lubricant additives specifically for internal combustion 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) 2013 Objectives

• Develop the first prototype fully-formulated engine oil using an ionic liquid as an anti-wear additive.

• Perform bench tribological evaluation of the prototype IL-additized engine oil.

• Conduct full-size multi-cylinder engine tests to evaluate the aging and wear performance of the prototype IL-additized engine oil.

• Perform standard engine dynamometer tests to demonstrate improved fuel efficiency.

FY 2013 Accomplishments

• High-temperature, high-load (HTHL) full-size multi-cylinder engine tests confirmed the excellent anti-wear performance for the IL-additized engine oil.

• Sequence VID engine dynamometer tests demonstrated an improved fuel economy by >2% for this IL-additized engine oil benchmarked against the Mobil 1™ 5W-30 oil.

• In addition, accelerated catalyst aging tests suggest that the IL additive may potentially have less adverse impact on three-way catalysts compared to the conventional additive zinc dialkyl-dithiophosphate (ZDDP).

Future Directions

This project was completed on September 28, 2013.

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. A new class of more effective lubricants could therefore lead to huge energy savings. Based on an ORNL U.S. patent on IL lubrication, ORNL and GM signed an agreement on May 28, 2009, to investigate the potential of using ILs as lubricants and/or lubricant additives specifically for internal combustion engines. ILs are, as the name indicates, composed solely of cations and anions instead of neutral molecules. Their unique chemical and physical properties, such as inherent polarity, high thermal stability, non-flammability, low volatility, and low viscosity-pressure coefficient, offer 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 and multifunctional including anti-wear/extreme-pressure, friction modifier, anti-corrosion, detergent, etc., and potentially allow the use of lower viscosity engine oils to improve...
fuel economy. The second approach is more cost effective and easier to penetrate into the current lubricant market.

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

RESULTS

The project team, in collaboration with the Lubrizol Company, conducted engine oil formulation to develop the first prototype automotive engine oil using the IL \([\text{P}66614]\text{[bis(2-ethylhexyl)phosphate, DEHP]}\) as the anti-wear additive. A polyalpha olefin polyalphaolefin 4 cSt base oil was used as the base fluid and the treat rate of \([\text{P}66614]\text{[DEHP]}\) was 1.0 wt%. The rheology properties are shown in Table 1. The kinematic and high-temperature, high-shear (HTHS) viscosities were determined using the ASTM standards D7279 and D5481, respectively. The IL-additized engine oil has ultra-low viscosities, which are substantially lower than the newest SAE 0W-16 engine oil.

Table 1. Kinematic and HTHS Viscosities

<table>
<thead>
<tr>
<th></th>
<th>cSt @ 40°C</th>
<th>cSt @ 100°C</th>
<th>HTHS (cP @150°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobil 1™ 5W-30 engine oil</td>
<td>64.3</td>
<td>11.4</td>
<td>3.11</td>
</tr>
<tr>
<td>Mobil Clean™ 5W-30 engine oil</td>
<td>56.1</td>
<td>10.1</td>
<td>3.06</td>
</tr>
<tr>
<td>SAE XW-20 engine oil</td>
<td>&gt;6.9, &lt;9.3</td>
<td>&gt;2.6</td>
<td></td>
</tr>
<tr>
<td>SAE XW-16 engine oil</td>
<td>&gt;6.1, &lt;8.2</td>
<td>&gt;2.3</td>
<td></td>
</tr>
<tr>
<td>Proposed SAE 12 grade</td>
<td>&gt;2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Proposed SAE 8 grade</td>
<td>&gt;1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IL-additized engine oil (300 mL batch)</td>
<td>25.5</td>
<td>5.38</td>
<td>1.93</td>
</tr>
<tr>
<td>IL-additized engine oil (6-gallon batch)</td>
<td>25.5</td>
<td>5.38</td>
<td>1.85</td>
</tr>
</tbody>
</table>

*SAE J300, Engine Oil Viscosity Classification, SAE International, April 2013.

Tribological bench tests were conducted on the IL-additized prototype engine oil at the GM Tech Center. Ball-on-disc rolling-sliding tests were carried out on a Mini Traction Machine (MTM-2) to generate the Strubeck curves as well as evaluate the wear behavior. The Strubeck curves of the three oils are plotted in Figure 1. The prototype IL-additized engine oil showed 20-33% friction reduction in mixed and elastohydrodynamic lubrication compared with the two commercial Mobil 5W-30 engine oils. The wear rates are compared in Figure 2, where the prototype IL-additized engine oil showed 38% and 92% less wear than the Mobil 1™ and Mobil Clean™ 5W-30 oils, respectively. This is particularly encouraging when considering the ultra-low kinematic and HTHS viscosities of the IL-additized oil.

HTHL engine dynamometer tests were carried out on the prototype IL-additized engine oil at the GM Tech Center to evaluate its engine wear protection and aging behavior at extreme engine operation conditions. Tests were conducted for 100 hours at 2,700 rpm speed, 120 N load, and 145°C oil sump temperature. The oil consumption of the IL-additized oil in the HTHL test was small and comparable to the Mobil 1™ 5W-30 engine oil. The HTHS viscosity of the IL-additized oil was slightly higher by the end of the engine test, from 1.85 to 2.03 cP.
at 150°C, as shown in Table 2. The wear-related metallic elements in the oil samples at different test intervals in the HTHL engine test were quantified using inductively coupled plasma-atomic emission spectroscopy. Very encouragingly, the low-viscosity IL-additized oil showed similar amounts of iron (main indicator of engine wear) and less copper (indicator of bronze bearing wear) compared to the Mobil 1™ 5W-30 oil. This suggested that the IL-additized oil provided adequate engine wear protection despite its ultra-low viscosity.

### TABLE 2. Kinematic and HTHS Viscosities of HTHL Tested Oils

<table>
<thead>
<tr>
<th>Test time (hr)</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mobil 1™ 5W-30 oil</td>
<td>cSt @ 40°C</td>
<td>64.2</td>
<td>58.4</td>
<td>55.2</td>
<td>55.1</td>
<td>56.8</td>
</tr>
<tr>
<td></td>
<td>cSt @ 100°C</td>
<td>11.4</td>
<td>10.2</td>
<td>9.7</td>
<td>9.5</td>
<td>9.7</td>
</tr>
<tr>
<td></td>
<td>HTHS (cP) @ 150°C</td>
<td>3.11</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IL-additized oil</td>
<td>cSt @ 40°C</td>
<td>25.5</td>
<td>27.5</td>
<td>28.2</td>
<td>28.7</td>
<td>29.5</td>
</tr>
<tr>
<td></td>
<td>cSt @ 100°C</td>
<td>5.4</td>
<td>5.6</td>
<td>5.7</td>
<td>5.7</td>
<td>5.8</td>
</tr>
<tr>
<td></td>
<td>HTHS (cP) @ 150°C</td>
<td>1.85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The GF-5/Sequence VID fuel efficiency engine dynamometer tests (ASTM D 7589) were conducted at InterTek Automotive Research using a 2008 Cadillac SRX 3.6-L High Feature V-6, 4-cycle engine. The baseline oil was an SAE 20W-30 engine oil without friction modifier or viscosity improver. Results are shown in Figure 3. The fuel economy in running the Mobil 1™ 5W-30 engine oil was 1.92% higher than the baseline. In contrast, the prototype IL-additized engine oil improved the fuel efficiency by 4.18% and 3.68% over the baseline 20W-30 oil in the two repeat tests, an average of 3.93% improvement. This demonstrates an average 2.01% higher fuel efficiency compared to the Mobil 1™ 5W-30 engine oil. This has met the DOE Vehicle Technologies Office’s goal of 2% fuel efficiency improvement via lubricant advances by 2015.

ORNL researchers set up an accelerated aging system to compare the effects of the IL [P66614][DEHP] and a commercial secondary ZDDP additive on three-way catalysts. A typical metric for the evaluation of three-way catalyst performance is based on temperature measurements at a given conversion rate for oxides of nitrogen, CO and hydrocarbons. Results are compared in Figure 4 and show that the temperature increase for the IL-exposure was 20-70°C less than that for the ZDDP-exposure. This suggests potentially less adverse impact on three-way catalysts for the IL-additized engine oil compared to oils with ZDDP.

### CONCLUSIONS

This project has successfully developed a new group of oil-miscible ILs for engine lubrication. Working with a leading oil formulation company, a prototype IL-additized low-viscosity engine oil has been produced. HTHL engine tests showed excellent anti-wear performance for the prototype oil in both fresh and aged conditions. Sequence VID engine dynamometer tests of this IL-additized oil demonstrated an improved fuel economy by 3.93% and 2.01% benchmarked against the 20W-30 baseline and Mobil 1™ 5W-30 engine oils, respectively. In addition, accelerated catalyst aging tests were conducted on the IL additive and results suggested potentially less poisoning effects on three-way catalysts compared to ZDDP.
III. Fuel Property Effects on Advanced Combustion Regimes

FY 2013 PUBLICATIONS/PRESENTATIONS


SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

Overall 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) 2013 Objectives

- Project management plan updated
- Spray work completed and desirable fuel properties identified
- Fuels identified for optical engine testing
- Models validated and available for use
- External testing replaces internal ignition quality tester operation
- Low temperature tri-propylene glycol methyl ether (TPGME) kinetic mechanism developed and verified

FY 2013 Accomplishments

- Continued the development of a master list of oxygenated fuels and measurement of key properties of select oxygenates.
- Conducted ignition delay tests on several test methods for cetane rating to better understand cetane rating variations. Identified a significant cetane number difference for different test methods across different TPGME blends.
  - Completed combustion spray vessel studies. Evaluated six fuel blends; neat n-dodecane, n-hexadecane with 50%, 33%, and 15% TPGME, 50% TPGME with a mixture of 23% m-xylene and 77% n-dodecane, and neat methyl decanoate.
  - Completed model development and validation using a grouped chemistry representation to model different cetane fuels. Published results at the 2013 SAE Congress and in an Energy & Fuel journal.
  - Identified issues with low temperature chemistry in the TPGME model which caused predicted ignition delay to increase with increasing TPGME, counter to experimental results (TPGME: >60 derived cetane number). Ultimately, this caused misfire in simulations with greater than 80% TPGME.
  - Subcontracted with Lawrence Livermore National Laboratory (LLNL) to further develop the TPGME low-temperature kinetics models. LLNL has nearly completed the kinetic model development and validation.
  - Investigated various methods for modeling oxygenated and non-oxygenated fuels. Continued to tune and validate models to help select test fuels, hardware, and boundary condition changes to demonstrate non-sooting diesel combustion.
  - Selected optical engine test fuels and developed a test matrix.
  - Acquired high-pressure fuel system hardware with a nozzle suite based on computational fluid dynamics (CFD) modeling.

Future Directions

- Further investigate the influence of cetane number test methods.
- Continue to improve and use models to guide fuel selection and boundary conditions.
- Validate and use fuel and combustion models to understand the effect of fuel properties on ELOC and identify combustion design changes needed to facilitate non-sooting diesel combustion.
- Conduct optical engine experiments.
- Complete the analysis of spray study results.
- Demonstrate non-sooting diesel combustion on an engine with modern power density requirements.
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 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, 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 further developed and used for fuel selection. Investigation of cetane number of TPGME and TPGME blends uncovered differences in cetane number and derived cetane number measurements from various measurement systems.

Fuels to support SNL spray lab testing and optical engine experiments were selected based on the fuel oxygen ratio and cetane number as well as other factors including low toxicity, ease of lab use, and availability of detailed chemistry mechanisms. Fuels were chosen to evaluate the influence of fuel oxygen ratio, the presence of aromatics and the oxygenate structure on soot behavior in ELOC.

High-pressure fuel system hardware was acquired to upgrade the single-cylinder engine fuel system to facilitate engine demonstration in 2014. The fuel system hardware included a suite of nozzle configurations that are expected to improve ELOC operation based on computational fluid dynamic analysis.

Modeling

Surrogate models were further developed to characterize spray and combustion properties of three different diesel fuels. Computations were performed using a grouped chemistry representation to model different fuel compositions. Model results were compared against single-cylinder engine data at various operation conditions, including conventional and low-temperature combustion conditions. Model prediction compared well at all operating conditions and under a variety of parameter sweeps including exhaust gas recirculation rate, injection timing and intake temperature.

A reduced combined TRF-TPGME mechanism with 50 species and 173 reactions was also explored for use in modeling spray combustion chamber data with TPGME-NHD mixtures. Comparing constant volume simulation results against spray tests uncovered an issue with the low-temperature TPGME mechanism. Improvements to the kinetics models were investigated, and LLNL was subcontracted to improve the TPGME low temperature chemistry model. LLNL has added the low-temperature chemistry reactions and updated reaction rate estimates and reaction pathways for the existing high-temperature reactions. The model has been validated against shock tube data generated at National University of Ireland, Galway. The model will be evaluated by UW.

Multiple modeling approaches have been investigated to account for the effect of oxygenated fuels on particulate matter emissions. Model results were compared against existing single-cylinder data. Reasonable agreement has been obtained comparing cylinder pressure and heat release; however, soot emissions trends do not appear to match experimental results. Separate tuning of the soot model for oxygenated and non-oxygenated fuels will be investigated.

Spray Work and Optical Engine

SNL has completed a set of experiments characterizing ELOC and providing a detailed
understanding of spray evaporation, mixing, ignition, lift-off stabilization, and soot formation. The testing included a new optical technique to provide quantitative line-of-sight soot measurement in a diesel spray. The ambient temperature and pressure variation will identify the conditions where ELOC can be achieved. An atypical trend between ignition delay and flame lift-off was observed with TPGME, suggesting it may be a good ELOC fuel. Using different blends of TPGME and n-hexadecane, fuel oxygen ratio was found to have a strong influence on the boundary conditions in which soot was observed as well as both the amount and the location of soot in a diesel spray.

Blends of 50% TPGME in a fuel with zero and 23% aromatics was found to have only a small influence on the boundary conditions that produce soot. The presence of aromatics increased both ignition delay and flame lift-off, possibly offsetting the negative effect of aromatics on soot formation. The presence of aromatics increased soot in the spray. Further analysis is needed to better understand the influence of aromatics.

Limited testing comparing G50 (50% TPGME, 50% n-hexadecane) and methyl decanoate were not able to demonstrate the influence of oxygenate structure due to confounding with cetane number and flame lift-off. Further data analysis is needed to compare the fuels at the same fuel-oxygen equivalence ratio.

CONCLUSIONS

- The atypical relationship between ignition delay and flame lift-off length for TPGME may make it a good candidate fuel for ELOC.
- Fuel oxygen ratio and flame lift-off length are key parameters influencing the ability to achieve ELOC. Fuel aromatics and fuel oxygenate structure also likely play a role, but require further analysis.
- A fuel surrogate approach has been used successfully to model the effect of different cetane numbers under various engine operating conditions.
- An improved TPGME kinetic mechanism has been developed and is almost ready to be used for comparison against SNL spray data.
- The high-pressure fuel system will be installed near year-end to facilitate demonstration of ELOC with oxygenated fuels.

FY 2013 PUBLICATIONS/PRESENTATIONS

2. UW and FMC published and presented the following paper at the 2013 SAE Congress: “Surrogate Diesel Fuel Models for Low Temperature Combustion, SAE 2013-01-1092.”
3. LLNL has submitted the following paper to the 35th Annual Combustion Symposium: “Experimental and kinetic modeling study of the shock tube ignition of TPGME.”
INTRODUCTION

Cars and trucks with GDI engines have been in commercial production since the late 1990s but have only become common in the U.S. fleet in the past four years. Smaller displacement, turbocharged GDI engines will likely replace larger displacement engines as one means for manufacturers to meet higher light-duty vehicle fuel economy regulations. GDI engines tend to produce more PM than their port fuel-injected counterparts as well as with diesel vehicles equipped with diesel particulate filters [1-6]. Controlling PM from GDI engines helps meet DOE goals of enabling high-efficiency engine technologies and reducing pollutants.

The Energy Independence and Security Act (2007) sets specific goals for the use of renewable fuels (36 billion gallons by 2022). Ethanol will make up the bulk of the renewables, but isobutanol is also gaining momentum as a renewable fuel. Isobutanol can be made in similar production facilities to ethanol and its vapor pressure and energy density more closely match gasoline than ethanol. Because of the impact of mobile sources on air quality, any large-scale change in engine efficiency technology and fuel may have far-reaching effects. Thus, there continues to be interest by DOE in seeing the effects of the convergence of two current technologies, GDI and alcohol fuel blends, on emission levels of PM and other pollutants.

APPROACH

The experimental approach was designed to examine the effects of gasoline-alcohol blends on PM characteristics. GDI engines generate the most exhaust PM under fuel-rich conditions, typical of start-up and acceleration. Thus, for this study, the A/F, as well as the real-time soot concentration, was measured during acceleration transients to determine a representative operating point. The engine was a 2.0-L light-duty engine modified with an engine control system to allow changes in injection and ignition timing, and more details are available in Szybist, et al [7]. Gasoline, as well as gasoline blended with ethanol or butanol, was used as fuel. The PM was collected and characterized in several different ways: size, number concentration, morphology,
RESULTS

The renewable fuel blends examined in this study included 30% gasoline in ethanol (E30), and 48% isobutanol in gasoline (iBu48) as compared to gasoline (E0). Beyond low-level blends like the current 10% ethanol (E10), E30 has been identified as a potential high octane rating fuel that will enable fuel efficient technologies such as low-speed and high boost without engine knock concerns [8]. The iBu48 blend is not envisioned as a future fuel, but was selected to match the oxygen content of the E30 blend, since fuel oxygen content is thought to affect PM formation [2]. A critical part of this experiment was to determine a steady-state operating condition that represented acceleration transients, since the majority of GDI PM is often produced during acceleration. A steady-state operating condition was needed to collect PM over a several hours for characterization. To determine the condition, the $A/F$, as represented by lambda ($\lambda$), and soot levels during various load transients on a similar engine with a transient-capable engine controller were measured for several engine speeds. Figure 1 shows results from a transient test at 2,600 rpm, in which the throttle position was changed from 30 to 60%. Soot concentration was measured with an AVL Microsoot sensor. The A/F ratio for steady-state testing was selected to be slightly higher than the minimum $\lambda$ value of 0.89 from these tests due to operational temperature concerns.

For analysis of elemental and organic carbon (OC) content of GDI PM, single dilution exhaust from the micro-tunnel diluter was filtered through pre-fired 47-mm quartz filters. The filters were analyzed using the NIOSH 5040 thermo-optical transmission method [9] and corrected for gaseous adsorption artifacts [3]. The results are shown in Figure 2. The data were highly variable for OC, most likely for two reasons: 1) based on visual observation of filters, the sampling times were short (<5 min) to prevent the accumulation of too much carbon. This short sampling interval may have resulted in a non-equilibrium condition for the gaseous hydrocarbons, and thus variability; 2) in general, GDI PM is ~90% elemental carbon, so small changes in OC can lead to variability. Based on these data, the PM was 43%, 85%, and 95% elemental carbon for E0, E30, and iBu48, respectively. The higher OC content for E0 is consistent with the chemical speciation results, detailed in an upcoming paper [10], which showed higher levels of adsorbed hydrocarbon species.

Size distributions (a minimum of six per fuel) were taken for all three fuels using double-dilution that was consistent with the European Particulate Measurement Protocol (PMP) [11] and the averaged, dilution-corrected values are compared in Figure 3. E0 emits the most particles which is to be expected from the higher aromatic content of the fuel and the highest mass concentration. The iBu48 falls in between E30 and E0 both in terms of particle numbers and peak particle size. The larger peak particle size for E30 is unexpected. In previous research, our laboratory determined that switching from E0 to E20 reduced peak particle size for steady state, stoichiometric operation at moderate load [2]. The rich operation may be the cause of the difference.
CONCLUSIONS

Several PM characterization methods have been applied to PM from a GDI engine operating on gasoline and gasoline-alcohol blends. A rich A/F and medium load were chosen to represent a vehicle acceleration condition, since we observed 10-20 times more PM emissions during load transients. EC was the dominant fraction of the PM, and size distributions showed that GDI PM under these conditions is dominated by particles from 70–90 nm, similar to uncontrolled diesel engine PM. Rich operation, whether at cold start or during load changes, will likely remain the cause of the highest GDI emissions. Future work will identify fuel effects on PM oxidation to further guide selection of emissions control strategies such as GPFs.

REFERENCES


FY 2013 PUBLICATIONS/PRESENTATIONS


IV. PETROLEUM DISPLACEMENT
FUELS/FUEL BLENDING COMPONENTS
Iv.1  Impact of Fuel Metal Impurities on the Performance and Durability of DOC, DPF, and SCR Systems

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DOE Technology Development Manager: Kevin Stork

Subcontractor: SGS-ETC, Aurora, CO

Funding Partners:
• National Biodiesel Board, Jefferson City, MO
• United Soybean Board, Chesterfield, MO

Research Partners:
• Todd Toops, Michael Lance – Oak Ridge National Laboratory
• Rasto Brezny – Manufacturers of Emission Controls Association

Overall 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 (ASTM) specifications for these metals in biodiesel.

Fiscal Year (FY) 2013 Objectives

- Determine if the rate of acceleration, used in accelerated catalyst aging experiments, has an influence on catalyst performance.
- Quantify how the rate of accelerated aging impacts the deposition of fuel-borne metals onto the diesel oxidation catalyst (DOC) and selective catalytic reduction (SCR) catalysts.
- Quantify how the rate of accelerated aging impacts the catalytic activity of the DOC and SCR catalysts.

FY 2013 Accomplishments

- Completed accelerated aging experiments with three separate exhaust aftertreatment systems. Each system was aged at a different rate of acceleration; 7x, 14x, and 28x.
- Materials characterization of aged catalysts showed that increasing the rate of accelerated aging increases the amount of fuel-borne K captured by the DOC and SCR catalysts.
- Emissions characterization of the aged catalysts showed that the inlet portion of the most rapidly aged catalysts had significant changes in catalytic activity.

Future Directions

Evaluate the impact of fuel-borne metal impurities on the full-useful-life durability of a heavy-duty engine platform. Accelerated aging will simulate 435,000 miles of operation for a Cummins ISL engine.

INTRODUCTION

Metallic fuel contaminants such as Na, K, Ca, and Mg may be introduced into diesel fuel through a number of different sources. As one example, biodiesel production relies on sodium hydroxide or potassium hydroxide to catalyze the reaction of vegetable oils with methanol to form methyl esters. In this process, residual amounts of Na or K can be left behind [1]. These metal 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. Alkali metals are well known poisons for catalysts and have been shown to negatively impact the mechanical properties of ceramic substrates [2]. 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 previous research studies the impact of these fuel-borne metal impurities was investigated by conducting accelerated aging experiments that simulate full-useful-life exposure to these metals. The ASTM standard for biodiesel (ASTM D6751) effectively limits a B20 to 1 ppm Na+K and 1 ppm Ca+Mg. In order to accelerate exposure to these metals, a test fuel was doped with higher quantities of metal than normally allowable. The 150,000 mile full-useful-life requirement of a Ford F250 was simulated in 100 hours by doping a 20% biodiesel in diesel fuel (B20) with 14 ppm of K. This represented a 14x rate of acceleration for metal exposure. To investigate how the rate of accelerated aging impacts the catalyst, two additional experiments were run: 50 hours with B20...
containing 28 ppm K and 200 hours with B20 containing 7 ppm K. This generated three systems aged at three different rates of acceleration, however, each system was exposed to the same total amount of fuel-borne K.

**APPROACH**

For accelerated aging, these full exhaust systems were placed onto an accelerated aging platform which was described in earlier studies [3]. The accelerated aging platform consisted of a Caterpillar 2008 C9 ACERT engine. By retrofitting the engine with exhaust emission controls, it served as a platform for exposing various catalysts to exhaust gas from fuels containing metal impurities. The exhaust was retrofitted with a fuel injector upstream of a diesel oxidation catalyst. This injector was used to inject fuel that burned over the DOC creating hot exhaust temperatures typical of a diesel particulate filter (DPF) regeneration event.

Fuel dopant levels were selected to simulate full-useful-life metal exposure coming from B20 at three different rates of accelerated aging: 7x, 14x and 28x. As the K dopant level was increased the duration of engine operation was reduced such that the total exposure to K would be identical in all three tests. These levels and durations of testing were chosen to achieve 150,000 miles worth of metal exposure, assuming normal vehicle operation with a B20 blend containing 1 ppm K.

At the completion of catalyst aging and vehicle emissions testing the catalyst bricks were cored and sectioned for detailed post mortem analysis. The exhaust system consisted of two DOC and two SCR bricks mounted in series. Catalyst cores with approximately one inch diameter were taken down the length of each of these DOC and SCR bricks close to the radial center of each brick. Each catalyst core was then equally divided into four parts, as shown in Figure 1. From the inlet to outlet direction, the four parts were labeled as Inlet, Mid 1, Mid 2, and Outlet, respectively.

The harvested samples were analyzed for K content in the catalyst washcoat by scanning electron microscopy-energy dispersive X-ray. Measurement of the CO, hydrocarbon, and NO oxidation activity of the DOC samples and the NO conversion of the SCR samples was conducted in a bench flow reactor.

**RESULTS**

The accelerated aging experiments generated three exhaust systems, all exposed to the same total quantity of K, but at different rates of exposure.

Figures 2 and 3 show the concentration of K that was measured in the washcoat of the aged DOCs and SCR, respectively. In each case we see that the concentration of K is highest at the inlet to the catalyst and decreases down the length. Also of note is that the rate of accelerated aging has a large impact on the K concentration in the catalyst washcoats. This is most pronounced at the inlet position of the DOC where the K concentration increases from 1.5% to 2.9% to 8.7% as the rate of accelerated aging is increased from a factor of 7x to 14x to 28x.

Figure 4 shows the T90 light-off temperature of C3H6 for the aged DOCs. These data illustrate the impact that rate of accelerated aging has on the catalyst deactivation. The light-off temperature for the inlet of the most rapidly aged catalyst was 77°C higher than the least rapidly aged catalyst. This is consistent with the nearly 6-fold increase in K found in the washcoat of this catalyst. The light-off for the catalyst aged at a 14x rate of acceleration is only 8°C higher than that of the catalyst aged at a 7x rate of acceleration.

Figure 5 illustrates the emissions performance for these SCR catalysts aged at the different rates of acceleration. This plot shows the percent NO conversion, measured in a bench flow reactor, over a range of temperatures. As seen in the plot, the un-aged catalyst and the catalyst aged at a 7x rate of acceleration have similar performance. The catalyst aged at a 14x rate of acceleration has similar performance above about 250°C, but slightly reduced performance below 250°C. The catalyst aged at a 28x rate of acceleration has decreased performance throughout the entire temperature range.

**CONCLUSIONS**

The present work was undertaken to elucidate how the acceleration rate of catalyst aging impacts the amount of fuel-borne metals that are captured by the
**Figure 2.** K Concentration in Aged DOC Samples

**Figure 3.** K Content in Aged SCR Samples
Williams – National Renewable Energy Laboratory

IV. Petroleum Displacement Fuels/Fuel Blending Components

X-ray was employed to investigate the impact of the acceleration rate on the distribution of K in the aged catalysts. It was found that the K concentrations in aged DOC and SCR samples progressively decreased along the catalysts from inlet to outlet. Interestingly, in spite of the same total amount of K exposure, the most rapidly aged catalysts exhibited elevated K concentrations and a measureable impact on catalyst performance. However, the system aged at a 14x rate of acceleration was similar in performance to the least rapidly aged system, suggesting some threshold rate of acceleration for catalyst aging experiments.

REFERENCES


FY 2013 PUBLICATIONS/PRESENTATIONS

Overall Objectives

- Assess the quality of biofuels to determine if the 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) 2013 Objectives

Collaborate with the Coordinating Research Council (CRC) to survey the quality of 85% ethanol/15% gasoline blend (Flex Fuel) and mid-level ethanol blends from blender pumps across the United States

FY 2013 Accomplishments

- Seventy-three samples, including gasoline, mid-level ethanol blends, and Flex Fuel, were collected from 20 stations, predominantly in the midwestern United States
- All the Flex Fuel samples were on specification for ethanol content, with the exception of one, with extremely high ethanol content. Four of these samples failed to meet the required volatility.
- The ethanol content of the mid-level ethanol samples was highly variable, between 3-10% different from the level on the pump label
- Photographs of the sample pumps showed little standardization and consistency, potentially leading to confusion among consumers

Future Directions

- A final report will be published on the results from the blender pump survey
- Additional work will include a survey of the quality of Flex Fuel in the next fiscal year

INTRODUCTION

In 2012, the U.S. gasoline market was about 134 billion gallons [1], and the fuel ethanol market was 13.3 billion gallons [2]. Almost all fuel ethanol is used in gasoline as a 10 volume percent (vol%) blend (E10). A significantly smaller amount is used in Flex Fuel which is a fuel compliant with ASTM International (ASTM) Specification D5798. Mid-level ethanol blends (MLEBs) are an emerging blend of Flex Fuel and gasoline, containing more than 10 vol% ethanol and less than 50 vol% ethanol. MLEBs are typically sold as discrete blends, such as 20 vol% (E20), and 30 vol% (E30). The argument for offering MLEBs is to offer consumers with Flex Fuel vehicles additional fuel choices at the pump. The recent U.S. Environmental Protection Agency waiver allowing up to 15% ethanol in gasoline (E15) in 2001 and newer cars, trucks, and sport utility vehicles should increase the volume of MLEBs in the marketplace.

MLEBs are sold via blender pumps, typically in the midwestern United States. A blender pump draws fuel from two separate storage tanks and mixes the fuels to produce the desired ethanol blend ratio. In traditional gas stations, a blender pump is often used to get midgrade gasoline by mixing the regular and premium grade fuels. In a station that offers MLEBs, the blends are generally made by mixing Flex Fuel with regular gasoline [3].

APPROACH

The sampling was conducted in January and February. The timing of the sampling was deliberate to target Class 4 Flex Fuel, which would be the largest contrast to the Class 1 fuels sampled in a previous blender pump survey [4]. Class 4 has recently been added to D5798 for many areas in the winter months, and should allow more samples to meet the revised volatility specifications.

Using the U.S. Department of Energy’s Alternative Fuels Data Center [5], twenty blender pump stations were identified. Each station was contacted to verify it sold mid-level ethanol blends. A contractor visited each station and collected a 1-liter sample each of the pump gasoline, Flex Fuel, and all MLEBs offered at each station. At each station, the pump was purged with three liters of fuel to prevent carryover between blends.
Photographs were taken at every station to determine the configuration of the blender pumps in the market. The photographs showed the number of hoses, and blends dispensed from each hose at each station.

RESULTS

Samples were collected from 20 stations, though only 19 stations were dispensing MLEBs. One station responded affirmatively prior to sample collection that they were selling MLEBs, however when the contractor arrived for the sample, only gasoline and Flex Fuel were being sold. Another station was inadvertently visited in the transition season between Class 3 and Class 4. The Flex Fuel from this station could meet either volatility requirement.

Figure 1 shows the ethanol content measured in all of the samples collected from the 20 stations. In general, the ethanol content in the gasoline varied little between samples. Interestingly, 11 samples were ethanol-free gasoline and 9 samples were E10. In most areas of the country, E10 is the only gasoline available. However, due to the rural location of blender pumps, state and federal regulations do not require oxygenated gasoline to be offered. The contractor was not given direction to sample the E10 specifically and it appears random whether the contractor collected ethanol-free gasoline or E10 at each station.

One Flex Fuel sample contained almost 95 vol% ethanol content, well above the specification maximum of 83 vol%. The remaining ethanol samples were well within the specification range of 51-85 vol%. The MLEB samples showed the highest variability in ethanol content. The largest deviation was an E40 with 30 vol% ethanol content, two E30s with 22 vol% ethanol content, and an E20 with 12 vol% ethanol content. In general, stations that sold multiple MLEB products either trended high or low in ethanol content together. The most notable exception was an E20 with 22 vol% ethanol and an E30 with 26 vol% ethanol content. These samples were supplied by separate blender pumps at the same fueling island.

Figure 2 shows the vapor pressure measured for all of the samples collected from the 20 stations. The vapor pressure of the Flex Fuel samples improved from previous surveys, with 80% of the samples on specification, compared to 30% and 12% in previous Flex Fuel surveys [6]. As expected, the sample with very high ethanol content had extremely low vapor pressure.

In addition to understanding blender pump fuel properties, an additional objective of this survey was...
Six of the stations which offered a single MLEB alongside Flex Fuel, offered the two products from separate hoses.

Three of the stations listed an octane number for the MLEBs that they offered.

- Six of the stations which offered a single MLEB alongside Flex Fuel, offered the two products from separate hoses.
- Three of the stations listed an octane number for the MLEBs that they offered.

Vapor Pressure for all Fuel Samples

![Figure 3. Example of Station Offering Higher Ethanol Blends from the same Hose as E10](image)
CONCLUSIONS

In this work, 73 samples were collected from 20 separate blender pump stations primarily located in the midwestern United States. Volatility Class 4 was targeted, with samples collected in February of 2013. Samples were analyzed by Southwest Research Institute® for ethanol content and vapor pressure. In addition, detailed photographs of the stations were collected at the time of sampling. Key findings in this survey are listed in the following:

- For the E10 samples there was very little variation in ethanol content.
- For the MLEB samples variability in ethanol content was higher, typically failing to meet the advertised ethanol level by 3 to 4 vol%, and in one case was off by 10 vol%.
- One of the 20 Flex Fuel samples was above the allowable limits for ethanol content.
- Four of the 20 Flex Fuel samples had volatility below the minimum requirement for Class 4.
- In general, there were many differences in the style and labeling of the dispensers surveyed in this study. Five of the 20 dispensers offered higher MLEBs (>E15) from the same hose as E10 or E15. These five dispensers create the potential for introduction of residual amounts of higher ethanol fuel than is acceptable in non-Flex Fuel vehicles.

The locations in the previous studies were rural, in areas that were not required to offer ethanol blends. Future work may consider another summertime survey, particularly in areas where specific requirements are in place for gasoline, to determine if these gasolines have any impact on Flex Fuel properties compared to gasolines found in rural areas. Future work may also consider a wider distribution of sampling locations, including states where only one or two blender pumps may be located.

REFERENCES

**IV.3 Understanding Biodiesel In-Use Performance Issues**

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**Overall Objectives**

- Develop a detailed understanding of issues that are preventing biodiesel blends from attaining drop-in fuel status.

**Fiscal Year (FY) 2013 Objectives**

- Quantify factors causing precipitate formation from biodiesel blends above cloud point (CP).
- Measure the long-term (3-year) storage stability of 5% biodiesel (B5) and 20% biodiesel (B20) blends and determine best methods for monitoring stability.
- Determine the impact of B20 on transit bus oxides of nitrogen (NOx) emissions for engines covering the full range of emission standards in the market today.

**FY 2013 Accomplishments**

- Revealed that some methods for measuring diesel CP may not accurately capture the CP of biodiesel blends, and that biodiesel blends containing saturated monoglycerides (SMG) are prone to polymorphic phase transformation. These observations may explain the “precipitate above CP” phenomenon.
- Determined that monitoring of biodiesel blend Rancimat induction time is the most effective way to monitor blend stability during storage.
- Showed that B5 and B20 blends can be stored for up to three years under clean storage conditions if the 100% biodiesel (B100) is of adequately high stability (B100 Rancimat induction time of 6 hr).
- Demonstrated that engine emissions certification level has a dominant effect on transit bus NOx, with the kinetic intensity of the duty cycle being the secondary driving factor.
- Showed that selective catalytic reduction (SCR) systems on the two 2010+ model year buses tested are effective at reducing NOx to near the detection limit on all duty cycles and fuels, including B100.

**Future Directions**

- Factors affecting SMG precipitation, crystal growth, crystal shape, and ability to clog a fuel filter have not been fully explained and a more detailed explanation is likely to facilitate low-cost solutions to filter clogging problems.
- Biodiesel blends as currently specified may not have adequate stability for modern, high-pressure common rail fuel injection systems, especially for situations where consumers do not rapidly consume the fuel.
- Additional data are needed to understand how fuels in general affect emissions of 2010+ model year heavy-duty vehicles during cold starts and low-speed, low-load operation when exhaust temperature may not be adequate for NOx reduction.

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**INTRODUCTION**

Biodiesel consists of fatty acid methyl esters [1] and is typically blended with diesel fuel at up to 20 vol%. Over 1 billion gallons of biodiesel was consumed in the United States in 2011 and 2012 [2], with projections for as much as 1.7 billion gallons in 2013 [3]. Biodiesel exhibits life cycle greenhouse gas emission reductions relative to petroleum diesel of over 75% [4] and is considered an advanced biofuel under the Renewable Fuel Standard [5]. Because biodiesel is a new and developing fuel, there are a number of handling and use issues that have not been fully resolved. These include occasional engine or dispenser fuel filter clogging in cold weather, concerns regarding long-term storage stability, and the potential for NOx emissions to increase, especially for transit buses. Studies conducted in 2013 addressed aspects of all three of these issues.

**APPROACH**

The effect of SMG on CP and final melting temperature (FMT) was examined by spiking B5, B10, and B20 blends with reagent-grade SMG. Four commercial diesel fuels and four vacuum-distilled or very low impurity content B100 from a range of
feedstocks were employed. CP was measured primarily by ASTM D5773, a very sensitive light scattering method, and by ASTM D5771 and D7689 which are both light transmission methods. CP is measured by cooling a sample under controlled conditions until the formation of solid particles is detected. FMT (measured by freezing the sample and reheating until solids disappear) was measured using the D5773 apparatus.

Long-term storage stability of biodiesel blends was studied in experiments simulating up to three years of storage. Aging was simulated by holding samples at 43°C to accelerate oxidation using the ASTM D4625 procedure. B100 containing both low and high levels of polyunsaturated fatty acid chains were utilized, blended into both a hydrotreated and a hydrocracked diesel fuel at 5 vol% and 20 vol%. Peroxide value was determined by iodometric titration with American Oil Chemists’ Society Official Method Cd 8h-90, modified for potentiometric endpoint detection, using a Metrohm 809 Titrando automatic titrator with platinum electrode. Acid value was measured following ASTM D664, Method B, for biodiesel and blends using the same automatic titrator with pH sensing electrode. Rancimat induction time was measured following EN 15751 using a Metrohm 873 Biodiesel Rancimat.

Six buses spanning engine build years 1998 to 2011 were tested on a heavy-duty chassis dynamometer with petroleum diesel and B20 blends. Several duty cycles with a range of kinetic intensity were employed. The buses selected represented the majority of the current national transit fleet as well as hybrid and SCR systems that are increasing penetration in the fleet. Emissions were measured using a full-flow dilution tunnel and analysis procedures derived from Code of Federal Regulations Section 40, Part 86, Subpart N.

RESULTS

Low-Temperature Operability

For CP measured by ASTM D5773, we found that some biodiesel blends exhibit what appears to be two CP results: an early signal increase at higher temperature followed by a more obvious sharp increase later in the run. We refer to these features as early CP and late CP, respectively. Figure 1 shows example D5773 light scattering plots depicting results for a sample with two CP results, as well as a sample that shows a single CP. The sample exhibiting two CP results was made from a B100 spiked to contain a total of 0.01 wt% SMG in the B5 blend. The second sample was blended using a vacuum-distilled B100 (residual SMG in this sample was negligible), also as a B5 blend. The addition of just a small amount of SMG causes the appearance of the early CP. Depending on which point is chosen for the CP, there can be a large impact on the results. In this example, the difference between the early and late CP is almost 8°C.

We have not observed this effect for petroleum diesel. B5 and B20 blends prepared using B100 collected as part of a quality survey [6] were analyzed using three CP methods (D5771, D5773, and D7689). Examination of the D5773 results revealed that most samples exhibited the early and late CPs. Figure 2 compares the results between the three methods when using D5773 with early CP and late CP. The D5773 late CP results are much more in line with results from the other methods, and by extension, with the referee method, D2500. Blends prepared from distilled B100 spiked with SMG also show D5773 CPs closer to those measured with D5771 and D7689 when the late CP is used. Once the amount of SMG is above about 0.03 wt% in the blend, the early CP becomes dominant enough that this is where CP is determined by D5773 when using the automated method. Because this early CP may be missed by other methods, samples with SMG content in this range may be particularly prone to unexpected filter clogging above the measured CP.

In previous work [7,8] we have shown that in B100, SMG precipitates as a metastable gel that can transform into the stable β polymorph over time or upon heating via solvent-mediated polymorphic phase transformation. We proposed that this transformation could account for many of the unanticipated occurrences of fuel filter clogging by precipitate formation above the CP in biodiesel blends. The polymorphic transformation can manifest itself as a large signal increase during warming of the samples at 1.5°C/min in light scattering plots, and the FMT is significantly higher than the CP. The polymorphic phase conversion can also occur in biodiesel blends. Figure 3 shows FMT and CP as a function of spiked SMG content.

FIGURE 1. Light scattering plots for B5 blends containing 0.01% SMG and prepared from a vacuum-distilled B100.
for blends of a vacuum-distilled B100 in a very low CP No. 1 diesel fuel. Above about 0.01 wt% SMG the FMT-CP difference increases to 20°C or higher, indicating the transformation of α-SMG into the most stable and lower solubility β form. At lower concentrations, apparently all of the SMG dissolves before undergoing transformation at this heating rate.

**Long-Term Storage Stability**

Induction times of the B5 blends over three years of simulated storage are shown in Figure 4. Each group of four blends is divided by Biodiesel C or D with an initial B100 induction time of 3 or 6 hours. All of the B5 blends have an initial induction time greater than 12 hours. At 39 weeks of aging (simulated three years), none of the B5 blends is below the 6-hour minimum induction time specified by ASTM D7467 for B6 to B20 blends. B20 blend induction times are shown in Figure 5. The initial induction times of the B20 blends are lower than those of the B5 blends; however, these are again at 12 hours or greater. All but two of the B20 blends remain above the 6-hour minimum induction time by 39 weeks of aging. The two blends that fail induction time were prepared with high polyunsaturated B100 having an initial B100 induction time of 3 hours.

The acid values of all of the blends did not increase for the entire 39 weeks with the exception of the least stable B20 blend. This blend reached an acid value of 0.3 mg KOH/g by the end of the test interval, which is the maximum value set by ASTM D7467. Similarly, the peroxide value of this sample was the only one to increase significantly during the test. At 29 weeks of aging, a notable increase in peroxide value was detected and this continued rapidly, reaching a value of 112 mmol O₂/kg by 39 weeks. All other B20 blend peroxide values remained below 5 mmol O₂/kg, and all B5 blend peroxide values remained below 2 mmol O₂/kg. The results show that monitoring of biodiesel blends in storage using Rancimat induction time allows aging fuels to be identified prior to formation of undesirable peroxides and acids, which will occur below an induction time of about 4 hrs.

**Transit Bus NOx Emissions**

Several conclusions can be drawn from this work. Figure 6 shows the Manhattan cycle NOx emissions from each bus. The emissions certification level of a transit bus engine is the largest determining factor for
Figure 4. Induction times of B5 blends. A. Hydrocracked diesel blends, B. Hydrotreated diesel blends. Error bars are calculated from the published reproducibility of EN 15751.

Figure 5. Induction times of B20 blends. A. Hydrocracked diesel blends, B. Hydrotreated diesel blends. Error bars are calculated from the published reproducibility of EN 15751.
NOx emissions. Each certification level reduced NOx emissions roughly in half from the previous certification level, and 2010 SCR NOx aftertreatment effectively reduced NOx to near detection levels. The exception is the 2008 hybrid bus, which had emissions similar to a pre-2007 bus, a possible effect of hybridization that has been observed before [9]. The kinetic intensity of a drive cycle determines the NOx emissions of any individual bus. All buses without NOx aftertreatment demonstrated higher NOx emissions on more intense stop and go, slow average speed, high stops per mile, and high kinetic intensity test cycles (not shown). For buses without NOx aftertreatment the fuel used on each bus caused a minor or not statistically significant change in NOx emissions. Low aromatic diesel generally lowered NOx emissions while a B20 blend of either certification diesel or low-aromatic diesel did not consistently show a statistically significant increase.

CONCLUSIONS

- Transit bus emission testing demonstrated that engine emissions certification level has a dominant effect on transit bus NOx, with the kinetic intensity of the duty cycle being the secondary driving factor. Choice of fuel had minor, and in most cases not statistically significant effects on NOx. This research also showed that SCR systems on the two 2010+ model year buses tested are effective at reducing NOx to near the detection limit on all duty cycles and fuels, including B100.

REFERENCES


IV. Petroleum Displacement Fuels/Fuel Blending Components


FY 2013 PUBLICATIONS/PRESENTATIONS


**Overall 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) 2013 Objectives**

- Improve analytical 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.

**FY 2013 Accomplishments**

Developed a thermal/pyrolysis method to analyze soot from gasoline direct injection combustion utilizing state-of-the-art thermal/pyrolysis gas chromatography-mass spectrometry.

**Future Directions**

- Perform analyses with capillary electrophoresis mass spectrometry of organic acid anions in exhaust condensates.
- Evaluate size-separated soot PM derived from engine combustion of non-petroleum-based fuel for determining unique soot chemistries for the different size ranges of soot particles.

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**INTRODUCTION**

Light-duty vehicles with direct injection gasoline (GDI) engines have been in commercial production since the late 1990s but have only become common in the U.S. fleet in the past four years [1-2]. Most manufacturers offer several passenger car and light-duty truck/sport utility vehicle models with GDI engines, and it is widely accepted that smaller displacement, turbocharged GDI engines will replace larger displacement engines as one means for manufacturers to meet the more stringent future light-duty vehicle fuel economy regulations. GDI engines can be more fuel efficient, in particular under fuel-lean operating conditions, and turbocharged engines can also offer a performance benefit due to the higher volumetric efficiency at high load [3]. However, GDI engines tend to produce more PM than the very low level of modern port fuel-injected engines [4-9], with PM mass levels exceeding those of diesels equipped with diesel particulate filters, as well as conventional port fuel-injected vehicles [4,10,11].

Because modern engines, including GDI engines, have low PM emissions rates, novel sampling and analytical methodology was developed specifically to achieve direct analysis of the organic hydrocarbon compounds from the PM filter samples. This approach used a combination of gentle vacuum to harvest PM from the filter surface without the need for solvent extraction and its attendant risks of biasing, volatiles loss, and contamination.

**APPROACH**

During recent research on the organic extraction of non-petroleum-based fuel PM emissions, a problem arose surrounding the interfaces between the non-polar compounds and the separation of aromatic anhydrides and aromatic carboxylic acids when using capillary electrophoresis, an aqueous platform method. The solution to this problem was the implementation of a multi-shot pyrolyzer injector coupled via a thermal desorption/pyrolysis sampling unit into a gas chromatograph-mass spectrometer (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 pyrolytically removed and analyzed, thereby reducing the complexity of the analysis results, both chromatographically and during mass spectral structure determination. Also, this method...
allows for a solvent-free extraction of organic compounds from soot, thus shortening the total analysis time and reducing cost.

The three fuels investigated in this study were a gasoline (E0), a 30% ethanol blend gasoline (E30), and a 48% isobutanol blend (iBu48). E30 was chosen to maximize octane enhancement while minimizing ethanol-blend level and iBu48 was chosen to match the same fuel oxygen level as E30. While it is recognized that iBu48 would likely never be a marketplace fuel, it was determined that the GDI soot oxidation study would benefit from having soot generated with gasoline-alcohol blends having the same fuel oxygen level.

After collection, a novel soot transfer method was developed which incorporates the transfer of the soot from the filter directly to the sample vessel for thermal desorption/pyrolysis sampling unit into a GC-MS by use of mild but focused vacuum suction. 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 and separated using a Restex Rxi-5ms column (30 m, 350 μm inside diameter, 0.25 μm). The gas chromatograph’s temperature program began at an initial temperature of 40°C for 3 min, followed by a ramp from 40°C to 320°C at 6°C per min and then was held at 320°C for 5 min. The analytes were analyzed by a mass spectrometer, which was scanned from 35 daltons to 550 daltons at a 1-sec scan rate.

RESULTS

The thermal analysis of the soot sample was conducted by purging the sample with helium for 30 sec then thermally desorbing at 300°C using a Frontier Laboratories LTD multi-shot pyrolyzer (EGA/PY-3030D). The desorbed compounds were then transferred into the GC-MS. The desorbed sample was analyzed using the same GC-MS conditions as described previously. Figure 1 shows the results of the thermal desorption ramp of the 1-mg soot sample. There was a 10-fold improvement 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.

The PM from each of the three fuels was subjected to a two-step thermal desorption/pyrolysis process as detailed previously. Each peak on the GC-MS chromatogram shown in Figure 2 represents a distinct organic species, and the height and area of the response is proportional to the amount of that species of organic material in the sample. The E0 PM has richer chemistry and higher amounts of individual species. The exception is the peak at 26.6 min, pyrene, the amount of which is higher for the iBu48.

Figure 3 overlays chromatographs from the pyrolysis of the three soot sources, which reveals that the compounds formed are light mono-aromatics. Note that the prior temperature history of the soot sample was much too high for these compounds to be present as adsorbed molecules, so the source of these molecules must be the breakdown of the soot matrix itself. Benzene, toluene, and styrene can be expected to form the major structural components of soot. Of interest is the presence of methyl propenoate for the E30 sample that is not present in the E0 or iBu48. Methyl propenoate is an unsaturated ester and thus may represent a portion of the soot structure that incorporated fuel oxygen into the backbone. Such insights can offer additional indications of soot formation mechanisms in GDI combustion.

CONCLUSIONS

The advanced chemical characterization effort has focused on two areas: ethanol systems and organic carbon analysis. The soot thermal/pyrolysis method and characterization efforts have led to the identification of compounds that make up a large fraction of the organic carbon. Future efforts will focus on refining the thermal/pyrolysis method for improved chemical speciation of both polar and non-polar organic carbon in one analysis. Accurate identification of PM-bound species can improve
understanding of soot formation in advanced, high-efficiency engines.

REFERENCES


IV.5 Unconventional Hydrocarbon Fuels

Overall Objectives

- Facilitate the successful introduction of future fuel feedstocks which will help reduce the 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) 2013 Objectives

- Complete an evaluation of nuclear magnetic resonance (NMR) diffusion-ordered spectroscopy (DOSY) and heteronuclear correlation (HETCOR) experiments on a variety of fuel samples, and provide recommendations on the use of this technique for identifying important fuel substructures.
- Obtain and analyze a deep-hydrotreated pyrolysis oil sample to identify unique traits and analytical challenges.
- Attend an Analytical Work Group meeting between Natural Resources Canada (CanmetENERGY) and PNNL for the purpose of fostering a collaborative relationship and information exchange.

FY 2013 Accomplishments

- Completed contributions to two Coordinating Research Council (CRC) Advanced Vehicle/Fuel/Lubricants (AVFL) Reports [1,2] detailing $^{13}$C and $^1$H NMR sub-structure analyses and assignments for three Fuels for Advanced Combustion Engine (FACE) diesel blends and 10 advanced alternative and renewable diesel fuels. $^{11}$ PNNL consolidated the NMR sections from two PNNL reports [3,4] and one CanmetENERGY report into the two CRC reports [5].

$^{11}$FACE diesel blends are developed under guidance from the CRC. Reports may be found at the CRC website, http://www.crcao.com/publications/advancedVehiclesFuelsLubricants/index.html.

- Continued development of new NMR approaches for identifying structure-property relationships of diesel fuels, including distortionless enhancement of polarization transfer (DEPT), 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.
- Developed strategies for the separation of pyrolysis oil into aqueous and organic soluble components to allow NMR quantification of each component.
- Continued collaborative efforts with CRC FACE Working Group, and the alternative and surrogate fuels subcommittees, through contributed NMR analyses of fuels and technical discussions.
- PNNL and CanmetENERGY met in Edmonton, Alberta, Canada to discuss collaborative opportunities and shared analytical approaches.

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 CanmetENERGY on analytical correlation of fuel properties and material compatibility investigations.
- Continue collaborative work with members of the CRC’s Working Group and the alternative and surrogate fuels subcommittees.

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 unanticipated problems with engine and fuel system components, and can impact our understanding of advanced combustion and aftertreatment 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, seal swell, and other performance parameters. 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**

Diesel samples from a variety of sources were obtained through our collaborations with other national laboratories and with AVFL Committee members. Unconventional 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 rebleds of three FACE diesel fuels. Biofuels analyzed included products of raw and hydrotreated pyrolysis oils and oils resulting from hydrothermal liquefaction.

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 distribution of the components and is expected to correlate with lubricity, soot formation, kinematic viscosity, and cloud point [6]. 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 engine development and 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 those parameters. Collectively, this is a multi-year approach to realize the integrated benefits of the analytical tools being applied to assess fit-for-service and structure-property correlations.

**RESULTS**

While PNNL did not receive FY 2013 funds for this work, limited research was continued using funds carried over from FY 2012.

PNNL has successfully validated the use of two-dimensional HETCOR NMR spectroscopy techniques, such as HSQC and HMBC, as a means of identifying not only fuel composition (i.e., aromatic, naphthenic, and paraffinic carbons), but also as a means of making substantially more detailed substructural assignments than would be possible using solely one-dimensional (1-D) NMR techniques. Through PNNL’s collaborations with the CRC, PNNL has published two reports, the first detailing the analyses of three rebleded FACE diesel fuels [4], and the second detailing the analyses of 14 fuels from commercial, unconventional, and renewable sources [3]. PNNL consolidated the NMR analyses with contributions from CanmetENERGY [5], which were assembled into two CRC reports containing comprehensive analyses of these fuel sets [1,2]. Portions of these reports are expected to be published in the peer-reviewed literature. Additionally, we anticipate using this data to contribute to developing structure-property/performance correlations, such as to lubricity and seal swell.

Building upon our FY 2012 efforts utilizing two-dimensional NMR techniques to elucidate more detailed structural information from fuel samples, PNNL has
continued to apply HETCOR techniques to the set of fuel samples mentioned above. The approach PNNL and others have applied to one-dimensional NMR spectra is to define discrete regions belonging to specific chemical environments. Because of the large number of different molecules that make up a single fuel sample, this approach clearly has limitations. Chemical environments often overlap and the contributions cannot be accounted for using defined regions. Two-dimensional NMR techniques, or more complex pulse sequences, can allow overlapping regions to be at least partially disentangled. Figure 1 shows the HSQC spectrum of the aromatic region for the rebinned FACE diesel, FD2B. HSQC correlates the proton and carbon NMR spectra, and shows only hydrogen-bearing carbon types. Along the x- and y-axes are labeled the respective one-dimensional NMR regions typically assigned to proton and carbon types. Carbons without protons attached (such as internal, and methyl- or naphthene-substituted carbons) are not shown in HSQC spectra, and these regions are expected to be blank. NMR resonances observed in these regions of the HSQC spectra therefore must contain an attached hydrogen, and clearly demonstrate a limitation of relying only on discrete spectral regions. Another example of spectral overlap can be shown by examining the distribution of the HSQC spectrum along the x-axis ($^1H$ NMR resonances). In the $^1H$ NMR, aromatic systems having one, two, or three fused rings are known to overlap. By correlating the spectrum with the $^{13}C(\text{1H})$ NMR in an HSQC spectrum, systems containing different numbers of fused aromatic rings may be distinguished. This is shown in Figure 1, where the small set of resonances in the upper left represents protons attached to carbons that are part of systems containing three fused rings (like anthracene). The elongated set of resonances in the center represents protons attached to carbons part of systems containing two fused rings (like naphthalene), and the circular region represents molecules containing individual aromatic rings. Projection of these resonances

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**FIGURE 1.** Aromatic region of an HSQC spectrum for FACE diesel fuel, FD4B. This two-dimensional NMR spectrum is a contour plot showing the correlation of protons attached directly to carbons of the surrogate fuel components. The horizontal axis represents the $1^H$ NMR and the vertical axis represents the $^{13}C(\text{1H})$ NMR. HSQC and other two-dimensional NMR techniques are particularly useful for resolving areas of overlapping NMR resonances.

In this case, there are three distinct groupings of resonances. The upper left represents species containing three fused aromatic rings, the elongated center grouping represents species containing two fused aromatic rings, and the roughly circular grouping in the center right represents monoaromatic species.
to the x-axis would resemble a typical one-dimensional \(^1\)H NMR, and shows the overlap that would be observed for these aromatic species. While two-dimensional NMR techniques such as HSQC and HMBC are more complex and more time consuming to obtain, for cases where overlap of important species is expected, these techniques can improve our understanding of the species present.

Similarly DEPT provides greater fidelity for group assignments in areas where carbon types overlap. This is particularly true in the aliphatic region of a fuel spectrum where methyls, methylenes, methines, and quaternary carbons can significantly overlap. Figure 2 shows the DEPT spectrum for a commercial diesel fuel. As described in the caption for Figure 2, the fully edited DEPT contains one subspectrum for each carbon type. One shortcoming of DEPT is that particularly intense resonances in one subspectrum can affect the other subspectra, obscuring a small area, making it difficult to assess the potential for coincidental overlap of different carbon types. As an example, in Figure 2, this can be seen by residual resonances in Figure 2 (b, c, and e) from the intense δ and ε methylene carbon resonances in Figure 2(d) at about 29.75 ppm. Nevertheless, DEPT can provide valuable information in a simple format and has been undertaken as part of the process to assess the quantification of 2-methyl-alkanes in fuels. This assessment will be a part of the PNNL contribution to the simplified, or “surrogate,” fuel project under development as part of a CRC activity led by Dr. Charles Mueller of Sandia National Laboratories and William Cannella of Chevron. Contributions from 2-methyl-alkanes have implications for both octane and cetane number [7]. By using DEPT resonances assigned to 2-methyl-alkanes can be determined, and quantitatively assessed using one-dimensional NMR techniques.

Pyrolysis oils and bio-based oils have proven to be challenging to analyze quantitatively using the NMR techniques applied at PNNL. Derived from biological sources, the oils have an exceptionally high ionic strength, as well as a high water content making it difficult to separate from the organic material. The former makes NMR analysis difficult because of signal reflectivity issues, making the sample lossy, and the latter creates sample solubility issues for some NMR solvents.

To overcome these problems researchers at PNNL opted to separate the oil into aqueous and organic phases utilizing several separation steps. These steps included an acid wash to protonate acidic sites deprotonated during pyrolysis, a classic diethyl ether/water separation, followed by filtration through Celite\(^6\) to remove residual pyrolysis char. Careful drying of the organic phase, and use of an internal standard will allow the carbon types from both phases to be compared. Figure 3 shows \(^1\)C\(^{1}\)H NMR spectra for the extracted aqueous and

![FIGURE 2](image)

**FIGURE 2.** Fully edited Distortionless Enhancement of Polarization Transfer (DEPT) spectrum of a commercial diesel fuel. (a) Composite \(^1\)C\(^{1}\)H NMR spectrum. Edited \(^1\)C\(^{1}\)H NMR spectrum of (b) quaternary carbons (no hydrogens attached), (c) tertiary carbons (one hydrogen attached), (d) secondary carbons (two hydrogens attached), and (e) primary carbons (three hydrogens attached).
organic phases of a pyrolysis oil. The organic phase, shown in Figure 3(a), has a high aromatic content that could be further upgraded to increase aliphatic content, and the aqueous phase, Figure 3(b), is poor in aromatic and aliphatic content, but rich in poly-ols, which are poorly resolved in spectra of samples containing a mixture of both phases. Quantifying the distribution between aqueous and organic phases will assist with understanding the chemical processes used to produce bio-oil from natural feedstocks, as well as understand when specific qualities are sufficiently present to introduce the upgraded oils into traditional refinery feedstocks. Methods for quantifying bio-based oil content are still under development, particularly since aqueous/organic separations are strongly dependent upon the source and treatment of individual bio-based oils.

**CONCLUSIONS**

- PNNL continued expanding a “toolkit” of NMR approaches that can be used for quantitatively determining the important molecular structures contained in fuel samples. Depending on the level of detail needed for the application, different tools can be utilized.
- Two-dimensional heteronuclear correlations, like HSQC and HMBC, and less complex correlations, like DEPT, can provide quantitative structural and substructural information that is not able to be resolved in using one-dimensional NMR techniques.
- Analysis of bio-based oils, while known to be complex, can be accomplished using a combination of wet chemistry separation steps, and quantitative NMR analysis.

**REFERENCES**

5. H.D. Dettman, NMR Carbon Type Analyses of Diesels Derived from Diverse Feedstocks, in, Natural Resources Canada, CanmetENERGY–Devon, Devon, Alberta, Canada, 2012.


**FY 2013 PUBLICATIONS/PRESENTATIONS**


Overall Objectives

- To develop an agile decision-analysis tool to enable rapid exploration and analysis of a wide range of transportation fuel pathways and vehicle technologies.
- To evaluate fuel and vehicle technologies on multiple criteria, including total cost, greenhouse gas emissions, and energy security.
- To create an online resource, Megajoule.org, for sharing estimates of key quantities used for energy analysis.

Fiscal Year (FY) 2013 Objectives

- To expand analysis of biofuels including updating biomass supply curves and extending advanced biofuels production technologies and infrastructure.
- To extend the Analytica Transportation Energy Assessment Model (ATEAM) user interface and provide online access to model documentation directly from within ATEAM.
- To populate Megajoule.org, an online energy database to find, review, and share estimates of key quantities used in energy analysis, with key numerical estimates used in ATEAM.
- To develop ten policy briefs applying ATEAM to analyze key issues affecting adoption of alternative technologies and the future of the U.S. vehicle fleet.

FY 2013 Accomplishments

- Updated estimates for biomass supply curves using results from the “billion-ton update” (DOE 2011) to improve biomass supply curves. Compared cellulosic ethanol and other advanced biofuels pathways, including “drop-in fuels” that need less distribution infrastructure. Examined the portfolio effects of uncertainty results from research and development on biofuels.
- Calibrated ATEAM with reference to the Annual Energy Outlook (AEO) 2013 model projections, to meet vehicle survival curves, past sales shared by vehicle technology, vehicle distance travelled, and vehicle efficiency for on-road performance and emission factors. The calibration allows direct comparison of ATEAM projections against the widely used AEO projections for alternative scenarios and sensitivity analysis.
- Developed a web-based ATEAM user guide using direct links from the ATEAM model to corresponding webpages, and cross links within the guide for ease of access.
- Applied ATEAM to analyze ten key policy issues relating to the U.S. vehicle fleet and adoption of new fuels and technologies, reported in ten ATEAM policy briefs summarized in this report.
- Extended Megajoule.org, including improvements to the user interface and internal structure, and a set of new estimates and sources, probabilistic projections. In 2013, it drew 277 new visitors from 43 countries, up from 129 new visitors from 24 countries in 2012. Twelve estimates, 17 sources, and two technology records about corn ethanol, cellulosic ethanol, and plug-in hybrid vehicles (PHEVs) were added.

Future Directions

- Update and expand the set of ATEAM policy briefs to address additional policy issues of concern to the government and private sectors, including current and new policies and programs to promote electric vehicles, biofuels, and improved efficiency.
- Develop a simplified version of ATEAM to allow easier use and collaborative analysis for policy research and educational use.

IV.6 Decision Analysis Tool to Compare Energy Pathways for Transportation
INTRODUCTION

Advanced biofuels, batteries, and PHEVs are just a few of the new automotive technologies being developed, with the goal of reducing transportation costs, greenhouse gas emissions, and oil consumption. Given the 12 to 15 years that 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 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 ATEAM public domain, open source, and extensible to provide a basis for collaboration and dialog among groups from government, universities, industry, and non-governmental organizations to explore and compare their perspectives on these important and sometimes controversial issues.

APPROACH

The focus of ATEAM Version 0.9 developed in the previous phase was on the U.S. fleet of light-duty and heavy-duty vehicles. In this phase, we expanded and applied ATEAM to analyze a set of ten key policy issues. 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, including costs and learning rates for batteries and a wider range of biofuels. We focused primarily on technologies such as standard gasoline internal combustion engines (ICEs), flexible-fuel ICEs, hybrid-electric vehicles (HEVs), battery electric vehicles with 100 mile range (BEV-100), plug-in hybrid electric vehicles with 10 mile and 40 mile ranges (PHEV-10 and PHEV-40) for light-duty vehicles, liquified natural gas (LNG) vehicles, compressed natural gas (CNG) vehicles, liquefied petroleum gas (LPG) vehicles, diesel, and gasoline for heavy duty vehicles. Figure 1 shows the top influence diagram overview of ATEAM.

To project the effect of new technologies and costs on the market penetration of these vehicle technologies, we looked at incremental vehicle costs, infrastructure costs, fuel costs, market penetration potential, fuel availability and scalability, and relevant tax incentives. We refined the representation of early adopter penalty cost to represent consumer preferences or aversion to switching to new and unfamiliar technologies. We calibrated the implied penalty for each technology relative to gasoline ICE technology that results in the actual market share by technology in the base year (2012) as the initial early adopter penalty. Sales share of each vehicle technology is estimated using a logit model based on the vehicle levelized lifecycle cost per mile of each technology. 

![ATEAM's Top level Influence Diagram and User Interface](image-url)
Learning effects that reduce the cost of new technologies, such as biofuels and batteries, are assumed to be a function of cumulative production. Such learning has the potential to transform the economics of alternative fuel vehicles. At the same time, the positive mutual feedback loop between adoption rates and costs of these new technologies creates high sensitivity to initial assumptions and make it challenging to understand the dynamic behavior of these systems. We used ATEAM to explore these behaviors and identify situations in which policies can find leverage points in which small initial investments can give rise to large long-run benefits.

RESULTS

The primary results of our analysis with ATEAM are presented in a series of 10 ATEAM policy briefs:

Strategies for offsetting the ethanol blend wall: This brief compares two policies to absorb higher levels of ethanol from the 10% volumetric ethanol blend including a switch to a 15% blend (E15) for all vehicles from 2001 on, and a rapid expansion of 85% ethanol in gasoline (E85) fueling infrastructure. It finds in all fuel consumption scenarios that the E85 expansion allows full consumption of projected levels of corn ethanol production through 2040. In the AEO reference case, the E15 scenario allows full corn ethanol consumption through 2040. However, in the ATEAM baseline case the E15 expansion scenario runs into the blend wall within 10 years, due to higher fuel economy and the adoption of vehicles that do not use gasoline.

How could Renewable Fuel Standard (RFS) accelerate production of advanced biofuels? We explored the impact of RFS policy and increased advanced biofuel credit (ABC) prices—i.e., price of waivers to RFS mandated use of advanced biofuels set by the Environmental Protection Agency (EPA)—up to $1.50 or $2.50/gallon of gasoline equivalent (GGE) on the advanced biofuel production as shown in Figure 2. RFS provides the economic incentive to accelerate production. The initially small percentage of advanced biofuels blended into gasoline causes a minimal increase in gasoline price in early years (under 1%). But, the accelerated production would bring costs down the learning curve over time, so that by 2022, advanced biofuels would likely be competitive with gasoline without mandate or subsidy. After that, costs drop substantially below gasoline prices, resulting in substantial savings in fuel cost and greenhouse gas (GHG) emissions (Figure 3). A tornado chart (Figure 4) shows how these results might be affected by the uncertain assumptions.

Indirect effects of an RFS waiver on GHG emissions from livestock: In the summer of 2012, the increased mandate for corn ethanol from the (RFS) coupled with a severe drought in corn growing regions, drove the price of corn and corn-fed beef to record highs, resulting in demands that EPA waive the RFS for corn ethanol. However, beef production itself has a high carbon footprint. Our analysis shows that an RFS waiver that lowers the price of corn would also increase beef consumption, and so increase GHG emissions to a degree comparable with the direct effects on GHG emissions of decreased biofuel consumption.

What if battery costs drop by a factor of five in five years? Plug-in vehicles (PIVs) promise to reduce GHG emission and gasoline consumption, but the high cost of batteries is a major obstacle to increasing market share for PIVs. We explore the potential effect of R&D if it achieves the target reduction in battery costs by a factor

![Figure 2](image-url)  
*FIGURE 2. Projected prices of gasoline, corn ethanol, and drop-in biogasoline from cellulosic biomass. The orange line depicts an ABC price plus cost of gasoline—i.e., the cost against which blenders compare the price of advanced biofuels. ABC price starts at $1.50/GGE in 2014, declining linearly to zero in 2022. The effect is to make biogasoline competitive with gasoline starting in 2014. The resulting accelerated production of biogasoline brings it down the learning curve so that it costs significantly less than gasoline post 2022 without further market intervention.*
of five in five years, set by Energy Secretary Chu in 2012. Figure 5 shows recent estimates of future battery costs from various sources. We find that achieving this 5 by 5 target could accelerate PIV adoption in 2020 from 0.9% in the AEO reference scenario to 4.5% of the 5 by 5 target scenario. The resulting PIV stock share by 2030 is 21.1%, much higher than 1.3% of the AEO reference scenario, and would reduce liquid fuel consumption by 36%. 
IV. Petroleum Displacement Fuels/Fuel Blending Components

How do battery learning rates affect adoption of electric vehicles? Assuming a positive feedback loop between PIV penetration and battery cost due to learning effects creates high sensitivity to early adoption rates for PIVs. For example, doubling current PIV tax credits would accelerate adoption, and so reduce battery cost by 21% by 2019, leading to substantially lower costs and higher adoption rates that would continue after the credit is ended (Figure 5). The net present value of the total investment in the PIV incentive program in early years is projected to be a small fraction of net present value cost savings in the longer term, as well as significantly reducing GHG emissions and petroleum consumption.

What if Americans buy smaller cars? After decades of increasing popularity, light trucks (including sport-utility vehicles, minivans, and pick-up trucks) have begun to lose market share to cars, reaching 46% in 2012. A scenario projecting increasing preference for cars, ultimately reaching 80% sales share by 2040, would result in a 3% decline in liquid fuel consumption and light-duty GHG emissions relative to AEO 2013 baseline. A status quo scenario, with trucks retaining their current 46% sales share would result in a 1% increase in liquid fuel consumption and GHG emissions by 2040.

Scrap vs. Save; effects of changing average vehicle lifetime: There has been a modest trend to longer average vehicle lifetimes for light-duty vehicles. Earlier vehicle retirement leads to significant fuel savings, by substituting more efficient or alternative fuel vehicles, but total transportation cost increases due to the additional capital cost of replacing the retired vehicles. Emissions associated with vehicle manufacturing reduces the overall GHG savings from earlier retirements, but results in significant GHG savings in later years.

What if there is a sudden spike in oil prices? A sudden spike in oil price to $200/barrel in 2015 and consequent increased prices for gasoline and diesel would increase purchase of alternative fuel vehicles such as HEVs and PIVs, with some small continuing effect after prices return to normal. A more extended spike for five years has a much larger effect as expected.

How would a carbon tax change the U.S. vehicle fleet composition? Adding a carbon tax of $10/ton CO$_2$ in 2015 (increasing at 5%/year thereafter) would have a modest effect in reducing vehicle miles driven and shifting consumer preference for more efficient vehicles, reducing both oil consumption and GHG emissions.

How would a large gasoline tax affect the U.S. vehicle fleet? Current U.S. taxes on gasoline average $0.49/gallon, much lower than most other advanced countries, such as Germany, with taxes about $4.00/gallon. If the U.S. increased oil taxes starting in 2015, rising linearly to 100% of pretax cost by 2020, making them comparable to Europe and Japan, it would reduce oil consumption by light-duty vehicles by 19% by 2020, increase sales share of alternative fuel vehicles from 3% to 30%.

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**Figure 5.** Recent projections of battery cost in $/KWh for the National Academy of Science (NAS, 2013) Mid and Low scenarios; DOE Vehicle Technologies Office (2013) High, Mid, and Low scenarios; Target 5 by 5, Secretary Chu's R&D target of reducing costs by a factor of five in five years announced in 2012; and learning rate with Low (10%), Mid (17.5%), and High (25%) cost reduction per doubling in cumulative battery production.
CONCLUSIONS

We have demonstrated the value and flexibility of ATEAM by applying it to explore and illuminate a wide range of policies and uncertainties. These include “push” policies to accelerate adoption of innovative technologies by increased R&D and incentives to encourage early adopters, and “pull” policies, such as fuel taxes or carbon taxes, that increase the economic competitiveness of low-carbon technologies by internalizing some of the currently external economic costs of petroleum use. These studies have shown how incentives to accelerate adoption of batteries and advanced biofuels are modest investments, relative to the likely large, long-run benefits expected once learning reduces their costs, to make them competitive with or cheaper than petroleum-based fuels.

FY 2013 PUBLICATIONS/PRESENTATIONS

ATEAM Policy Briefs


Overall Objectives

Determine if and at what levels biomass-derived oxygenates are scientifically and commercially feasible in drop-in fuels for both diesel and gasoline applications.

Fiscal Year (FY) 2013 Objectives

- Quantify the impact of residual oxygenate compounds, typical of those remaining after hydroprocessing of biomass pyrolysis oils to approximately 3 wt% oxygen, on the performance properties for both diesel and gasoline.
- Quantify the impact of oxygenated blending components that could be produced thermochemically from biomass on gasoline and diesel properties.
- Measure air pollutant emission impacts of diesel oxygenates.

FY 2013 Accomplishments

- The effects of phenolic, carbonyl, and ether compounds derived from biomass on gasoline and diesel properties were quantified. Phenol itself exhibits a high water solubility and melting point. It cannot likely be present in fuel above trace levels.
- Diisoamyl ether and pentyl pentanoate were shown to be technically viable diesel blending components.
- Emission impacts of both residual and blending component oxygenates were measured.

Future Directions

- Evaluate effects of these oxygenates on fuel storage stability and gum formation.

- Apply solubility parameter theory to assess the compatibility of oxygenate blends with fuel system elastomers.
- Complete several 300-hr engine durability tests with residual phenolic oxygenates.
- Conduct experiments to measure the impact of oxygenated aromatic compounds on air pollutant emissions from a spark-ignited, direct-injection engine.

INTRODUCTION

A DOE study has shown that by 2030 the U.S. will be capable of annually producing more than 1.3 billion tons of sustainable forest and agricultural waste as well as perennial crops that can be processed into biofuel [1]. A National Academy of Sciences study projects that 0.55 billion tons of biomass could be sustainably harvested in 2020, which could be used to produce 30 to 45 billion gallons of gasoline and diesel [2]. Biomass resources may be adequate for meeting the entire Renewable Fuel Standard requirement of 36 billion gallons of renewable fuels by 2022.

Biomass provides the largest prospective supply of biofuel feedstock—adequate for production of more than 20 times the amount of biodiesel or renewable diesel that could be produced from fats and oils (about 2 billion gallons) [3] and more than two times the amount of ethanol or other biofuels (such as butanol) that can be produced by fermenting starch-derived sugars (about 15 billion gallons) [4]. Analysis using the Greenhouse Gas, Regulated Emissions, and Energy Use in Transportation model has shown that biomass-derived fuels have roughly 80% lower life-cycle greenhouse gas emissions than petroleum-derived fuels [5,6].

Processes being investigated for conversion of biomass to liquid fuels include fast pyrolysis (FP), acid depolymerization (AD), and base depolymerization (BD). All three of these approaches produce a high oxygen content product (40 wt% to 60 wt% oxygen) that must be upgraded. Hydroprocessing at high pressures, high temperatures, and low space velocities is required to remove the oxygen from these crude products. From current economic evaluations, as demonstrated in Figure 1 for fast pyrolysis [7], there is a clear economic advantage to only remove a portion of the oxygen from the pyrolysis oil. The projected cost of the hydroprocessing upgrading step nearly doubles when the
targeted oxygen content in the final product is reduced from 5 wt% to 0.02 wt% oxygen. Table 1 lists a number of biomass-derived phenolics and ketones that have been observed in partially upgraded pyrolysis products, along with their properties [8].

While FP produces a broad range of oxygenated compounds, AD and BD can be conceived as processes to produce a narrow range of specific oxygenates. Dimethyl and 2-methyl furans, along with methyl pentanoate, have been examined previously as high octane gasoline blending components [9]. Diesel blending oxygenates produced from biomass include pentyl pentanoate and diisoamyl ether, both shown in Table 1.

**TABLE 1. Oxygenates Examined in this Research Project**

<table>
<thead>
<tr>
<th>Class/Compound</th>
<th>Molecular Structure</th>
<th>Production Process</th>
<th>Fuel/Blending</th>
<th>Blend Range</th>
<th>Blending RON, MON</th>
<th>Cetane (or DCN)</th>
<th>Boiling Point (°C)</th>
<th>Melting Point (°C)</th>
<th>Water Soluble 20°C (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Blending Components</strong></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pentyl pentanoate</td>
<td></td>
<td>AD + HT + EST</td>
<td>Diesel</td>
<td>10-20%</td>
<td>29</td>
<td>203.7</td>
<td>-79</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>Di-isoamyl ether</td>
<td></td>
<td>AD + ETH</td>
<td>Diesel</td>
<td>10-20%</td>
<td>96</td>
<td>173</td>
<td>-69</td>
<td>Insoluble</td>
<td></td>
</tr>
<tr>
<td>4-Methyl anisole</td>
<td></td>
<td>FP or BD + HT or ETH</td>
<td>Gasoline/Diesel</td>
<td>5-15%/1-2%</td>
<td>166, 148*</td>
<td>&lt;15</td>
<td>174</td>
<td>-32</td>
<td>Insoluble</td>
</tr>
<tr>
<td><strong>Residual Components</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Methyl tetrahydrofuran</td>
<td></td>
<td>AD+HT, or FP + HT</td>
<td>Gasoline</td>
<td>1-2%</td>
<td>81-90, 74-78</td>
<td>78</td>
<td>-136</td>
<td>12.1</td>
<td></td>
</tr>
<tr>
<td>2-Hexanone</td>
<td></td>
<td>FP or BD + HT</td>
<td>Gasoline</td>
<td>&lt;1%</td>
<td>127.6</td>
<td>-55.5</td>
<td>1.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Methyl-acetophenone</td>
<td></td>
<td>FP or BD + HT</td>
<td>Diesel</td>
<td>&lt;1%</td>
<td>&lt;15</td>
<td>226</td>
<td>-20</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td></td>
<td>FP or BD + HT</td>
<td>Gasoline/Diesel</td>
<td>1-2%</td>
<td>153, 149</td>
<td>&lt;15</td>
<td>202</td>
<td>34.8</td>
<td>1.9</td>
</tr>
<tr>
<td>p-Cresol</td>
<td></td>
<td>FP or BD + HT</td>
<td>Gasoline/Diesel</td>
<td>1-2%</td>
<td>140, 113</td>
<td>&lt;15</td>
<td>211</td>
<td>23</td>
<td>0.5</td>
</tr>
<tr>
<td>2,4-Xylenol</td>
<td></td>
<td>FP or BD + HT</td>
<td>Gasoline/Diesel</td>
<td>1-2%</td>
<td>&lt;15</td>
<td>205</td>
<td>27</td>
<td>&gt;17</td>
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</tr>
<tr>
<td>Guaiacol</td>
<td></td>
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<td>Gasoline/Diesel</td>
<td>&lt;1%</td>
<td>&lt;15</td>
<td>222</td>
<td>5</td>
<td>2</td>
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<tr>
<td>4-Methyl guaiacol</td>
<td></td>
<td>FP or BD + HT</td>
<td>Gasoline/Diesel</td>
<td>&lt;1%</td>
<td>&lt;15</td>
<td>222</td>
<td>5</td>
<td>2</td>
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</table>

AD = acid depolymerization of cellulose and/or hemicellulose; BD = base catalyzed depolymerization of lignin; EST = esterification; ETH = etherification; FP = fast pyrolysis of biomass; HT = hydrotreating; DCN = derived cetane number; * octane number data for 4-methyl anisole from reference 10.
In this study we examine the potential of both residual (less than a few percent) and blending component (over 10%) oxygenates for fuels that are considered drop-in fuels.

**APPROACH**

Oxygenated compounds were obtained as reagent grade chemicals from commercial suppliers. These were blended into a certification diesel fuel and a hydrocarbon gasoline blendstock for oxygenate blending (BOB, sub-octane, class AA). Residual oxygenates were blended at 1 vol% or 2 vol%. The diesel blendstocks were blended at 2 wt% oxygen (20 vol% for diisooamyl ether and 10 vol% for pentyl pentanoate). The blends were characterized using standard test methods.

The fuels were tested in a 4-cylinder, turbocharged, 4.5-L John Deere PowerTech™ Plus common-rail, direct-injection diesel engine that meets off-highway Tier 3/Stage IIIA emissions specifications. Each of the fuel blends was tested at 50%, 75%, and 100% load. Exhaust was sampled through a dilution tunnel and CO (non-dispersive infrared), oxides of nitrogen (NOx) (chemiluminescence detector), unburned hydrocarbon (flame ionization detector), formaldehyde (Fourier transform infrared), and particulate matter (PM) (gravimetric) were determined.

**RESULTS**

The properties of the methyl anisole gasoline blend are reported in Table 2. The oxygenate increase Research Octane Number (RON) and Motor Octane Number (MON) to reach an anti-knock index (AKI) of 87. Methyl anisole had little effect on Reid Vapor Pressure (RVP), increased T<sub>50</sub> and T<sub>90</sub>. The results indicate that methyl anisole has desirable properties as a gasoline blendstock. Of the residual oxygenates, phenol increased the phase separation temperature to -26°C, while m-cresol increased it to -32°C at 1 vol% and 2 vol% respectively. Hexanone significantly increased gum formation. Blending these residual oxygenates with 10% ethanol in gasoline (E10) rather than BOB eliminated these negative effects.

Property results for the diesel blend components are shown in Table 3. Diisooamyl ether significantly improved cetane number and conductivity, having little effect on other properties. Pentyl pentanoate apparently contained some residual acid as acid value of the blend increased significantly over that of the base diesel. Conductivity and lubricity improved, with little change to other properties. Both oxygenates appear to be viable as diesel blending components. In general the residual oxygenates had little or no effect on diesel properties. An exception was 4-methyl guaiacol which affected thermal stability, reducing reflectance to 89%, although this change may not be practically significant. While this level of stability may be adequate for most diesel fuel uses, the reduction in stability is notable and worth additional research. The phenolics p-cresol and 2,4 xylenol also lowered derived cetane number (DCN) almost 3 points.

The potential diesel blending components pentyl pentanoate and di-isooamyl ether exhibited decreased CO (Figure 2) and increased NOx under some conditions. Only small changes in PM emissions were observed. The heat release rate profiles of all of the fuel blends were similar with the exception of diisoamyl ether 20%. The diisoamyl ether 20% blend has a higher DCN (47.3) compared to all of the other fuel blends leading to a shorter ignition delay. Several of the residual oxygenated components, such as p-cresol exhibited disproportionately large changes in emissions considering that the component was blended at only 2%. For example, the p-cresol blend resulted in a 10% increase in CO, 15% decrease in hydrocarbons and 6% decrease in NOx at multiple loading conditions. These results may be related to the lower DCN of the blend, but indicate that further study of the effects of these residual oxygenates is warranted.

**CONCLUSIONS**

- Methyl anisole was tested as a gasoline blend component at nominally 10 vol% and found to have desirable octane number and volatility properties.
Phenol and p-cresol caused a significant increase in phase separation temperature when blended into gasoline. Hexanone caused an increase in gum formation. All were blended as residual oxygenates at 2 vol%. Additional research on the phase and chemical stability of these oxygenates is ongoing.

- Both diisoamyl ether and pentyl pentanoate were tested as diesel blend components and neither caused any negative property effects.

- Residual oxygenates had no effect on diesel properties, with the exceptions of 4-methyl guaiacol which reduced thermal stability, and p-cresol/2,4-xyleneol which significantly reduce DCN.

- Oxygenated diesel blend components generally reduced CO emissions. Residual oxygenates had unexpected effects in some cases suggesting that further study is warranted.

REFERENCES


**FY 2013 PUBLICATIONS/PRESENTATIONS**


**IV.8 Emissions and Operability of Gasoline, Ethanol, and Butanol Fuel Blends in Recreational Marine Applications**

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DOE Technology Development Managers:
Steve Przesmitzki and Kevin Stork

**Overall 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) 2013 Objectives**

- Characterize particulate matter (PM) emissions of 10 vol% blend of ethanol in gasoline (E10) and 16 vol% blend of iso-butanol in gasoline (iB16) compared to indolene
- Quantify emissions performance over the full useful engine life for E10 and iB16 compared to indolene for a range of test engines
- Perform field testing of vessels operated on tri-fuel blends
- Assess the impact of extreme fuel dilution on engine oil performance

**FY 2013 Accomplishments**

- Operation on E10 and iB16 was found to result in a 15-30% reduction in total PM emissions due to a significant reduction in organic carbon emissions accompanied by a moderate increase in elemental carbon emissions
  - A test over the full Environmental Protection Agency (EPA) useful life of six recreational marine engines ranging from 10 HP to 200 HP indicates that hydrocarbon plus oxides of nitrogen (HC+NOx) emissions limits are met even after 350 hours of deterioration with E10 and iB16
  - Over 100 hours of field testing of two vessels on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends comprised of 5 vol% ethanol, 8 vol% iso-butanol, and 87 vol% gasoline were successfully completed
  - Scuffing load showed a near-linear decrease with increased amount of bio-derived fuel blend content up to 20-25% at 50% oil dilution

**Future Directions**

- Perform end-of-season testing on recreational marine engines operated on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends
- Expand laboratory and field tests to include operation on mid-level blends with 5 wt% oxygen including 15 vol% ethanol blends, 24 vol% blend of iso-butanol in gasoline, and a tri-fuel blend
- Conduct cold start, fuel system, and fuel stability/long-term storage tests

**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]. Assuming that all alternatives were introduced as blends of ethanol and gasoline, this mandate is estimated to result in a theoretical ethanol blend level of 24-29 vol% in 2022 [2]. In order to further increase the renewable fuel fraction in transportation fuels, the U.S. EPA granted a waiver for use of 15 vol% ethanol blends 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 operating strategies without closed-loop feedback
controls 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 [4]. This project is specifically designed to assess the suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications. The main focus is the quantification of performance, efficiency and emissions on a range of widely used marine engines through laboratory and field testing with butanol blends compared to gasoline and ethanol blends.

**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 tested for end of life emissions, 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**

To ensure a comprehensive assessment, experiments were conducted on a range of commonly used recreational marine engines covering a range of technologies, engine sizes, and power ratings. An overview of the engines and specifications as well as the respective focus area for the performed tests is given in Table 1.

The current phase of the project focuses on a comparison of ethanol and iso-butanol blends at constant fuel oxygen content of 3.5 wt% relative to the indolene baseline. Results reported here include an assessment of PM characteristics and useful life emissions assessment for E10 and iB16, field testing of a tri-fuel blend with 5 vol% ethanol and 8 vol% iso-butanol content as well as assessment of fuel dilution effects on engine oil performance.

**PM Emissions Assessment**

Two 90-HP engines with different cylinder configurations (I-3 and I-4) and combustion cycles (two-stroke and four-stroke) were selected for PM emissions testing. Fuel grade ethanol and neat bio iso-butanol were splash blended with base indolene certification fuel to create the E10 and iB16 test fuels for PM testing. Mass particulate emissions were determined gravimetrically using a partial flow sampling system which collected an emissions sample at the base of the engine power head prior to water injection in the mid section of the outboard engine. 90mm Pall Emfab™ Teflon® glass fiber filters were stabilized in a constant temperature/constant humidity glove box prior to initial weighing and stabilized for two hours prior to final weighing. A weighted composite particulate sample (five modes on one filter) was collected by varying the sample time of the partial flow sampling system to match the five-mode International Council of Marine Industry Associations weighted test cycle (ISO8178). Two back-to-back samples were collected for each of the three test fuels.

After total mass PM determinations, the extractable organics (referred to as the soluble organic fraction) were removed by Soxhlet extraction for 24 hours using dichloromethane. After extraction, each filter was stabilized overnight and re-weighed to determine the percentage of elemental carbon and organic carbon.

As indicated in Figure 1, both alcohols, on average, increased elemental carbon, reduced organic carbon, and...
reduced total PM compared to baseline indolene test fuel for both engines tested.

The aforementioned results for total PM are consistent with published data on closed-loop automotive engines operating on increasing amounts of ethanol [5,6]. However, the trends for increased elemental carbon are somewhat contrary to published data. This may be due to the lack of closed-loop engine control, and changes in overall air/fuel ratio as a result of the enleanment effects of the fuel.

**Full Useful Life Emissions**

Six engines from three different engine manufacturers (Mercury, Evinrude, Tohatsu) in a power range from 10 HP to 200 HP were selected to run for their full 350-hour EPA useful life according to the International Council of Marine Industry Associations weighted duty cycle. One engine from each set of two test engines from each engine manufacturer accumulated hours operating on E10, and the other engine accumulated hours operating on iB16. Baseline emissions and final deteriorated emissions were recorded for each of the six engines. As indicated in Figure 2, final HC+NOx emissions after 350 hours of deterioration followed similar trends between the E10 control engine and the iB16 test engine. Regardless of the test fuel used during engine deterioration, all test engines passed the final HC+NOx EPA Part 1045 standards (dashed line).

The Tohatsu engine operating on E10 experienced more deterioration because of the variability of carburetion rather than effects of the test fuel.

**Tri-Fuel Blend Field Testing**

There are several pathways for the introduction of iso-butanol to the market. From a refiner’s perspective, the inherently low Reid Vapor Pressure (RVP) of neat iso-butanol may help to lower the overall finished gasoline RVP, particularly when blended at 16 vol%. Comingling ethanol and iso-butanol has some advantages such as the ability of butanol to trim the overall RVP [7], minimize depression in the distillation curve, and improve water tolerance of the finished gasoline. Moreover, if iso-butanol is introduced into the market, tri-fuel blends consisting of gasoline, ethanol, and butanol will inevitably occur. To account for this scenario, a 9-RVP tri-fuel blend comprised of 5 vol% ethanol, 8 vol% iso-butanol, and 87 vol% gasoline was evaluated over the summer boating season on two boats: a 26’ Premier pontoon with twin 135 HP Evinrude DFI engines and a 16’ Angler with a single 90 HP Yamaha EFI engine. Baseline laboratory emissions tests were conducted prior to placing the engines in the field for hour accumulation. The baseline emissions results relative to indolene certification fuel are presented in Figure 3. The increase in HC, NOx, CO, and CO₂ emissions observed with the Evinrude DFI 2-stroke engine is less than 10% for all measured components suggesting only slight changes in
operational characteristics due to changes in air/fuel ratio compared to indolene. On the other hand the Yamaha EFI 4-stroke engine showed a reduction in HC and CO emissions with a simultaneous increase in NO\textsubscript{x} and CO\textsubscript{2} emissions consistent with enleanment due to the reduced energy content of the tri-fuel blend compared to indolene. After official baseline testing occurred, emissions results have been verified on a second Evinrude 135HP engine operating on tri-fuel and Indolene. The results of this additional test also indicate very similar emissions output on both fuels. The Evinrude carbon monoxide emissions from the tri-fuel are inconsistent with results from other outboard engines operated on E10. However, based on previous testing, DFI has typically resulted in less CO enleanment relative to multi-port fuel injection. Nonetheless, additional engine testing and combustion analysis on tri-fuel will be conducted in effort to better understand the effects. At the time of this report the engines had accumulated over 100 hours of field operation on the tri-fuel blend and were being prepared for final emissions testing.

**Effect of Fuel Dilution on Engine Oil Performance**

Although the measured fuel dilution in the crankcase is in the 4-7% range [8], it is well known that the level of fuel dilution in the engine ring pack is usually substantially higher. Those higher levels of dilution can make the ring-liner contact interface more susceptible to scuffing failure. In the scuffing test with used oil from a Yamaha engine boat test reported last year, gasoline fuel dilution resulted in less than 5% reduction in scuffing load while E10 and iB16 contamination of the oil resulted in as much as 25% reduction in scuffing load. Consequently, scuffing tests were conducted with surrogate fluids consisting of marine engine oil containing different levels (up to 50%) of three fuels—gasoline, E10 and iB16. Scuffing tests were conducted with a block-on-ring contact configuration using a step load increase protocol. Tests were conducted at a constant speed of 1,000 RPM with initial contact load of 50 N, followed by 25 N increase every minute until scuffing occurred as indicated by a sudden rapid rise in friction coefficient. The load at which scuffing occurred is judged to be an indication of scuffing life or scuffing resistance. The higher the load, the better the scuffing protection by the lubricant. Figure 4 shows the results of average scuffing loads for various surrogate fluids in comparison with fresh marine engine oil. Any level of fuel dilution resulted in a noticeable decrease in scuffing load. Scuffing load reduction ranges from 5% to as much as 25%. These results suggest that the presence of fuel in the engine oil will result in a decreased load carrying capacity of the engine oil, i.e., reduction in protection against scuffing. Furthermore, fuels containing bio derived components (E10 and iB16) showed a near-linear decrease in scuffing load with increasing amount of fuel in the oil.
Laboratory and field testing on a range of recreational marine engines from 10 HP to 200 HP was performed using gasoline-alcohol blends with a constant oxygen content of 3.5 wt%. The tested fuels included E10, iB16, and a 5 vol% ethanol, 8 vol% iso-butanol, 87 vol% gasoline tri-fuel blend. The results support the following conclusions:
FY 2013 PUBLICATIONS/PRESENTATIONS


SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. Oyelayo Ajayi received NMMA Environmental Achievement Award “for innovative research and outstanding contribution to the recreational boating industry”

REFERENCES


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.


## V. Acronyms, Abbreviations and Definitions

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$\eta_{th}$</td>
<td>Thermodynamic cycle efficiency</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Ratio of specific heats</td>
</tr>
<tr>
<td>$\mu$</td>
<td>Micro-liter</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Fuel/air-equivalence ratio</td>
</tr>
<tr>
<td>$\eta_{f,ig}$</td>
<td>Gross indicated fuel-conversion efficiency</td>
</tr>
<tr>
<td>$^\circ$F</td>
<td>Degrees Fahrenheit</td>
</tr>
<tr>
<td>% w/w</td>
<td>% weight/weight</td>
</tr>
<tr>
<td>1-D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D-GC</td>
<td>2-dimensional gas chromatograph</td>
</tr>
<tr>
<td>2-D</td>
<td>Two-dimensional</td>
</tr>
<tr>
<td>ABC</td>
<td>Advanced biofuel credit</td>
</tr>
<tr>
<td>AC&amp;F</td>
<td>Advanced Combustion and Fuels</td>
</tr>
<tr>
<td>AD</td>
<td>Acid depolymerization</td>
</tr>
<tr>
<td>ADC</td>
<td>Advanced distillation curve</td>
</tr>
<tr>
<td>AEO</td>
<td>Annual Energy Outlook</td>
</tr>
<tr>
<td>A/F</td>
<td>Air/fuel ratio</td>
</tr>
<tr>
<td>AFR</td>
<td>Stoichiometric air/fuel ratio</td>
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<tr>
<td>AHRR</td>
<td>Apparent heat release rate</td>
</tr>
<tr>
<td>AKI</td>
<td>Anti-knock index</td>
</tr>
<tr>
<td>AMN</td>
<td>Alpha methyl naphthalene</td>
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<tr>
<td>APBF</td>
<td>Advanced petroleum-based fuels</td>
</tr>
<tr>
<td>API</td>
<td>American Petroleum Institute</td>
</tr>
<tr>
<td>ARPA-E</td>
<td>Advanced Research Projects Agency-Energy</td>
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<tr>
<td>ASTM</td>
<td>ASTM International, a standards setting organization</td>
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<table>
<thead>
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<th>Abbreviation</th>
<th>Description</th>
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<tr>
<td>atdc, ATDC, aTDC</td>
<td>After top-dead center</td>
</tr>
<tr>
<td>aTDC$_f$</td>
<td>After firing top-dead center</td>
</tr>
<tr>
<td>ATEAM</td>
<td>Analytica Transportation Energy Analysis Model</td>
</tr>
<tr>
<td>a.u.</td>
<td>Arbitrary units</td>
</tr>
<tr>
<td>AVFL</td>
<td>Advanced Vehicles Fuels and Lubricants</td>
</tr>
<tr>
<td>AW</td>
<td>Anti-wear</td>
</tr>
<tr>
<td>B5</td>
<td>5% biodiesel</td>
</tr>
<tr>
<td>B6</td>
<td>6% biodiesel</td>
</tr>
<tr>
<td>B20</td>
<td>20% biodiesel</td>
</tr>
<tr>
<td>B100</td>
<td>100% biodiesel</td>
</tr>
<tr>
<td>BAC</td>
<td>Benzalkonium chloride</td>
</tr>
<tr>
<td>BD</td>
<td>Base depolymerization</td>
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<tr>
<td>BDC</td>
<td>Bottom dead center</td>
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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

BEV-100 Battery electric vehicle with 100 mile range

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

BZT Benzethonium chloride

CA50 Crank angle at which 50% of the combustion heat release has occurred

CARB California Air Resources Board

CDC Conventional diesel combustion

CF Certification fuel

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
<table>
<thead>
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<th>Acronym</th>
<th>Definition</th>
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<tr>
<td>CRC</td>
<td>Coordinating Research Council</td>
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<tr>
<td>CSM</td>
<td>Colorado School of Mines</td>
</tr>
<tr>
<td>CSFT</td>
<td>Cold soak filtration test</td>
</tr>
<tr>
<td>CT</td>
<td>Carbon-bond type</td>
</tr>
<tr>
<td>CTAB</td>
<td>Cetyl trimethyl ammonium bromide</td>
</tr>
<tr>
<td>CuME</td>
<td>FAME derived from Cuphea oil</td>
</tr>
<tr>
<td>DCN</td>
<td>Derived cetane number</td>
</tr>
<tr>
<td>DEER</td>
<td>Diesel Engine Emissions Reduction</td>
</tr>
<tr>
<td>degCA</td>
<td>Degrees crank angle</td>
</tr>
<tr>
<td>DEPT</td>
<td>Distortionless enhancement of polarization transfer</td>
</tr>
<tr>
<td>DI</td>
<td>Direct-injection</td>
</tr>
<tr>
<td>DISI</td>
<td>Direct-injection spark ignition</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-like carbon</td>
</tr>
<tr>
<td>DNPH</td>
<td>2,4-dinitorophenylhydrazine</td>
</tr>
<tr>
<td>DOC</td>
<td>Diesel oxidation catalyst</td>
</tr>
<tr>
<td>DODA</td>
<td>Dimethyldiacetadyclammonium chloride</td>
</tr>
<tr>
<td>DODAPS</td>
<td>N-Dodecyl-N, N-dimethyl-3-ammonio-1-propanesulfonate</td>
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<tr>
<td>DOSY</td>
<td>Diffusion-ordered spectroscopy</td>
</tr>
<tr>
<td>DPF</td>
<td>Diesel particulate filter</td>
</tr>
<tr>
<td>DRIFTS</td>
<td>Diffuse reflectance infrared Fourier-transform spectroscopy</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
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<tr>
<td>E0</td>
<td>Gasoline with no ethanol</td>
</tr>
<tr>
<td>E10</td>
<td>10% ethanol, 90% gasoline fuel blend</td>
</tr>
<tr>
<td>E15</td>
<td>15% ethanol, 85% gasoline fuel blend</td>
</tr>
<tr>
<td>E20</td>
<td>20% ethanol, 80% gasoline fuel blend</td>
</tr>
<tr>
<td>E30</td>
<td>30% ethanol, 70% gasoline fuel blend</td>
</tr>
<tr>
<td>E50</td>
<td>50% ethanol, 50% gasoline fuel blend</td>
</tr>
<tr>
<td>E85</td>
<td>Nominally 85% ethanol/15% gasoline blend which can actually range from 51–83% per ASTM D5798</td>
</tr>
<tr>
<td>ECM</td>
<td>Engine control module</td>
</tr>
<tr>
<td>ECS</td>
<td>Emission control system</td>
</tr>
<tr>
<td>ECU</td>
<td>Electronic control unit</td>
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<td>EDAX</td>
<td>Energy-dispersive X-ray spectroscopy</td>
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<td>EEPS</td>
<td>Engine exhaust particle sizer</td>
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<td>EGO</td>
<td>Exhaust gas oxygen</td>
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<td>EGR</td>
<td>Exhaust gas recirculation</td>
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<td>EHL</td>
<td>Elastohydrodynamic lubricant</td>
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<tr>
<td>EHN</td>
<td>Ethyl hexyl nitrate</td>
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<td>EIVC</td>
<td>Early intake valve closing</td>
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<td>ELOC</td>
<td>Extended lift-off combustion</td>
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<td>EOI</td>
<td>End of injection</td>
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<td>EPA</td>
<td>Environmental Protection Agency</td>
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<td>EPMA</td>
<td>Thermodynamic cycle efficiency</td>
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<tr>
<td>ETC</td>
<td>Environmental Testing Corporation</td>
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<td>ETE</td>
<td>Ethyltetrahydrofurfuryl ether</td>
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<tr>
<td>Exx</td>
<td>xx% ethanol, 100-xx% gasoline fuel blend</td>
</tr>
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<td>FACE</td>
<td>Fuels for Advanced Combustion Engines</td>
</tr>
<tr>
<td>FAME</td>
<td>Fatty acid methyl ester</td>
</tr>
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<td>FE</td>
<td>Fuel economy</td>
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<tr>
<td>FFV</td>
<td>Flexible-fuel vehicle; flex-fuel vehicle</td>
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<td>FID</td>
<td>Flame ionization detector</td>
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<td>FMC</td>
<td>Ford Motor Company</td>
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<td>Flex Fuel</td>
<td>Nominally 85% ethanol/15% gasoline blend which can actually range from 51–83% per ASTM D5798</td>
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<td>Final melting temperature</td>
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</tr>
<tr>
<td>FSN</td>
<td>Filter smoke number</td>
</tr>
<tr>
<td>FTP</td>
<td>Federal Test Procedure</td>
</tr>
<tr>
<td>FTP-75</td>
<td>Federal Test Procedure for LD vehicles</td>
</tr>
<tr>
<td>FU</td>
<td>Fleet utility</td>
</tr>
<tr>
<td>FUL</td>
<td>Full useful life</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>GC-FID</td>
<td>Gas chromatography/flame ionization detector</td>
</tr>
<tr>
<td>GC-FIMS</td>
<td>Gas chromatography field ionization mass spectrometry</td>
</tr>
<tr>
<td>GC-MS</td>
<td>Gas chromatography – mass spectrometry</td>
</tr>
<tr>
<td>GDI, GDi</td>
<td>Gasoline direct injection</td>
</tr>
<tr>
<td>GGE</td>
<td>Gasoline gallon equivalent</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gas</td>
</tr>
<tr>
<td>GISFC</td>
<td>Gross indicated specific fuel consumption</td>
</tr>
<tr>
<td>GPF</td>
<td>Gasoline particulate filter</td>
</tr>
<tr>
<td>GTDI</td>
<td>Gasoline turbocharged direct injection</td>
</tr>
<tr>
<td>GTL</td>
<td>Gas to liquid</td>
</tr>
<tr>
<td>HC</td>
<td>Hydrocarbon</td>
</tr>
<tr>
<td>HCCI</td>
<td>Homogeneous Charge Compression Ignition</td>
</tr>
<tr>
<td>HD</td>
<td>Heavy-duty</td>
</tr>
<tr>
<td>HECC</td>
<td>High-efficiency clean-combustion</td>
</tr>
<tr>
<td>HETCOR</td>
<td>Heteronuclear correlation</td>
</tr>
<tr>
<td>HEV</td>
<td>Hybrid electric vehicle</td>
</tr>
<tr>
<td>HFET</td>
<td>Highway Fuel Economy Test</td>
</tr>
<tr>
<td>HFRR</td>
<td>High frequency reciprocating rig</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>HMBC</td>
<td>Heteronuclear multiple bond correlation</td>
</tr>
<tr>
<td>HMN</td>
<td>Heptamethylnonane (2,2,4,4,6,8-heptamethylnonane, a diesel primary reference fuel)</td>
</tr>
<tr>
<td>HPLC</td>
<td>High-performance liquid chromatography</td>
</tr>
<tr>
<td>HRA</td>
<td>Home refueling appliance</td>
</tr>
<tr>
<td>HRR</td>
<td>Heat release rate</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High-resolution transmission electron microscopic</td>
</tr>
<tr>
<td>HSDI</td>
<td>High-speed direct injection</td>
</tr>
<tr>
<td>HSQC</td>
<td>Heteronuclear single quantum coherence</td>
</tr>
<tr>
<td>HTML</td>
<td>High temperature, high load</td>
</tr>
<tr>
<td>HVA</td>
<td>Hydraulic valve actuator</td>
</tr>
<tr>
<td>iB16</td>
<td>16 vol% blend of iso-butanol in gasoline</td>
</tr>
<tr>
<td>iB24, IB24</td>
<td>24 vol% blend of iso-butanol in gasoline</td>
</tr>
<tr>
<td>iBu48</td>
<td>48 vol% blend of iso-butanol in gasoline</td>
</tr>
<tr>
<td>ICE</td>
<td>Internal combustion engine</td>
</tr>
<tr>
<td>ICOMIA</td>
<td>International Council of Marine Industry Associations</td>
</tr>
<tr>
<td>IL</td>
<td>Ionic liquid</td>
</tr>
<tr>
<td>ILSAC</td>
<td>International Lubricants Standardization and Approval Committee</td>
</tr>
<tr>
<td>IMEP&lt;sub&gt;g&lt;/sub&gt;</td>
<td>Indicated mean effective pressure, gross</td>
</tr>
<tr>
<td>IMEP&lt;sub&gt;net&lt;/sub&gt;</td>
<td>Indicated mean effective pressure, net over all four strokes</td>
</tr>
<tr>
<td>IQT™</td>
<td>Ignition Quality Tester</td>
</tr>
<tr>
<td>ISFC</td>
<td>Indicated specific fuel consumption</td>
</tr>
<tr>
<td>ISCO</td>
<td>Indicated specific carbon monoxide</td>
</tr>
<tr>
<td>ISHC</td>
<td>Indicated specific hydrocarbons</td>
</tr>
<tr>
<td>ISNO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>Indicated specific emissions of nitrogen oxides</td>
</tr>
<tr>
<td>ITE</td>
<td>Indicated thermal efficiency</td>
</tr>
<tr>
<td>IVD</td>
<td>Intake valve deposit</td>
</tr>
<tr>
<td>kPa</td>
<td>Kilopascals</td>
</tr>
<tr>
<td>KIVA</td>
<td>Combustion analysis software developed by Los Alamos National Laboratory</td>
</tr>
<tr>
<td>LC/MS</td>
<td>Liquid chromatography with mass spectrometric detection</td>
</tr>
<tr>
<td>LD</td>
<td>Light-duty</td>
</tr>
<tr>
<td>LED</td>
<td>Light-emitting diode</td>
</tr>
<tr>
<td>LEV</td>
<td>Low Emission Vehicle</td>
</tr>
<tr>
<td>LFT</td>
<td>Learned fuel trim (or long-term fuel trim)</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value; latent heat of vaporization</td>
</tr>
<tr>
<td>LIVC</td>
<td>Late intake valve closing</td>
</tr>
<tr>
<td>LL</td>
<td>Liquid length</td>
</tr>
<tr>
<td>LNG</td>
<td>Liquefied natural gas</td>
</tr>
<tr>
<td>LPG</td>
<td>Liquefied petroleum gas</td>
</tr>
<tr>
<td>LTC</td>
<td>Low-Temperature Combustion</td>
</tr>
<tr>
<td>LTFT</td>
<td>Low temperature flow test; long-term fuel trim</td>
</tr>
<tr>
<td>LTHR</td>
<td>Low-temperature heat release</td>
</tr>
<tr>
<td>MAG</td>
<td>Monoglycerides</td>
</tr>
<tr>
<td>MBT</td>
<td>Maximum (spark advance) for best torque</td>
</tr>
<tr>
<td>MCE</td>
<td>Multi-cylinder engine</td>
</tr>
<tr>
<td>MECA</td>
<td>Manufacturers of Emission Controls Association</td>
</tr>
<tr>
<td>µl</td>
<td>Micro-liter</td>
</tr>
<tr>
<td>MFB</td>
<td>Mass fuel burned</td>
</tr>
<tr>
<td>MFB50</td>
<td>Crank angle where 50% of heat release has occurred</td>
</tr>
<tr>
<td>MFC</td>
<td>Model Fuels Consortium, a consortium run by Reaction Design to improve kinetic modeling tools and fuels and engine modeling tools.</td>
</tr>
<tr>
<td>MIL</td>
<td>Malfunction indicator lamp</td>
</tr>
<tr>
<td>MIT</td>
<td>Massachusetts Institute of Technology</td>
</tr>
<tr>
<td>ML</td>
<td>Mixed lubrication</td>
</tr>
<tr>
<td>MLEB</td>
<td>Mid-level ethanol blend</td>
</tr>
<tr>
<td>MOAT</td>
<td>Morris one-at-a-time</td>
</tr>
<tr>
<td>MON</td>
<td>Motor Octane Number</td>
</tr>
<tr>
<td>ng</td>
<td>Nano-gram</td>
</tr>
<tr>
<td>NHD</td>
<td>N-hexadecane</td>
</tr>
<tr>
<td>NMHC</td>
<td>Non-methane hydrocarbon</td>
</tr>
<tr>
<td>NMOG</td>
<td>Non-methane organic gases</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Nitrogen dioxide</td>
</tr>
<tr>
<td>NOx</td>
<td>Oxides of nitrogen</td>
</tr>
<tr>
<td>NVO</td>
<td>Negative valve overlap</td>
</tr>
<tr>
<td>OA</td>
<td>Oleic acid</td>
</tr>
<tr>
<td>OC</td>
<td>Organic carbon</td>
</tr>
<tr>
<td>ODT</td>
<td>Octadecane thiol</td>
</tr>
<tr>
<td>OEM</td>
<td>Original Equipment Manufacturer</td>
</tr>
<tr>
<td>O-POM</td>
<td>Organic-coated polyoxometalate</td>
</tr>
<tr>
<td>OSC</td>
<td>Oxygen storage capacity</td>
</tr>
<tr>
<td>PAG</td>
<td>Polyalkylene glycol</td>
</tr>
<tr>
<td>PAH</td>
<td>Polycyclic aromatic hydrocarbon</td>
</tr>
<tr>
<td>PAO</td>
<td>Polyalphaolefin</td>
</tr>
<tr>
<td>PCCI</td>
<td>Pre-mixed charge compression ignition</td>
</tr>
<tr>
<td>% w/w</td>
<td>% weight/weight</td>
</tr>
<tr>
<td>PFI</td>
<td>Port fuel injection, port fuel injected</td>
</tr>
<tr>
<td>PGM</td>
<td>Platinum group metal</td>
</tr>
<tr>
<td>Acronym</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>PHEV</td>
<td>Plug-in hybrid electric vehicle</td>
</tr>
<tr>
<td>PHEV-10</td>
<td>Plug-in hybrid electric vehicle with 10 mile electric range</td>
</tr>
<tr>
<td>PHEV-40</td>
<td>Plug-in hybrid electric vehicle with 40 mile electric range</td>
</tr>
<tr>
<td>SOC</td>
<td>Start of combustion; soluble organic compound</td>
</tr>
<tr>
<td>SOF</td>
<td>Soluble organic fraction</td>
</tr>
<tr>
<td>SOI</td>
<td>Start of injection</td>
</tr>
<tr>
<td>SRC</td>
<td>Standard Road Cycle</td>
</tr>
<tr>
<td>ST</td>
<td>Spark timing</td>
</tr>
<tr>
<td>SULEV</td>
<td>Super Ultra-Low Emissions Vehicle</td>
</tr>
<tr>
<td>SwRI®</td>
<td>Southwest Research Institute®</td>
</tr>
<tr>
<td>T_{bdc}</td>
<td>Bottom-dead-center temperature</td>
</tr>
<tr>
<td>T50</td>
<td>Temperature for 50% evaporated</td>
</tr>
<tr>
<td>TAN</td>
<td>Total acid number</td>
</tr>
<tr>
<td>TDC</td>
<td>Top-dead center</td>
</tr>
<tr>
<td>TDC_{exc}</td>
<td>Top-dead center (of gas-exchange strokes)</td>
</tr>
<tr>
<td>TDO</td>
<td>Thermal deoxygenation</td>
</tr>
<tr>
<td>TET</td>
<td>Tetralin</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermo-gravimetric analysis</td>
</tr>
<tr>
<td>THC</td>
<td>Total hydrocarbon</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TMB</td>
<td>1,2,4-trimethylbenzene</td>
</tr>
<tr>
<td>TPD</td>
<td>Temperature-programmed desorption</td>
</tr>
<tr>
<td>TPGME</td>
<td>Tri-propylene glycol methyl ether</td>
</tr>
<tr>
<td>TPO</td>
<td>Temperature-programmed oxidation</td>
</tr>
<tr>
<td>TRC</td>
<td>Transportation Research Center</td>
</tr>
<tr>
<td>TSI</td>
<td>Threshold sooting index</td>
</tr>
<tr>
<td>TWC</td>
<td>Three-way sooting index</td>
</tr>
<tr>
<td>ULEV</td>
<td>Ultra-Low Emission Vehicle</td>
</tr>
<tr>
<td>ULEV</td>
<td>Ultra-Low Emission Vehicle</td>
</tr>
<tr>
<td>ULG 91 RON</td>
<td>Unleaded gasoline 91 Research Octane Number</td>
</tr>
<tr>
<td>ULG 95 RON</td>
<td>Unleaded gasoline 95 Research Octane Number</td>
</tr>
<tr>
<td>ULSD</td>
<td>Ultra-low-sulfur diesel</td>
</tr>
<tr>
<td>UTG</td>
<td>Unleaded test gasoline</td>
</tr>
<tr>
<td>VOT</td>
<td>Vehicle Technologies Office</td>
</tr>
<tr>
<td>VVO</td>
<td>Variable valve actuation</td>
</tr>
<tr>
<td>WOT</td>
<td>Wide-open throttle</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>ZDDP</td>
<td>Zinc dialkyl-dithiophosphate</td>
</tr>
</tbody>
</table>

**V. Acronyms, Abbreviations and Definitions**

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