U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

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## VEHICLE TECHNOLOGIES OFFICE

# FY 2014 Annual Progress Report -
## Fuel & Lubricant Technologies

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# FY 2014 Progress Report for Fuel & Lubricant Technologies

Energy Efficiency and Renewable Energy
Vehicle Technologies Office

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# Executive Summary

## Advanced Fuels and Lubricants for an Efficient, Clean and Secure U.S. Vehicle Transportation System

On behalf of the Department of Energy's Vehicle Technologies Program (VTP), we are pleased to introduce the Fiscal Year (FY) 2014 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 subprogram 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  Although world events late in 2014 have resulted in a precipitous decline in crude oil prices, over the long-term it is expected that transportation fuels will 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, natural gasoline, 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 and biomass-derived feedstocks on finished fuels is an area of relatively new concern to engine manufacturers, regulators and users. While in some cases it may be seen as a challenge for engines to be tolerant to more diverse fuels, it may also be an opportunity to change the fuel composition and properties for emerging combustion strategies. Advanced engine technologies can be optimized by matching fuel composition to the combustion system, in addition to helping compliance with new emissions standards. The Fuel & Lubricant Technologies subprogram activities focus on the properties and quality of the finished fuels derived from these sources, not primarily on their production.

The goals of the Fuel & Lubricant Technologies subprogram 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.

From 2009-2012, the Fuel & Lubricant Technologies subprogram conducted a 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 (15% ethanol and 85% gasoline) to be used in 2007 and newer light-duty vehicles (2010) and a second partial waiver for 2001 to 2006 light-duty vehicles (2011). The impact of E15 and E20 on vehicles and other engines, materials compatibility, evaporative emissions, and vehicle driveability were investigated. More recently, the Fuel & Lubricant Technologies subprogram 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 subprogram 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 the United States to use less petroleum in transportation. In 2013, a U.S. DRIVE fuels technology team was initiated and continued work in 2014, culminating in a plan to evaluate potential properties of new lower carbon fuels for future, high-efficiency engines and combustion regimes. The initial plan for pre-competitive research includes an emphasis on low carbon spark-ignition (SI) and compression ignition (CI) engine fuels for high efficiency; fuels to enable advanced, low temperature combustion engines; a new metric for measuring the anti-knock index of fuels used in SI engines; and the determination of a new ignition delay metric for advanced low temperature combustion engines. 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. Although fast-fill compressed natural gas stations are increasing every year, expected to reach over 800 in 2015, liquid fuels primarily diesel, currently dominate the market for heavy over-the-road trucks. The Fuel & Lubricant Technologies subprogram works closely with the Advanced Combustion Engine R&D subprogram of the VTP, which is focused on removing critical technical barriers to commercialization of higher efficiency, advanced internal combustion engines in light-duty, medium-duty, and heavy-duty vehicles. Fuel & Lubricant Technologies subprogram activities are also coordinated with appropriate DOE/industry technical teams; the light-duty automotive, heavy-duty engine, and energy industries; and federal, state, and local government agencies. Some activities are undertaken in coordination with the Biomass Program, the Hydrogen and Fuel Cells Program, and the Office of Fossil Energy (via the Fuels Cross-Cut Team) to ensure maximum synergy and to avoid duplication of effort.

## Program Goals

The Fuel & Lubricant Technologies Program has the following goals for 2020:

- Demonstrate cost-effective lubricant system with 4% fuel economy improvement relative to 2013 base fluids
- Demonstrate expanded operational range of advanced combustion regimes to >95% of the light-duty Federal Test Procedures
- 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 Technologies Office) 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 with lowest possible greenhouse gas (GHG) emissions.

## 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.

In contrast to 2005, the events of the fourth quarter of 2014 have had an opposite effect. Declining demand for petroleum, particularly gasoline, and the decision by some OPEC members to continue production levels, have led to a dramatic drop in energy prices, almost as severe as the drop precipitated by the recession of 2008. Diesel fuel prices have dropped as well, but to a lesser extent due to the continued strong demand for diesel as the economy grows. It is expected that oil prices will recover somewhat in 2015, but there is a high degree of uncertainty in the predictions. 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 subprogram focuses on tailoring petroleum-based fuels to accommodate and enable more efficient use, and on increasing use of renewable and non-petroleum-derived fuels for the long-term. For example, oil-sand-derived fuels from Canada, 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 which 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, 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 (FFVs) that can use E85 (85% ethanol and 15% gasoline), gasoline, or any blend in between. These FFVs vehicles are currently optimized for gasoline operation. The Fuel & Lubricant Technologies subprogram is sponsoring the development of engines for the next generation of FFVs 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 E20 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 conventional diesel fuel. However, continuing quality problems with biodiesel resulted in fuel 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 subprogram partnered with the National Biodiesel Board to improve ASTM (an international standards organization) biodiesel fuel specifications and ensure that suppliers adhere to the specifications. Surveys of marketed biodiesel conducted by the Fuel & Lubricant Technologies subprogram in 2005, 2007, 2008, 2010, 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 subprogram is evaluating advanced petroleum-based fuels and non-petroleum-based fuels for their impact on engine-out emissions and emission control system efficiency and durability. For example, detailed research is being conducted on biodiesel combustion to understand its impact on NOx emissions and its ability to enhance the performance of diesel particulate filters. Optimized engine designs are being explored to use E85 with high efficiency while achieving very low emissions.

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

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 subprogram led a government-industry collaboration in demonstrating that the sulfur content of diesel fuel had to be reduced to enable the use of advanced emission control systems. Diesel vehicles need these advanced emission control systems, such as lean-NOx catalysts, to meet stringent emissions standards. Fuel & Lubricant Technologies subprogram-sponsored research led the EPA to require that all highway diesel fuel contain a maximum of 15-ppm sulfur. Before this ruling went into effect in 2006, diesel fuel for on-road use contained an average of 350-ppm sulfur, with a legal maximum of 500 ppm. 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 subprogram is conducting research that will yield substantial benefits to the energy security of our country, to our environment, and to our economy. By cooperating with other DOE programs to leverage synergies, this subprogram greatly improves the prospects for advanced fuels and advanced vehicle technologies.

## 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.

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# I. Introduction

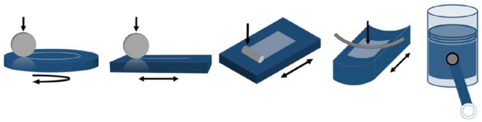
## Highlights of Significant FY 2014 Accomplishments

The following presents highlights of the Fuel & Lubricant Technologies project accomplishments in 2014.

### Fuels and Lubricants to Enable High-Efficiency 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.

- Oak Ridge National Laboratory is identifying important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology. In FY 2014 they: (1) Developed and implemented accelerated poisoning and aging protocols; (2) Developed laboratory experiments to mimic field use; and (3) Developed procedures and techniques in this project that can also be used to evaluate field durability. (Toops, report II.1)
- Argonne National Laboratory 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 2014 they; (1) Performed initial studies of wear analysis using profilometry and microscopy and revealed various types of wear mechanisms present in a used engine; (2) Initiated the development of test protocols to simulate scuffing, a major failure mechanism of concern to industrial collaborators; and (3) Identified benchtop tests that best simulate friction, wear, and failure mechanisms. (Demas, report II.2)

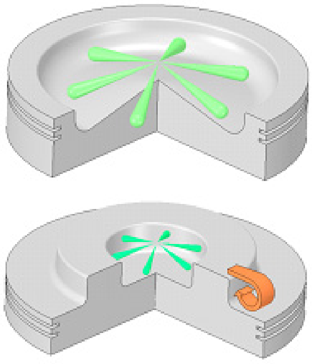


Schematics of laboratory test configurations (left-to-right: unidirectional ball-on-flat, reciprocating ball-on-flat, reciprocating cylinder-on-flat, reciprocating ring-on-liner, and floating liner) used to simulate engine tests. (Demas, report II.2)

- Argonne National Laboratory is developing and optimizing lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles. In FY 2014 they: (1) Established the minimum concentration for friction reducing nano-additive systems to be about 0.1%. Higher concentration did not produce any further friction reduction; (2) Determined that use of an appropriate encapsulator resulted in further enhancement of friction and wear performance; (3) Established the anti-wear mechanism of the nano-additive system via the formation of nano-sized and structured surface tribo-films by the additives; and (4) Observed that under severe sliding contact conditions many nano-additives reduced wear compared to current state-of-the-art lubricants. Encapsulation with oleic acid further enhanced the wear reduction. (Ajayi, report II.3)
- Argonne National Laboratory is seeking to develop a better understanding of the nature (structure), composition, and the mechanisms of formation of tribochemical surface films. In FY 2014 they: (1) Determined the thermal limit of tribochemical films from several commercially available lubricants to be in the range of 220°C to 250°C; (2) Identified the failure modes of tribochemical films under thermal loads to sudden film removal by increased shear stress or extensive oxidation; (3) Observed a peculiar effect of base-oil viscosity on boundary-lubrication friction behavior; (4) Analyzed tribochemical films by X-ray absorption near edge structure at the Advanced Photon Source; and (5) 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, report II.4)
- The Massachusetts Institute of Technology is identifying the best lubricant formulations for individual engine subsystems and 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 2014 they: (1) Demonstrated the ability to maintain the wear protection performance of a 15W40 lubricant in the valvetrain while using a 5W20 lubricant in the power cylinder. A friction reduction of 9% was demonstrated in low-speed, low-load operating condition; (2) Demonstrated an additional 1% reduction in total engine friction using

reduced antiwear additive in the power cylinder; and (3) Demonstrated contaminant protection of engine subsystems during a 250-hour oil aging test with a dual-loop lubricating system. (Cheng, report II.5)

- The Massachusetts Institute of Technology 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 2014 they: (1) Finalized their set of simulation-based turbocharged spark ignition engine performance maps for a range of different knock-suppressing fuels; (2) Validated a fundamentally-based chemical-kinetic methodology for predicting knock onset at peak cylinder conditions for different fuels; (3) Completed light-duty engine-in-vehicle simulations, using Automonie, quantifying the significant fuel economy benefits that knock suppression provides; and (4) Initiated work on onboard fuel separation to produce the high-octane ethanol stream this approach requires. (Heywood, report II.6)
- 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 2014 they: (1) Developed a novel two-zone piston bowl analytically; (2) conducted LD testing of analytically developed two-zone piston bowl with comparison to Open bowl; and (3) Demonstrated HD RCCI combustion at the rated power point (1,800 rpm, 21 bar indicated mean effective pressure). The data were acquired with a 12:1 compression ratio, but still had a 48% gross indicated efficiency with engine-out oxides of nitrogen below 0.25 g/kg-f and peak pressure rise rates below 10 bar/deg. (Reitz, report II.7)

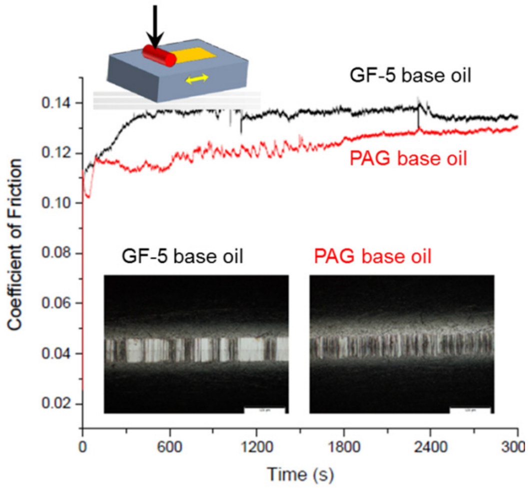


A novel two-zone piston bowl design was developed which addresses three of the major challenges associated with RCCI combustion. (Reitz, report II.7)

- Argonne National Laboratory is developing hybrid base-stock fluids as lubricants to minimize viscosity and thus improve fuel economy. In FY 2014 they: (1) Formulated hybrid base-stock mixtures with different polyalphaolefin (PAO)-ester ratios; (2) Measured rheological properties for hybrid base-stock blends. Various PAO-ester ratios showed substantially lower viscosity than mineral-based lubricants (over two-times reduction at both low and high temperature); (3) Evaluated traction coefficient under slide/roll contact for different PAO-ester ratios. All blended mixtures showed lower traction coefficient compared to pure PAO; and (4) Determined that friction and wear performance of all PAO-ester mixtures under sliding contact was superior to that of PAO alone. Up to 50% friction reduction and up to six times less wear were determined for the hybrid mixtures compared to PAO of similar viscosity. (Lorenzo-Martin, report II.8)
- Argonne National Laboratory is identifying and incorporating catalytically active non-ferrous metallic and ceramic ingredients in a nanocomposite coating that can derive carbon-based boundary films from long-chain hydrocarbon molecules of lubricating oils. In FY 2014 they: (1) Achieved a 2.2 µm-thick coating with very strong adhesion and confirmed a very smooth surface finish; (2) Ran many coating trials to further optimize the physical vapor deposition conditions in a commercial-scale coating unit and successfully produced a range of non-ferrous coatings on test samples for tribological evaluation; (3) Optimized the bonding, thickness, and surface finish of these coatings by effectively controlling the deposition parameters; and (4) Procured the sputtering targets for the synthesis of other non-ferrous coatings (NbN-Ni, NbN-Cu, WN-Ni, WN-Cu, MoN-Ni, etc.). (Erdemir, report II.9)
- Argonne National Laboratory is developing, optimizing, and implementing novel boron-based lubricant formulations to achieve higher fuel economy, longer durability, and better environmental compatibility in engines in order to reduce dependence on imported oil. In FY 2014 they: (1) Completed compatibility studies of surfactant-functionalized nanolubricant with base and fully formulated engine oils; (2) Optimized lubricant formulations based on boron chemistries; (3) Completed bench tribology studies of optimized lubricants, showing as much as 80% reduction in friction and more than two orders of magnitude reduction in wear; (4) Completed scuffing studies, showing 30 to 40% increase in scuffing load of formulated engine oils; (5) Completed surface analytical studies, revealing a boron-rich boundary film on rubbing surfaces; (6) Completed friction, wear, and scuffing studies with conventional and

PC-11 type diesel oils, showing 50% reduction in friction, as well as 30 to 40% improvement in wear rates and scuffing loads; and (7) Completed initial engine tests, showing as much as 2.5% fuel economy improvements under regimes where boundary and mixed lubrication prevail. (Erdemir, report II.10)

- Oak Ridge National Laboratory 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 2014: (1) Synergistic effects on friction and wear reductions were discovered when combining phosphonium-phosphate ILs with zinc dialkyldithiophosphate, while such synergy was not observed for other groups of ILs; (2) Mechanistic understanding is being achieved for the IL+ zinc dialkyldithiophosphate synergism; (3) Top candidate ILs have passed the standard no harm storage and elastomer compatibility tests, as required for automotive engine oil additives; and (4) The compatibility of the top-performing IL with other additives in the engine oil formulation is currently being investigated. (Qu, report II.11)
- 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 2014 they evaluated and compared various PAG oil formulations to the standard SAE 5W20 oil. Efforts included valvetrain wear measurements, traction coefficient measurements with and without additives, motored engine friction evaluations, fired engine dyno tests for fuel economy (ASTM Sequence VID) and wear assessments (ASTM Sequence IIIG and Sequence IVA tests) and chassis roll dynamometer fuel economy tests. (Gangopadhyay, report II.12)



Coefficient of Friction at 100°C (Gangopadhyay, report II.12)

- Northwestern University is developing novel lubricant formulations for improving vehicle fuel efficiency by at least 2% without adversely impacting vehicle performance or durability. In FY 2014 they: (1) Designed, synthesized, and characterized three major families of heterocyclic additives; (2) Found excellent boundary lubrication additives to reduce friction maximally by ~45% with the laboratory-scale tests; (3) Obtained a visible lubrication enhancement and friction reduction in the boundary lubrication regime using the as-synthesized additives in fully formulated 5W30 engine oil; (4) Conducted the first stage synthesis of a di-block PMMA-(LCB) polyalphaolefin copolymer; (5) Found organosilane functionalized nanoparticles reducing friction by forming significant tribo-layers; and (6) Developed a method for molecular dynamic-supported modeling of base fluids. (Wang, report II.13)
- Valvoline is developing novel lubricant formulations that are expected to improve the fuel efficiency of medium-duty, commercial and military vehicles by at least 2% without adverse impacts on vehicle performance or durability. In FY 2014: (1) Two engine oil candidates have been developed and modeling work showed they meet the target fuel economy improvements of greater than 2%. Tribological bench tests showed the Candidate 2 has better wear and friction performances than the baseline; and (2) Two axle oil candidates have been developed and modeling work showed they meet the target fuel economy improvement of greater than 0.5%. Mini traction machine tests showed that both candidates have lower friction than the baseline under most testing conditions. (Wu, report II.14)
- Ford Motor Company is formulating new polyalkylene glycol-based gear oils that will improve the fuel efficiency of light- and medium-duty applications by 2% over 75W140 grade axle oils without adverse impacts on vehicle performance or durability. In FY 2014 they initiated the dynamometer-based axle efficiency test. (Gangopadhyay, report II.15)
- Pacific Northwest National Laboratory is developing novel polymers with a hyperbranched architecture to be used as viscosity modifiers, and developing a fundamental understanding of polymer architecture and

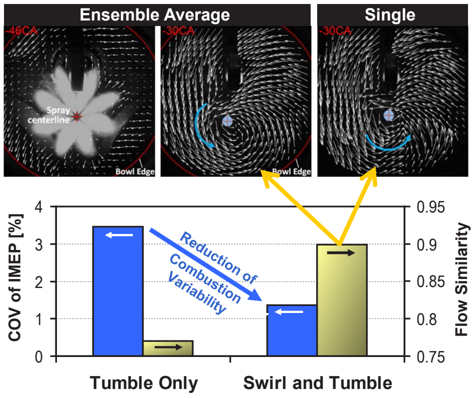
ability to affect the viscosity of a base oil. In FY 2014 they: (1) Established screening protocol (Brookfield viscometer) for viscosity index measurements at 40 and 100°C; (2) Synthesized several branched and hyperbranched polymers with adequate base oil solubility; and (3) Established collaborations with scientists at Argonne for high temperature, high shear testing. (Cosimbescu, report II.16)

- Pacific Northwest National Laboratory is designing and developing multi-functional base oils by incorporating chemical/material functionality responsible for one or more of the properties typically provided by lubricant additives, while maintaining or improving lubricant performance. In FY 2014: (1) A pin-on-disk wear measurement capability has been established coupled with a profilometer and software to enable evaluation of wear. This is an important milestone, as the set-up will benefit multiple tasks within the lube projects; (2) Initial base oil synthetic strategies led to several candidates; (3) Implemented methodology for tribological additive task, and started preliminary tests of known additives; and (4) Completed initial calculations using model base oil compounds. (Cosimbescu, report II.17)

### 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.

- Oak Ridge National Laboratory is investigating the opportunities and challenges that advanced transportation fuels, including renewable fuels, have on advanced combustion regimes and emerging engine technologies. In FY 2014 they: (1) Attained the 2014 technical target of demonstrating biodiesel blends allowed an improvement in reactivity controlled compression ignition (RCCI) operating range allowing for a simulated 75% coverage of the federal city and highway driving cycles; and (2) Compared RCCI with conventional fuels and gasoline compression ignition with a 68 Research Octane Number gasoline for efficiency, load expansion and controllability on premixed pistons. (Curran, report III.1)
- Sandia National Laboratories 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 2014 they: (1) Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council in formulating and blending a set of diesel surrogate fuels with different compositional fidelities relative to a single target fuel; (2) Conducted optical-engine experiments on methyl decanoate in a mixing-controlled combustion mode, showing that this biodiesel component can effectively eliminate engine-out soot emissions; and (3) Developed and applied a new laser-induced incandescence imaging technique to show the distribution of soot in the entire region above the piston bowl throughout the expansion stroke, and used the images to estimate the total mass of in-cylinder soot as a function of crank angle. (Mueller, report III.2)
- Sandia National Laboratories 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 2014 they: (1) Demonstrated combined effects of gasoline-ethanol blend ratio and spark-timing strategy on exhaust soot; (2) Quantified and examined in detail factors that govern heat release rate and its variability when the stratification level is tailored to the fuel composition. This included optical measurements of spray variability, flow field and flame development; (3) Quantified lean stability limits and fuel efficiency gains for 85% ethanol and 15% gasoline (E85) and gasoline fuels; (4) Examined combined effects of intake heat and fuel type on the ability to achieve controlled end-gas autoignition for higher combustion efficiency for lean spark ignition operation; and (5) Conducted a combined optical/performance study of advanced multi-pulse transient plasma ignition for E85, explaining fundamental ignition requirements for stable ultra-lean combustion. (Sjoberg, III.3)



Spray-swirl interaction causes flows that are more repeatable from cycle-to-cycle. (Sjoberg, report III.3)

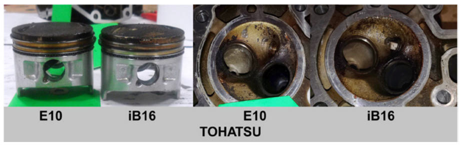
- Oak Ridge National Laboratory is investigating the opportunities and challenges of gasoline boiling range non-petroleum-based fuels on advanced combustion regimes and emerging engine technologies. In FY 2014 they: (1) Concluded through vehicle fuel economy estimates that for a vehicle with a downsized/downsped engine designed to run on 30% ethanol, the fuel energy density penalty associated with ethanol can be recovered by increased engine and vehicle system efficiency; (2) Found that homogeneous charge compression ignition is more compatible with larger engine displacement, and may be counter to current industry trends of downsizing and downspeeding; and (3) Completed the installation of a unique flexible multi-cylinder engine to pursue the Oak Ridge National Laboratory in-cylinder reforming strategy. (Szybist, report III.4)
- Ford Motor Company is identifying how fuel properties can be used to achieve controllable Extended Lift-Off Combustion with low oxides of nitrogen and particulate matter emissions. In FY 2014: (1) A model for tri-propylene glycol methyl ether blends has been validated for ignition delay, flame lift-off, soot location and soot magnitude at typical modern diesel engine boundary conditions; (2) Modeling suggested soot production is not only dependent on the fuel oxygen ratio, but also lift-off length and the number of carbon-carbon bonds in the fuel; (3) Using a newly validated oxygenate model, estimated the minimum fuel oxygen ratio to meet Low Emission Vehicle III particulate matter without a diesel particulate filter to be ~4.6% based on modeling results; (4) A 17% reduction in nozzle flow rate was possible while still meeting full-load requirements, which will help enable single-cylinder engine leaner lifted flame combustion operation; and (5) Leaner lifted flame combustion operation was achieved under realistic boundary conditions using a two-hole nozzle tip with T50 fuel. (Kurtz, report III.5)
- Oak Ridge National Laboratory 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 2014 they: (1) Demonstrated major fuel effects on GDI PM oxidation for both ethanol and isobutanol; and (2) Characterized start-stop PM emissions for a 2015 GDI vehicle operating on gasoline, gasoline-ethanol, and gasoline-isobutanol blends. (Storey, report III.6)
- The National Renewable Energy Laboratory is addressing technical barriers of inadequate data and predictive tools for fuel and lubricant effects on combustion, engine optimization, emissions, and emission control systems, and developing understanding of fuel chemical and physical properties that enable furtherance of the Advanced Combustion Engines Research and Development program for high-efficiency engines with cost-effective emission controls. In FY 2014 they: continued development of Ignition Quality Tester-based experimental and simulation research platform to characterize fuel ignition properties, and conducted a parametric study with the National Renewable Energy Laboratory's direct-injection, spark-ignition single-cylinder engine research facility to isolate various fuel chemistry effects with the potential to increase engine efficiency, including isolation of heat of vaporization fuel effects. (Zigler, report III.7)

### 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.

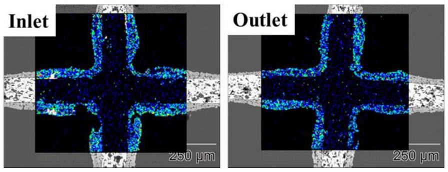
- Oak Ridge National Laboratory is identifying fuel properties and specific combustion products to provide data for a better understanding of the properties, combustion characteristics, and systems compatibility of advanced fuels and lubricants fuels. In FY 2014 they: (1) Developed a chemical analysis method for a defined soot particle size range utilizing a micro-orifice uniform deposit impactor and thermal/pyrolysis gas chromatograph-mass spectrometry; and (2) Measured nitroalkanes in the exhaust of a reactivity-controlled compression ignition engine. (Lewis, report IV.1)
- Pacific Northwest National Laboratory 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 2014 they: (1) Continued development of new nuclear magnetic resonance approaches for identifying structure-property relationships of diesel fuels, focusing on the two-dimensional nuclear magnetic resonance technique, single-bond proton-carbon correlation; (2) Continued collaboration with CanmetENERGY to develop structure-property relationships for diesel fuel lubricity using nuclear magnetic resonance and gas chromatography-field ionization mass

spectrometry data; and (3) Continued collaborative efforts with the Coordinating Research Council through participation in the Fuels for Advanced Combustion Engines Working Group, and contributions to the Coordinating Research Council Projects. (Bays, report IV.2)



Comparison of Pistons and Cylinder Heads (cylinder number 1) for the Tohatsu Engines Operated on E10 and iB16 (Wallner, report IV.3)

- Argonne National Laboratory is assessing the suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications. In FY 2014: (1) Engine cold-start performance was found to be nearly identical between iB16 and E10 fuel blends at 24°C. The data indicate a reduction in time to start at -1°C for the Mercury four-stroke outboard engine operating on iB16 compared to E10 fuel; (2) Engine tear-down inspections performed after full useful life durability testing indicate similar wear characteristics between control engines operated on E10 and test engines operated on iB16; (3) End of season testing performed on field test engines operated on tri-fuel blends indicate similar gaseous emissions and engine performance as E10 test fuels. All engines remained below the Environmental Protection Agency emissions standards for hydrocarbons plus oxides of nitrogen and carbon monoxide, and no engine runability or durability issues were encountered during the testing program; and (4) An additional 100 hours of field testing of two vessels operating 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. (Wallner, report IV.3)
- Argonne National Laboratory is developing physics-based nozzle flow and spray models for biodiesel from different feedstocks, developing chemical kinetic models for biodiesel from different feedstocks, developing computation fluid dynamics tools to perform engine simulations to gain further insights into biodiesel performance and emission characteristics. In FY 2014: (1) Five different fuels with different physical properties were simulated and in-nozzle characteristics such as cavitation, injection velocity and turbulence levels were determined; (2) A chemical kinetic mechanism to represent combustion characteristics of soy-based methyl ester was developed for computational fluid dynamics applications and this mechanism has been made available to the industry and academia; and (3) A comprehensive experimental campaign was performed to determine the combustion and emission characteristics of cuphea methyl ester and compared against diesel fuel. (Som, report IV.4)
- The National Renewable Energy Laboratory is developing a detailed understanding of issues that are preventing biodiesel blends from attaining drop-in fuel status. In FY 2014 they: (1) showed Furans and methyl aryl ethers such as anisole have excellent gasoline properties because of their insolubility in water, minimal impact on vapor pressure, and high blending octane numbers; (2) Phenol (and also the higher boiling cresol and guaiacol) cannot be used as drop-in fuel components because of their solubility in water and impact on phase separation temperature; (3) Ketones (represented by hexanone) have low octane number but did not negatively impact gasoline performance properties when blended at low levels; (4) Measurement of fine particulate matter emissions from a gasoline direct injection engine showed that particle number emissions could increase by up to a factor of three upon blending of the aromatic oxygenates, indicating no impact of the oxygen atom on particulate matter formation; and (5) Biomass pyrolysis oxygenates boiling in the diesel range are primarily phenolic and methyl aryl etherscompounds. (McCormick, report IV.5)
- The National Renewable Energy Laboratory is developing a fundamental understanding of how saturated monoglycerides (SMGs) may influence the co-crystallization of minor components in biodiesel and how this may affect the cloud point and cold weather performance (fuel filter clogging) of both the biodiesel and blends with diesel. In FY 2014 they: (1) Determined that the solubility of SMGs can vary greatly in different components of diesel fuel; (2) Demonstrated that SMGs can cause other components found in biodiesel to come out of solution at higher temperatures than expected by providing a surface for the compounds to co-crystallize on; (3) Demonstrated that SMGs in conjunction with other minor components leads to increased filtration times; and (4) Showed crystals containing monoolein physically appeared to stack higher on the filters than when only SMGs were present. (Chupka, report IV.6)



Electron Probe Micro-Analysis Maps of Na Collected from Cross-Sections of the Fully-Aged DOC 1 cm from the Inlet (left) and Outlet (right). (McCormick, report IV.7)

- The National Renewable Energy Laboratory is quantifying the impact of fuel metal impurities on the performance and durability of engine exhaust aftertreatment components. In 2014: (1) A heavy-duty aftertreatment system was aged for 1,001 hours, simulating the full useful life (435,000 miles) using a 20% blend of biodiesel in diesel fuel (B20) which was doped with Na to represent the allowable ASTM standard with a 14x acceleration factor; (2) Tailpipe oxides of nitrogen emissions were tested periodically throughout the aging process over the Federal Test Procedure and shown to increase to 0.41 g/bhp-hr with the fully-aged system, exceeding the family emission limit of 0.33 g/bhp-hr for engine and aftertreatment certification; (3) Diesel particulate filter weights were also taken periodically throughout the aging process and it was determined that biodiesel derived ash from the Na dopant was a significant contributor, estimated to account for over 80% of the total ash load (50 g/L); (4) Analysis of the aged components using electron probe microanalysis showed Na to be deposited throughout the thickness of the washcoat and along the entire diesel oxidation catalyst (DOC) length; and (5) Individual components of the aged system were replaced by new degreened parts and hot-start Federal Test Procedure tests showed 65% of the increased oxides of nitrogen emissions could be attributed to the aged diesel oxidation catalyst/diesel particulate filter and 35% was due to the degraded selective catalytic reduction catalyst. (McCormick, report IV.7)

## Special Honors/Recognitions

**1.** 2014 R&D 100 award winner: Ionic Liquid Anti-wear Additives for Fuel-efficient Engine Lubricants - Jun Qu, Huimin Luo, Sheng Dai, Peter Blau, Todd Toops, Brian West, Bruce Bunting, Mike Viola, and Ewa Bardasz. (Toops, report II.1)

**2.** 2014 Oak Ridge National Laboratory Significant Event Award (SEA): Development of lubricant that meets DOE goal of 2 percent vehicle fuel economy improvement - Jun Qu, Huimin Luo, Sheng Dai, Todd Toops and Peter Blau. (Toops, report II.1)

**3.** 2014 R&D 100 Award, jointly among ORNL, GM, Shell, and Lubrizol, Ionic liquid anti-wear additives for fuel-efficient engine lubricants. (Qu, report II.11)

**4.** C.J. Mueller received a Society of Automotive Engineers (SAE) Lloyd L. Withrow Distinguished Speaker award at the 2014 SAE International Congress and Exposition in Detroit, Michigan. (Mueller, report III.2)

**5.** Magnus Sjöberg received an SAE Excellence in Oral Presentation Award for a presentation of stratified DISI operation using E85 fuel at the SAE/KSAE 2013 Powertrains, Fuels & Lubricants meeting in Seoul, South Korea. (Sjoberg, report III.3)

**6.** Wisconsin Business Friend of the Environment Award in recognition of the unique emissions sampling equipment developed in support of the U.S. Department of Energy's search for a more environmentally friendly gasoline alternative. Wisconsin Manufacturing and Commerce May, 2014. (Wallner, report IV.3)

**7.** Press release announcing Gulf Racing Fuels supplying three new fuels for marine and all-terrain vehicle use containing 16.1 vol% iso-butanol (iso-butanol sourced from Gevo) http://www.biofuelsdigest.com/bdigest/2014/10/02/gevo-sells-isobutanol-to-gulf-racing-fuels-for-marine-and-off-road/ (Wallner, report IV.3)

**8.** Dr. Sibendu Som: High Performance Computing Innovation Excellence Award from International Data Corporation, June 2014. (Som, report IV.4)

**9.** Dr. Sibendu Som: Invitee to US-Frontiers of Engineering workshop organized by National Academy of Sciences (only 100 people under the age of 45 were invited). (Som, report IV.4)

## Patents Issued/Pending

**1.** O.O. Ajayi, C. Lorenzo-Martin, and G.R. Fenske, "A Tribochemical Synthesis Method for Producing Low-Friction Surface Film Coatings," U.S. Patent application (Pending). (Ajayi, report II.4)

**2.** J. Qu and H. Luo, "Ionic liquids containing symmetric quaternary phosphonium cations and phosphorus-containing anions, and their use as lubricant additives," U.S. Patent Application 14/184,754, filed on Feb. 20, 2014. (Qu, report II.11)

**3.** A patent application (14548850) was filed on Nov 20, 2014. (Wu, report II.14)

**4.** Provisional US Patent Application #62058613, "Ducted Fuel Injection," filed October 1, 2014. (Mueller, report III.2)

## 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 High-Efficiency 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.

- Oak Ridge National Laboratory is identifying important deactivation mechanisms of emissions control devices that are impeding the implementation of efficient lean-burn technology. In FY 2015 they will: (1) Investigate the impact of other new lubricant additive formulations on the catalytic activity of three-way catalyst, diesel oxidation catalysts, and selective catalytic reduction catalysts; and (2) Confirm location of Na in emissions control systems and determine if its presence was the cause of the observed deactivation. (Toops, report II.1)
- Argonne National Laboratory 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 2015 they plan to provide the ability to evaluate advanced technologies in terms of their performance and mechanisms (do the benchtop tests replicate the mechanisms expected in engines?) before they progress to the next level of validation testing. (Demas, report II.2)
- Argonne National Laboratory is developing and optimizing lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles. In FY 2015 they plan to: (1) Refocus the project to the development of a colloidal additive system in order to address the stability issue with nano-additive systems; (2) Develop and synthesize colloidal-based friction reducing, wear reducing, scuffing preventing, and thermal dissipating lubricant additives; (3) Evaluate the scuffing performance of potential nano-additive and colloidal additive systems with standard block-on-ring test protocol; (4) Analyze nano-structure of tribo-chemical films formed from nano-additive and colloidal systems using transmission electron microscopy with focused ion beam; (5) Evaluate the thermal properties and behavior of colloidal lubricant additive systems; and (6) Measure nanoscale mechanical properties of the tribo-chemical films formed from particulate colloidal additive systems. (Ajayi, report II.3)
- Argonne National Laboratory is seeking to develop a better understanding of the nature (structure), composition, and the mechanisms of formation of tribochemical surface films. In FY 2015 they plan to: (1) Conduct tribological performance evaluation in terms of scuffing and wear under severe contact conditions for additives that produce low-friction tribochemical films; (2) Evaluate the basic mechanisms of scuffing in engine components; (3) Determine and formulate constitutive equations to enable friction prediction and modeling at the lubricated interface; and (4) Develop empirical relationship between base-fluid viscosity and boundary-regime frictional behavior. (Ajayi, report II.4)
- The Massachusetts Institute of Technology is identifying the best lubricant formulations for individual engine subsystems and 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 2015 they plan to: (1) Continue to develop advanced power cylinder friction models incorporating local oil composition changes; (2) Experimentally investigate the effect of additive changes on valvetrain subsystem losses through parametric studies; (3) Experimentally investigate the effect of oil aging in separate lubricant subsystems under different operating conditions and with different additive packages; (4) Experimentally investigate opportunities for material selection in engine subsystems given the implementation of a dual-loop lubricating system; and (5) Further investigate the effect of oxidation in valvetrain lubricants. (Cheng, report II.5)
- The Massachusetts Institute of Technology 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 2015 they plan to: (1) Complete their experiments that determine the octane requirements of their turbocharged 2-liter engine at mid and low loads to explore the application of onboard membrane fuel separation (pervaporation);

(2) Quantify the knock-suppressed turbocharged engine fuel economy benefits in medium-duty vehicles; and (3) Analyze the single-cylinder spark ignition engine data from Cummins and compare it with their performance maps. (Heywood, report II.6)

- 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 2015 they will complete final reporting and publish a technical paper. (Reitz, report II.7)
- Argonne National Laboratory is developing hybrid base-stock fluids as lubricants to minimize viscosity and thus improve fuel economy. In FY 2015 they plan to: (1) Develop a thermodynamic model to predict rheological properties of binary and ternary fluid mixtures; (2) Conduct comprehensive characterization of rheological properties of additional hybrid base stocks produced from different chemistries and viscosities; (3) Evaluate friction and wear performance of fluid mixtures with optimized rheological properties; and (4) Evaluate the effect of model additives on friction and wear behavior of base-stock fluid mixtures. (Lorenzo-Martin, report II.8)
- Argonne National Laboratory is identifying and incorporating catalytically active non-ferrous metallic and ceramic ingredients in a nanocomposite coating that can derive carbon-based boundary films from long-chain hydrocarbon molecules of lubricating oils. In FY 2015 they plan to: (1) Develop and optimize non-ferrous coatings in nanocomposite form; (2) Optimize coating microstructure, adhesion, hardness, surface roughness, and chemistry; (3) Perform detailed characterization of chemistry and structure of the coatings using both surface and structure-sensitive techniques; and (4) Evaluate effects of coating composition on tribological behavior under boundary-lubricated sliding regimes. (Erdemir, report II.9)
- Argonne National Laboratory is developing, optimizing, and implementing novel boron-based lubricant formulations to achieve higher fuel economy, longer durability, and better environmental compatibility in engines in order to reduce dependence on imported oil. In FY 2015, based on the very encouraging results from rigorous bench and limited engine studies, more comprehensive engine and valvetrain tests should be conducted on the optimized lubricant formulations to determine their long-term engine-specific efficiency and durability benefits. Of particular interest in these tests will be the long-term additive-lubricant interactions (if any) and their impact on engine performance and efficiency. (Erdemir, report II.10)
- Oak Ridge National Laboratory is developing oil-soluble ionic liquids (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 FY 2015 they plan to: (1) Formulate a low-viscosity engine oil using the IL [P8888][DEHP] + zinc dialkyldithiophosphate as anti-wear additives; (2) Conduct Sequence VID/VIE engine dynamometer tests on the formulated IL-additized engine oil to demonstrate improved engine mechanical efficiency; (3) Investigate the effects of an IL-zinc dialkyldithiophosphate combination on three-way catalysts using an accelerated small engine test; and (4) Gain further fundamental understanding of the synergism between ILs and zinc dialkyldithiophosphate. (Qu, report II.11)
- 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 2015 they plan to: (1) Complete valvetrain wear measurements; (2) Complete analysis of tribo-films formed on contacting surfaces to understand friction reduction mechanism(s); (3) Complete any additional ASTM Sequence tests to demonstrate fuel economy, anti-oxidation and wear protection capabilities; and (4) Complete chassis roll dynamometer fuel economy and emission evaluations of fresh and aged oils. (Gangopadhyay, report II.12)
- Northwestern University is developing novel lubricant formulations for improving vehicle fuel efficiency by at least 2% without adversely impacting vehicle performance or durability. In FY 2015 they plan to: (1) Continue designing, synthesizing, and optimizing oil-soluble boundary lubrication additives and the copolymer viscosity modifier; (2) Develop lubricant formulations using the optimized boundary lubrication additives and the newly-synthesized copolymer viscosity modifier; (3) Conduct a comprehensive study on the tribological and rheological properties of the initial lubricant formulations; (4) Conduct detailed physical/chemical investigations of surface functionalizations and additive-surface

interactions; (5) Develop molecular dynamic simulations to visualize surface adsorptions of the additives and to predict molecular structure-viscosity relations. Investigate and model lubrication mechanisms; and (6) Transfer the successfully formulated lubricants from laboratory investigations to industrial tests. (Wang, report II.13)

- Valvoline is developing novel lubricant formulations that are expected to improve the fuel efficiency of medium-duty, commercial and military vehicles by at least 2% without adverse impacts on vehicle performance or durability. In FY 2015: (1) For engine oil, the next step is to run the National Renewable Energy Laboratory ISL 8.9-L engine fuel efficiency verification test. Improvement of around 2% against the baseline is anticipated; (2) For axle oil, the next step is to run the axle efficiency verification test and do reformulation if necessary. Greater than 0.5% improvement against the baseline is anticipated; (3) Transmission fluid preparation of multiple candidates for SAE #2 tests is underway. A candidate will be picked after comparison of multiple properties with the baseline; and (4) Conduct SAE J1321 test for the system of the aforementioned three types of lubricants at the Transportation Research Center Inc. in East Liberty, OH. Greater than 2% total fuel efficiency is expected. (Wu, report II.14)
- Ford Motor Company is formulating new polyalkylene glycol-based gear oils that will improve the fuel efficiency of light- and medium-duty applications by 2% over 75W140 grade axle oils without adverse impacts on vehicle performance or durability. In FY 2015 they plan to: (1) Complete analyzing tribo-films formed on contacting surfaces to understand friction reduction mechanism(s); (2) Complete laboratory bench rig friction and wear studies; (3) Conduct fatigue and micro-pitting studies at Argonne National Laboratory; and (4) Complete SAE International Technical Specification J2360 level tests (L-33-1 and L60-1). (Gangopadhyay, report II.15)
- Pacific Northwest National Laboratory is developing novel polymers with a hyperbranched architecture to be used as viscosity modifiers, and develop a fundamental understanding of polymer architecture and ability to affect the viscosity of a base oil. In FY 2015 they plan to: (1) Explore hybrid structures (comb, branched and star polymers) as well as dendronized polymers as potential next generation additives; (2) Re-evaluate molecular design targets based on tribological and high-temperature, high-shear data; and (3) Hyperbranched polymer systems will be studied further and novel structural permutations will be investigated to increase their lipophilic (non-polar) character. (Cosimbescu, report II.16)
- Pacific Northwest National Laboratory is designing and developing multi-functional base oils by incorporating chemical/material functionality responsible for one or more of the properties typically provided by lubricant additives, while maintaining or improving lubricant performance. In FY 2015 they plan to: (1) Evaluate at least three synthesized base oils for viscosity, wear and friction against unadditized commercial base oils; (2) Develop structure-property relationships based on the series of materials prepared and continue to develop the series of compounds; (3) Continue to investigate the potential of tribopolymers as a renewable in situ additive and expand beyond caprolactams and caprolactones; (4) Optimize testing conditions to achieve tribopolymers with known materials; (5) Continue to explore conformational and size changes using dynamic light scattering, diffusion-ordered spectroscopy, and small angle neutron scattering; and (6) Demonstrate the value of modeling in predicting viscosity changes with temperature of viscosity modifiers. (Cosimbescu, report II.17)

### 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.

- Oak Ridge National Laboratory is investigating the opportunities and challenges that advanced transportation fuels, including renewable fuels, have on advanced combustion regimes and emerging engine technologies. In FY 2015 they plan to: (1) Continue reactivity controlled compression ignition (RCCI) and single-fuel low-temperature combustion experiments with a variety of fuels on the stock diesel piston including transient effects; (2) 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 (i.e. ethanol and biodiesel); (3) Investigate the potential for alternative fuels to expand the drive-cycle coverage of advanced combustion leading to higher potential fuel economy and lowered emissions; (4) Evaluate gasoline compression ignition as compared to RCCI on the same engine, with the same hardware over a variety of gasoline-range fuels that seem well suited for gasoline compression ignition; and (5) Identify alternative fuels that may have high enabling potential for advanced combustion. (Curran, report III.1)

- Sandia National Laboratories 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 2015 they plan to: (1) Conduct engine tests on a target #2 diesel fuel and the set of corresponding diesel surrogate fuels described in this report to determine the level of surrogate-fuel compositional fidelity required to adequately match the target-fuel combustion performance; (2) Compare the combustion performance of methyl decanoate to that of an ether/diesel-fuel blend with similar properties at injection pressures up to 2,400 bar, to determine how oxygenate molecular structure affects the ability of a fuel to mitigate in-cylinder soot formation; and (3) Assess the efficacy of injecting fuel through in-cylinder ducts as a means to enhance mixing rates and mitigate in-cylinder soot formation, to enable the deployment of less expensive fuels and exhaust gas aftertreatment systems. (Mueller, report III.2)
- Sandia National Laboratories 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 2015 they plan to: (1) Examine the use of intake boost for load-range extension of stratified-charge operation; (2) 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; (3) Continue examination of well-mixed lean/dilute operation, using both regular spark and advanced multi-pulse ignition systems in combination with 0% to 30% ethanol-gasoline blends; and (4) Examine the effect of fuel type on combustion and fuel economy gain for spark ignition operation with partial fuel stratification. (Sjoberg, report III.3)
- Oak Ridge National Laboratory is investigating the opportunities and challenges of gasoline boiling range non-petroleum-based fuels on advanced combustion regimes and emerging engine technologies. In FY 2015 they plan to: (1) Investigate fuel effects of the exhaust gas recirculation dilution limits for spark ignition combustion both with and without simulated reformate; and (2) Characterize fuel-specific differences of the Oak Ridge National Laboratory in-cylinder reforming strategy on the flexible multi-cylinder engine. (Szybist, report III.4)
- Ford Motor Company is identifying how fuel properties can be used to achieve controllable Extended Lift-Off Combustion with low oxides of nitrogen and particulate matter emissions. In FY 2015 they plan to: (1) Complete study of tri-propylene glycol methyl ether and hydrocarbon fuels with different cetane rating methods to better understand cetane rating results and the disparity between test methods; (2) Complete modeling projects at University of Wisconsin in December 2014, finalizing the investigation of the effect of fuel structure on soot formation; (3) Use models to finalize an improved combustion system design to enable single-cylinder engine leaner lifted flame combustion; (4) Complete optical engine experiments using a six-hole nozzle and T50 fuel; and (5) Demonstrate non-sooting diesel combustion on a single-cylinder engine with modern power density requirements. (Kurtz, report III.5)
- Oak Ridge National Laboratory is quantifying fuel and lubricant effects on particulate matter (PM) formation in gasoline direction 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 2015 they plan to: quantify fuel effects on the GDI vehicle start-stop PM emissions, and evaluate fuel effects on the oxidation kinetics of the PM collected on gasoline particulate filter cores. (Storey, report III.6)
- The National Renewable Energy Laboratory is addressing technical barriers of inadequate data and predictive tools for fuel and lubricant effects on combustion, engine optimization, emissions, and emission control systems, and developing understanding of fuel chemical and physical properties that enable furtherance of the Advanced Combustion Engines Research and Development program for high-efficiency engines with cost-effective emission controls. In FY 2015 they plan to: continue expanding Ignition Quality Tester-based experimental and simulation research, and continue parametric gasoline direct injection single-cylinder engine research to isolate various fuel chemistry effects with the potential to increase engine efficiency, and correlate novel fuel ignition measurements adapted from the Ignition Quality Tester. (Zigler, report III.7)

### 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.

- Oak Ridge National Laboratory is identifying fuel properties and specific combustion products to provide data for a better understanding of the properties, combustion characteristics, and systems compatibility of advanced fuels and lubricants fuels. In FY 2015 they plan to evaluate the size dependent chemical composition of particulate matter derived from the combustion of advanced biofuels and biofuel blends. (Lewis, report IV.1)
- Pacific Northwest National Laboratory 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 2015 they plan to: (1) Continue to develop structure-property correlations built upon data obtained from current fuel sets; (2) Identify key molecular structures in unconventional fuels, which have the greatest impact on fuel properties and performance; (3) Continue to coordinate the interaction with CanmetENERGY on analytical correlation of fuel properties and material compatibility investigations; and (4) Continue collaborative work with members of the Coordinating Research Council's Working Group and the Alternative and Surrogate Fuels projects. (Bays, report IV.2)
- Argonne National Laboratory is assessing the suitability of butanol as a drop-in fuel for blending with gasoline for recreational marine engine applications. In FY 2015 they plan to: (1) Determine critical blend level for iso-butanol in laboratory test engines; (2) 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 (3) Perform end-of-season testing on recreational marine engines operated on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends. (Wallner, report IV.3)
- Argonne National Laboratory is developing physics-based nozzle flow and spray models for biodiesel from different feedstocks, developing chemical kinetic models for biodiesel from different feedstocks, developing computation fluid dynamics tools to perform engine simulations to gain further insights into biodiesel performance and emission characteristics. In FY 2015 they plan to: (1) Complete the engine experimental campaign with cuphea, jatropha, and karanja fuels in the single-cylinder Caterpillar engine at Argonne and compare against diesel fuel for combustion and emission characteristics: (2) Develop a computational fluid dynamics model to simulate nozzle flow, spray, combustion, and emission characteristics for cuphea methyl ester for comparison with diesel fuel; and (3) Develop a "work-flow" to efficiently develop comprehensive computational fluid dynamics models for different biofuels that may be of interest to this project which will involve collaborations with experimentalists at Argonne, Sandia National Laboratories, and the National Renewable Energy Laboratory and the chemical kinetics group at Lawrence Livermore National Laboratory. (Som, report IV.4)
- The National Renewable Energy Laboratory is developing a detailed understanding of issues that are preventing biodiesel blends from attaining drop-in fuel status. In FY 2015 they plan to: (1) Evaluate particle mass and number emissions from a broader range of oxygenate structures and fuel properties; (2) Analyze the cause of dimethylfuran oxidative instability and determine if simple antioxidant additives can mitigate this issue for this promising high octane gasoline oxygenate; (3) Research the knock resistance properties of biomass oxygenates in more detail including temperature effects on autoignition and kinetics; and (4) Perform more extensive combustion and emissions characterization of diesel oxygenates. (McCormick, report IV.5)
- The National Renewable Energy Laboratory is developing a fundamental understanding of how saturated monoglycerides (SMGs) may influence the co-crystallization of minor components in biodiesel and how this may affect the cloud point and cold weather performance (fuel filter clogging) of both the biodiesel and blends with diesel. In FY 2015 they plan: (1) Additionally characterize crystals containing co-crystallized components; (2) Expand to the test matrix to include other fuel minor components, notably water; (3) Evaluate the influence of SMGs on gel formation and rheology in biodiesel blends;

and (4) Determine how additives could prevent or alter crystallization of SMGs and other components to reduce the cloud point of the fuel and prevent fuel filter clogging. (Chupka, report IV.6)

- The National Renewable Energy Laboratory is quantifying the impact of fuel metal impurities on the performance and durability of engine exhaust aftertreatment components. In 2015 they plan: (1) Further investigation of the influence from accelerated testing is needed and should be explored by repeating testing at a lower acceleration factor or potentially without acceleration to determine a deterioration factor; and (2) Aging conditions and test cycle selection need to be evaluated to determine if they are representative of real world engine operation. (McCormick, report IV.7)

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# II. Fuels and Lubricants to Enable High-Efficiency Engine Operation while Meeting 2007-2010 Standards

The trend toward turbocharging and down-speeding spark-ignited engines for higher efficiency is constrained by the need to keep engine compression ratios low to avoid pre-ignition with current fuels. These research projects explore fuel properties that can both result in lower carbon emissions and enhanced efficiency. Lubricant projects target lower friction as a means of improving fuel economy for the entire fleet while maintain low emissions.

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# II.1 Compatibility of Emerging Fuels and Lubricants on Emissions Control Devices using Accelerated Aging Techniques

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## Overall Objectives

- Identify important deactivation mechanisms of emissions control devices that are impeding the implementation of advanced fuels and lubricants
  - 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) 2014 Objectives

- Identify deactivation mechanism in three-way catalysts (TWCs) from both ionic liquid (IL) and zinc dialkyl-dithiophosphate (ZDDP) lubricant additives
- Illustrate progression of phosphorous from the two lubricant additives and compare effects on catalytic activity
- Determine impact on heavy-duty emissions control devices from operating system with 20% biodiesel in diesel fuel (B20) at full-useful life (FUL) exposure, 435,000 miles with 1 ppm Na in fuel
  - Effort is relative to the 5 ppm Na+K limit in 100% biodiesel (B100)
- Report impact of high levels of fuel-borne sulfur on selective catalytic reduction (SCR) catalyst activity

## FY 2014 Accomplishments

- Identified location and extent of P effect
  - Showed that the IL-aged TWC was less affected by aging then the ZDDP-aged catalyst in the following areas:
  - Light-off temperature of CO, NO and $C_3H_6$
  - Water-gas-shift (WGS) reactivity
  - Oxygen storage capacity
- Identified form of the P and what it was bound to
- In collaboration with the National Renewable Energy Laboratory (NREL) and Cummins, observed significant increase in oxides of nitrogen (NOx) emissions after aging heavy-duty emissions control system (diesel oxidation catalyst-diesel particulate filter-SCR catalyst, DOC-DPF-SCR) to FUL with 1 ppm Na in the B20 fuel (Na at the specification limit)
  - Replacing the individual emissions control devices suggests that the DOC and DPF deactivation contributes significantly to lost NOx reactivity
  - This is likely due to the observed decreased NO to $NO_2$ activity that is important for the achieving the highest activity of the SCR system
- Published in SAE International Journal of Fuels and Lubricants and submitted manuscripts to Catalysis Today and International Journal of Engine Research
- Published book chapter entitled "Fe-zeolite functionality, durability and deactivation mechanisms in the selective catalytic reduction (SCR) of NOx with ammonia," which included in *$NH_3$-SCR technology for deNOx aftertreatment of Diesel exhausts* (Springer Publishing)

## Future Directions

- Investigate impact of other new lubricant additive formulations on the catalytic activity of TWC, DOC, and SCR catalysis
- Confirm location of Na in emissions control systems and determine if its presence was the cause of the observed deactivation

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## INTRODUCTION

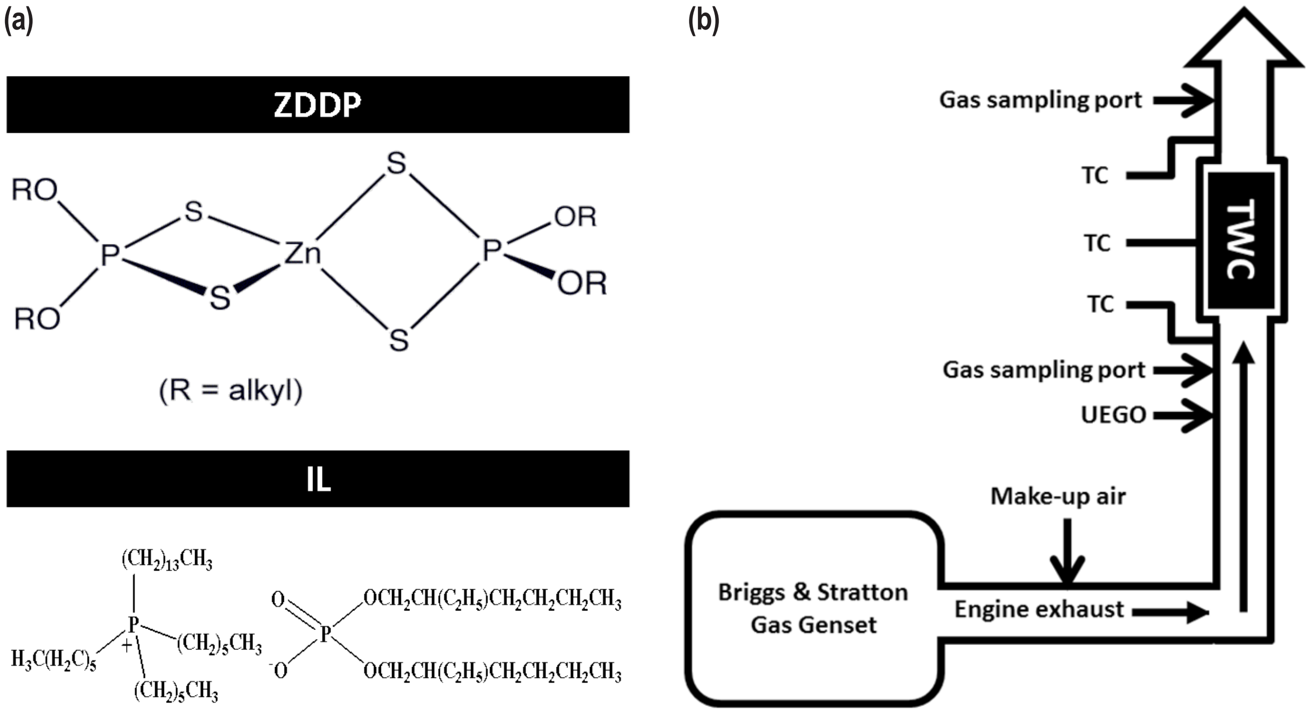
To enable new and emerging fuels to displace petroleum and advanced lubricants to improve efficiency, it is critical to evaluate their compatibility with existing and emerging emissions control devices. This effort develops and applies accelerated aging and poisoning techniques to the investigation of 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 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], thermal aging of lean-NOx traps [4-7] and SCR catalysts [8]. 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 ILs 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 [9-14]. In studying these processes we are hoping to either alleviate the concerns of the diesel vehicle industry or determine the deactivation mechanisms and suggest possible remedies. If the concerns can be alleviated it may be possible to increase the allowable biodiesel blend levels to 20% from the current 5% level.

## APPROACH

The investigation of aging mechanisms relies on accelerated techniques with the exact approach depending on the given concern. When necessary a representative engine will be employed but some approaches rely solely on bench flow reactors. In efforts this year, we employed a stoichiometric gasoline aging system to compare the impact of a novel IL lubricant additive to the industry standard, ZDDP, with respect to TWC chemistry. The chemistry of these two additives is shown in Figure 1a. The IL was added to the fuel and it underwent a combustion event before being exposed to the General Motors-provided TWCs. A schematic of the catalyst aging system is shown in Figure 1b. The amount of IL or ZDDP to be added to the fuel was based on the average oil consumption of several vehicles and was introduced through a 25-hour exposure with the TWC inlet temperature kept at 900°C. The TWCs that were exposed were thermally aged to FUL at General Motors before being used in the study such that the sensitivities of the P could be shown under their most vulnerable conditions. Bench reactor evaluation and extensive materials characterization were employed to evaluate the performance properties of the aged TWCs. In addition to standard light-off curves under stoichiometric operation, other functionalities, such as WGS activity, $CO+H_2O \rightarrow CO_2 + H_2$, and oxygen storage capacity were measured. For control measurements we also evaluated the FUL-TWCs in the as received state, and since additional thermal aging was occurring during our evaluation we aged a FUL-TWC without including the lubricant additives.

Additionally, we continued collaborating with NREL and Cummins to investigate the impact of Na, at the 5-ppm specification in biodiesel, on a heavy-duty emissions control system (DOC-DPF-SCR). The experimental details of this effort can be found elsewhere [13-14], but essentially NREL employed an accelerated technique to age a production exhaust system from a 2010 Cummins ISL. The long aging time of 1,000 hours dictated that only one exhaust system could be evaluated to the 435,000 mile FUL equivalent. Analysis of the aged catalysts included Federal Test Procedure emissions testing with the systems installed on a Cummins ISL at NREL, bench-flow reactor testing of catalyst cores at Cummins, and detailed materials characterization of the aged DOCs, SCRs, and DPFs at ORNL. This portion of



TC - thermocouple; UEGO - universal exhaust gas oxygen sensor

**FIGURE 1.** (a) Molecular structures of ZDDP and IL employed in the study. (b) These were added to the fuel and combusted using this accelerated catalyst aging system.

the project will only be briefly discussed this year as all of the analysis is not yet complete.

## RESULTS

After exposing the TWCs to both IL-18 and ZDDP, we initially measured the performance under stoichiometric conditions to determine the light-off reactivity. This involved flowing NO, CO and hydrocarbons with the precise amount of $O_2$ necessary to achieve full conversion of the reactants. Figure 2a displays the light-off temperatures at 50% gas conversion (i.e., T50) for NO, $C_3H_6$, and CO for inlet of the following parts: FUL as-received (FUL_AR), FUL no additive (FUL_NA), FUL with ZDDP (FUL_ZDDP), and FUL with IL-18 (FUL_IL). We can observe that all of the additionally aged catalysts have increased in T50 compared to the as received case, and more importantly that the T50 for FUL_IL in each case is lower than that for FUL_ZDDP, in fact, it is comparable to the no additive case for NO. While these differences are only on the order of 30°C the key observation is that the IL-18 does not introduce a different or more severe deactivation mechanism due to its differing chemistry than ZDDP. In looking at the WGS reactivity at 550°C in Figure 2b, a similar trend is observed as the ZDDP-aged TWC has the lowest reactivity, and although the FUL-IL TWC is affected after aging the impact is significantly muted. Similarly for oxygen storage capacity measurements (not shown) the ZDDP-aged TWCs were more affected than the IL-aged ones.

Further characterization of the devices was warranted to verify that the deactivation was indeed due to the P in the lubricant additives and to determine the differing nature of the P found on the TWCs. Elemental maps of P for the inlet, middle, and outlet parts of FUL_NA, FUL_ZDDP, and FUL_IL were obtained using electron probe microanalysis (EPMA) and are presented in Figure 3. In the case of FUL_NA, an overlayer of P can be observed at the inlet, but it is not observed in the middle and outlet parts. This layer originates from the FUL procedure that was accomplished using an engine that was running with ZDDP-containing lubricant. For the additive-exposed TWC, P not only covered the inlet washcoat surfaces, but also severely penetrated into the bulk. Moreover, we can observe an overlayer of P even for the middle and outlet parts of FUL_ZDDP. Despite a little difference observed for the EPMA maps of P between the inlets of FUL_ZDDP and FUL_IL, no overlay of P is observed for the middle and outlet parts of the IL-aged samples. This suggests that the form of the P in the exhaust originating from IL may be significantly different than when using ZDDP. To further study the interactions between P and

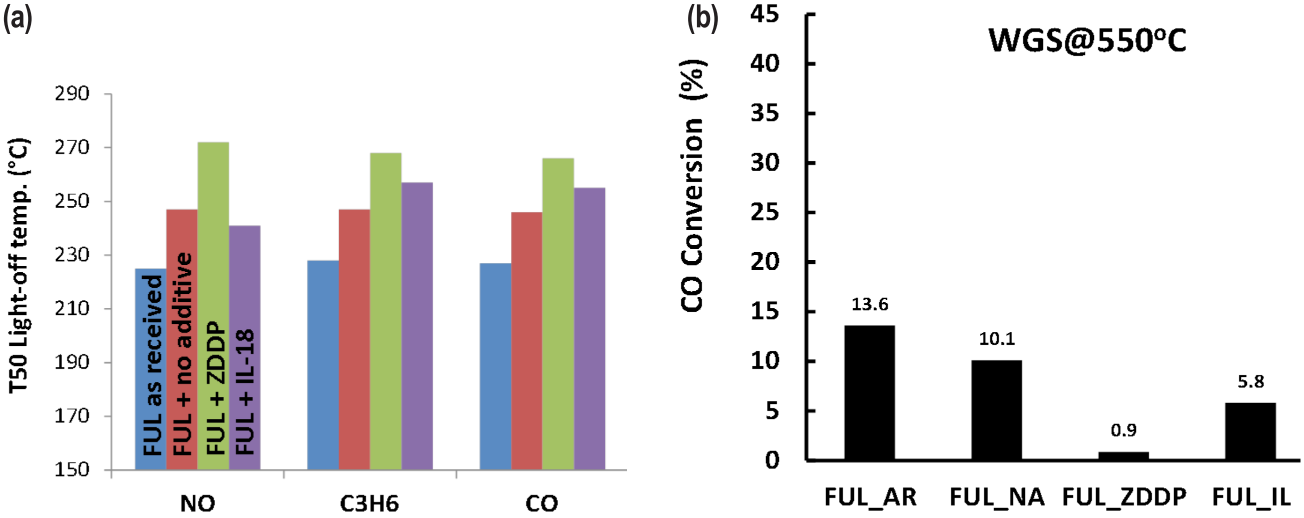


**FIGURE 2.** (a) TWC T50 light-off temperatures of NO, $C_3H_6$, and CO and (b) WGS reactivity at 550°C for FUL_AR, FUL_NA, FUL_ZDDP, and FUL_IL.

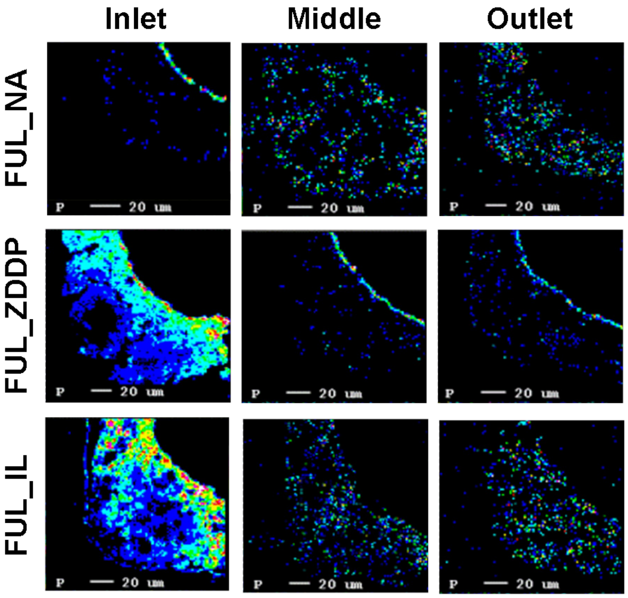


**FIGURE 3.** EPMA elemental maps of P for the inlet, middle, and outlet parts of FUL_NA, FUL_ZDDP, and FUL_IL.

the washcoat of the TWCs, electrospray analysis was performed to analyze the amounts of the P species in TWCs that can be dissolved into water. As it can be seen in Figure 4a, the water soluble concentration of such P species for FUL_IL is about five times higher than that of FUL_ZDDP. This implies that there are significantly more P species that weakly bond with the TWC washcoat when using IL as the additive. To confirm that the amount of P was comparable in both cases inductively coupled plasma mass spectrometry (ICP-MS) was performed to obtain the total mass percentage of P in the washcoat. Figure 4b illustrates that this is indeed the case as the P-level is higher in the FUL-ZDDP inlet portion of the catalyst.

Further characterization was performed on the bulk samples to identify the form of P in the TWC. Figure 5a displays the X-ray diffraction (XRD) patterns of FUL_AR, FUL_NA, FUL_ZDDP, and FUL_IL. The key observation in this comparison is that the FUL_ZDDP catalysts have significantly more bulk features than the other samples. Of particular note, the clear formation of peaks associated with zinc phosphate ($Zn_2P_2O_7$) and more importantly cerium phosphate ($CePO_4$). These peaks are notably missing from the other samples, or are significantly muted, and suggest that the P in this sample is directly interacting with an important component in the TWC, i.e. ceria. Interestingly with the FUL_IL sample there is no indication of a crystalline P-phase even though we know P is there from electrospray, ICP-MS and EPMA. Thus, P is likely present as an amorphous phase, so we employed nuclear magnetic resonance (NMR) to identify what it is bound to. The $^{31}P$ NMR spectra of the inlet parts of FUL_AR, FUL_NA, FUL_ZDDP, and FUL_IL are shown in Figure 5b. The area of focus is specifically around the peak associated with aluminum phosphate ($AlPO_4$) and indicates a significant peak for the IL-aged part, FUL_IL. Quantitative analysis indicates that there is about 10% more $AlPO_4$ in FUL_IL as compared with FUL_ZDDP. This fact suggest that, in IL aging, P may prefer to react with aluminum in the DOC washcoat to form $AlPO_4$, thus reducing its negative impact on cerium, i.e. suppressed formation of $CePO_4$ in FUL_IL, as indicated by XRD.

In addition to the lubricant additive study, a brief summary of the current results from the Na/biodiesel

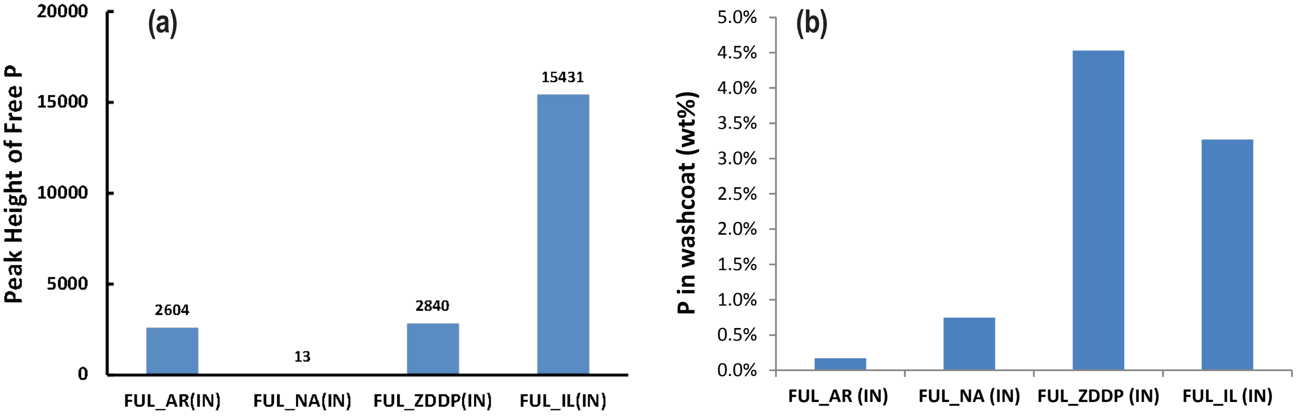


**FIGURE 4.** (a) Electrospray analyses of the P species that are water soluble in the TWC washcoat and (b) ICP-MS result of total P found in washcoats of each TWC.

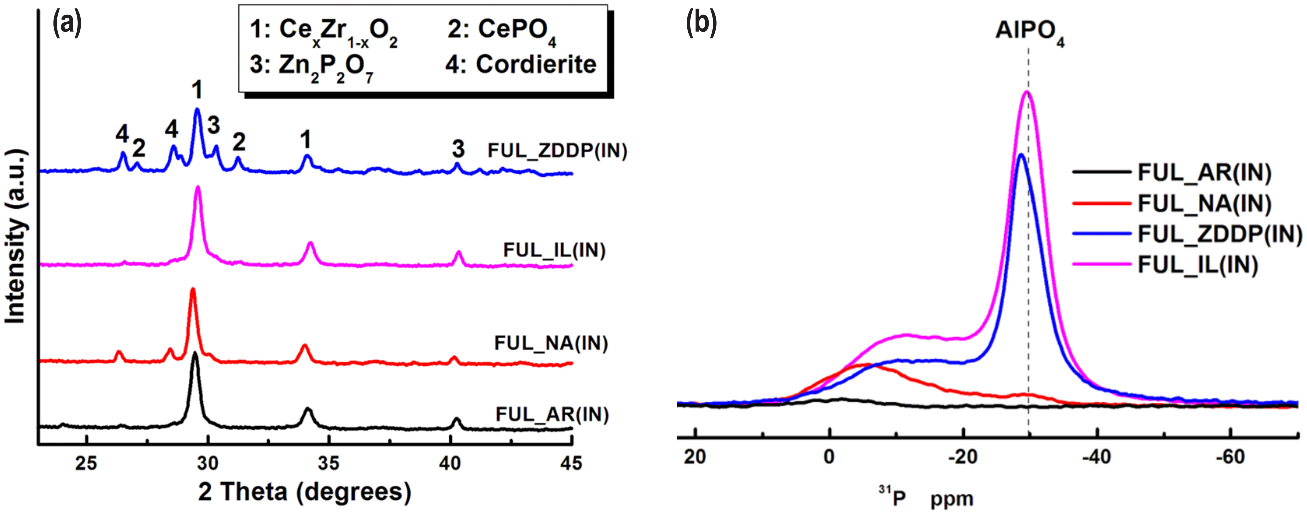


**FIGURE 5.** (a) XRD patterns and (b) $^{31}P$ NMR spectra of the inlet parts of FUL_AR, FUL_NA, FUL_ZDDP, and FUL_IL.

impact are presented this year with a more detailed summary reported next year. After exposing the emissions control system to a thermal and Na equivalent of ~210,000 miles, the NOx emissions rose above the engine certification value of 0.33 g/bhp-hr, far short of the 435,000 mile FUL requirement. Replacing aged DOC, DPF, and SCR devices with degreened parts and conducting hot-start Federal Test Procedure tests showed that 65% of the increase in NOx was due to the aging of DOC/DPF and 35% was from the SCR degradation. Both the DOC and DPF influence the NOx emissions by degrading the SCR feed-gas and the combined effect is non-linear. Figures 6a and 6b show EPMA maps of Na collected from cross-sections near the inlet and outlet of the DOC. Na was found at similar levels across the washcoat thickness and down the entire DOC length. The decrease of NOx oxidation function following aging is likely related to the accumulation and stabilization of Na contamination in the DOC. Detailed micro reactor analysis of the activity and functionality of the DOC will be a major part of the presentation. No Na was detected on the SCR (Figure 6c) which shows that the main effect of metals on the NOx emissions is likely through the effect on SCR feed-gas composition (degraded DOC and DPF NO oxidation).

## CONCLUSIONS

Efforts carried out this year were focused on the compatibility of a promising efficiency-improving lubricant additive, IL-18, and the long-term compatibility of fuel-borne Na on a heavy-duty emissions control system. The major findings are summarized here:

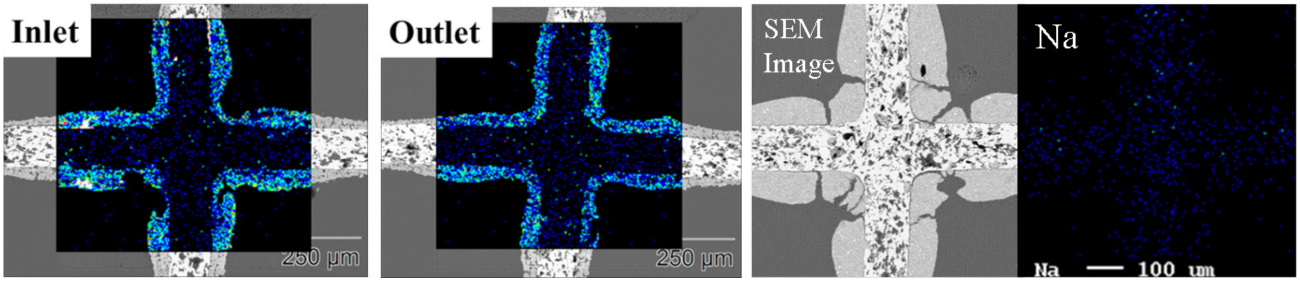


**FIGURE 6.** Scanning electron microscopy (SEM) micrographs and EPMA maps of Na collected from cross-sections of the following fully-aged emissions control system components: (a) DOC inlet, (b) DOC outlet and (c) SCR inlet.

- The catalytic reactivity in the IL-aged TWCs was consistently less impacted than the TWCs aged with the industry standard additive ZDDP
  - Light-off temperature, WGS reactivity and oxygen storage measured
- The IL-aged TWCs did contain significant P, but the interactions with the TWC components were less severe
  - P more water soluble on the IL-aged TWC
  - No formation of cerium phosphate
  - No observation of an overlayer with IL-aged samples
  - The formation of aluminum phosphate appears to be the preferred form of P in TWC to minimize impact
- In collaboration with NREL and Cummins, observed significant increase in NOx emissions after aging heavy duty emissions control system to FUL with 1 ppm Na
  - Lost activity is likely due to the lost activity in the DOC and DPF that prepares the exhaust for reactivity over the downstream SCR

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**2.** P. Ye, C.-X. Sun, M. Lapuerta, J. Agudelo, R. Vander Wal, A.L. Boehman, T.J. Toops, C.S. Daw, "Impact of Rail Pressure and Biodiesel Fueling on the Particulate Morphology and Soot Nanostructures from a Common-Rail Turbocharged DI Diesel Engine," accepted to International Journal of Engine Research.

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**5.** Todd J. Toops, Chao Xie, Michael J. Lance, "Compatibility of Emerging Fuels and Lubricants on Emissions Control Devices using Accelerated Aging Techniques," DOE 2013 Annual Progress Report.

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**13.** Chao Xie, Todd J. Toops, Michael Lance, and Jun Qu, "Impact of lubricant oil additives on the performance of three way catalysts" 2014 Cross-cut Lean Exhaust Emissions Reduction Simulations (CLEERS) Workshop, Dearborn, MI, April 29 – May 1, 2014.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

**1.** 2014 R&D 100 award winner: Ionic Liquid Anti-wear Additives for Fuel-efficient Engine Lubricants - Jun Qu, Huimin Luo, Sheng Dai, Peter Blau, Todd Toops, Brian West, Bruce Bunting, Mike Viola, and Ewa Bardasz.

**2.** 2014 Oak Ridge National Laboratory Significant Event Award (SEA): Development of lubricant that meets DOE goal of 2 percent vehicle fuel economy improvement - Jun Qu, Huimin Luo, Sheng Dai, Todd Toops and Peter Blau.

# II.2 Lab-Engine Correlation and In Situ Validation of Fuel-Efficient Engine Lubricant Technologies

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## Overall Objectives

- Develop accurate and reliable correlations between friction data and wear mechanisms from a select set of benchtop, fuel economy, durability, and reliability of engine tests
- Utilize the protocols, techniques, and knowledge established to work with industry to evaluate candidate solutions under a common set of conditions

## Fiscal Year (FY) 2014 Objectives

- Perform studies of wear analysis using profilometry and microscopy to reveal various types of wear mechanisms present in a used engine
- Initiate the development of test protocols to simulate scuffing, a major failure mechanism of concern to the automotive industry

## FY 2014 Accomplishments

- Broadened network of industrial collaborators
- Acquired engine components for in-use part evaluation
- Performed initial studies of wear analysis using profilometry and microscopy and revealed various types of wear mechanisms present in a used engine
- Initiated the development of test protocols to simulate scuffing, a major failure mechanism of concern to industrial collaborators
- 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 at top-dead-center (TDC) piston position; and performed baseline tests on candidate lubricants and additives and materials.

## Future Directions

Provide the ability to evaluate advanced technologies in terms of their performance and mechanisms (do the benchtop tests replicate the mechanisms expected in engines?) before they progress to the next level of validation testing.

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## 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, such that they can accurately screen technologies in the early stage of development and thus avoid testing technologies that will fail in the full-scale tests. Laboratory tests, such as the high-frequency reciprocating rig test, are rapid, cost-effective, and repeatable. They 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 the real world.

## RESULTS

During FY 2013, we reviewed existing test methods (e.g., ASTM G181-11) 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. After this review, laboratory tests using a reciprocating test rig were performed. The goal was to provide a means for preliminary, cost-effective screening and/or evaluation of candidate ring and liner materials. We performed tests under a range of loads, speeds, duration times, and temperatures using lubricants, materials, and surface finishes that replicate the engine environment at TDC piston position, where liquid lubrication is least effective, and most wear is known to occur. These tests demonstrated the differences in the frictional response between various lubricant/additive formulations, i.e., lubricants from different manufacturers and different concentrations of additives in the oil. Studies showed that temperature has a pronounced effect on the tribological behavior of a contact, and that tribochemical reactions are often driven or accelerated by increasing temperature. It was also found that boundary friction can vary significantly due to the formation of a tribofilm, tribochemical film, or other means of formation, such as physical mechanisms that might be responsible for friction reduction (for example, layered low-shear strength particles). We also investigated the effect various nanoparticles have on friction and wear when added to oil. Oxides and carbon-based additive were studied. We performed tests under laboratory conditions using a reciprocating test rig and two test configurations (ball-on-flat and ring-on-liner) at reciprocating speeds up to 5 Hz. These tests were performed over a range of temperatures up to 160°C using different oils. We found that the addition of most nanoparticles reduced the coefficient of friction of basestock oil. However, a positive effect was not observed when nanoparticles were added to partially or fully formulated oil. In many cases, a non-conductive boundary film separating the sliding surfaces formed.

Examination of the rubbed surfaces showed the pronounced formation of a thick tribofilm in some cases, while mild-to-severe polishing on the surface was also observed. We concluded that the contact configuration is important when nanoparticles are being evaluated, and caution has to be exercised when evaluating the friction and wear performance of nanoparticles in engine oil. Test geometries other than the ball-on-flat configuration, such as the ring-on-liner, may be used to reveal the true nature of a nanoparticle. The majority of the tests performed consisted of an initial speed ramp-up, then a 1-hour test at a constant speed, followed by a second speed "ramp" at the end at a specified load. This type of speed profile allows for the construction of a Stribeck curve, which is used to categorize friction regimes for sliding of lubricated surfaces. By performing tests with ramps, we can generate Stribeck curves and obtain information about the friction regime of a contact. To demonstrate the effectiveness of these types of tests to investigate different friction behavior, Stribeck curves were generated for two liner surfaces—a typical "plateau-honed" surface used on engine liners and a smoother "slide-honed" surface. In the engine, manufacturers use slide honing because it minimizes metal-to-metal contact between surface asperities and enables faster transition from boundary to mixed lubrication with respect to sliding speed. This effect was demonstrated in our laboratory testing.

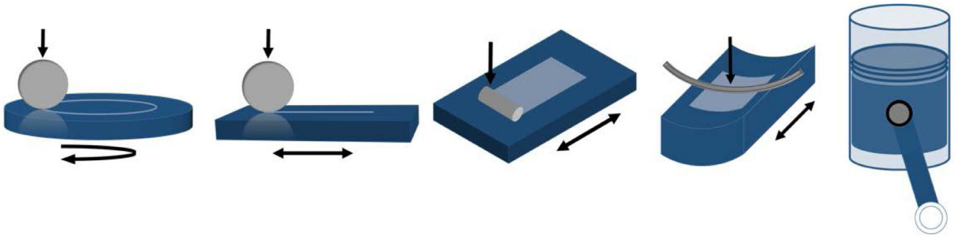

**FIGURE 1.** Schematics of laboratory test configurations (left-to-right: unidirectional ball-on-flat, reciprocating ball-on-flat, reciprocating cylinder-on-flat, reciprocating ring-on-liner, and floating liner) used to simulate engine tests.

Companies invest significant efforts in modeling friction behavior in an engine. Simulation tools that can mimic simple geometries are also available. During FY 2013, experimental results were compared with simulated results obtained from a model developed by Mahle Metal Leve S.A., which uses 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. There was good correlation between the experimental data and the simulated data for different liner finishes. However, deviations occurred in simulations with rings having an asymmetric profile. We speculated that more accurate inputs (i.e., Patir and Cheng's model [1] and MIT's deterministic model [2]) might provide better agreement. Such inputs require modification to the existing code and complex profilometric analyses. We have been working closely with Mahle to incorporate these changes into their simulation tool in the future.

In FY 2014, we started to focus on methods to reproduce the wear mechanisms/failures observed in actual engine components in tests using laboratory equipment/techniques. Phenomenological studies are needed to achieve this understanding. The first step was to obtain engine components for examination, including piston rings and cylinder liners supplied by our industrial collaborators. Laboratory tests that tried to simulate engine conditions (lubrication regime, temperature, load, and speed) were performed. For these tests, we obtained sets of piston rings from different engine tests operating under different modes (i.e., peaks in pressure and hours of operation). These were examined to characterize possible wear mechanisms seen in engines. Figure 2 shows the ring pack after a Federal Driving Cycle test with a peak cylinder pressure of 20 MPa. Evidence of scuffing marks can be seen at the top compression ring (Figure 2a). Scratches are evident along the sliding direction on the second ring (Figure 2b). Polishing wear was dominant on the oil-control ring (Figure 2c).

The ring pack was further examined by scanning electron microscopy (SEM). Examination of the top compression ring showed deposit formation around the edges and polishing wear toward the center. Scratches were evident at the edges while localized spalling was also observed. These details are shown in Figure 3. SEM images of the second ring and oil control ring can be seen in Figure 4. Examination of the second ring and the oil control ring showed evidence of general mild wear, local deep scratches, and local damage due to external abrasive particles.

A segment extracted from a cylinder liner near TDC was also examined. As seen from Figure 5, the formation of a tribofilm is evident. Figure 6a shows approximately the same region using SEM. The tribofilm on this area was analyzed using energy dispersive X-ray spectroscopy (EDXS). The spectrum is shown in Figure 6b. Peaks corresponding to S, P, and Ca were present on the tribofilm formed during tribological interaction, because the oil contains additives that consist of these elements. Other elements like Si and Fe are found in the cast iron material used for making cylinder liners.

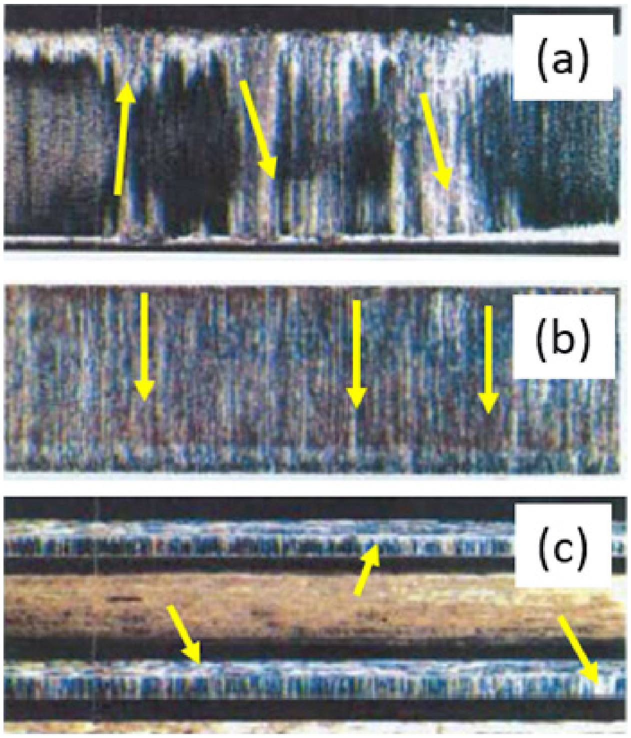

**FIGURE 2.** Ring pack from an engine tested under a Federal Driving Cycle test: (a) top compression ring, (b) second ring, and (c) oil-control ring.

After the aforementioned examination and other similar SEM/EDXS studies, we wanted to reproduce the conditions experienced by the ring pack in an actual engine. Since the study of oil control rings has not been the focus of previous work and substantial experience was gained during the study of top compression rings during the previous year, during FY 2014 we focused on oil-control rings. Oil-control rings experience starved conditions in an actual engine. "Starved" is the condition when the oil film thickness is insufficient to provide hydrodynamic lift, as it does if it is fully flooded. The goal was to reproduce starved lubrication in the laboratory using either gravity or air blow-off.

Because our reciprocating test rig is horizontal, draining under gravity would require significant modifications. Discussions with our industrial collaborators indicated interest in investigating both of these methods because some manufacturers have employed these with partial success. Figure 7 shows a

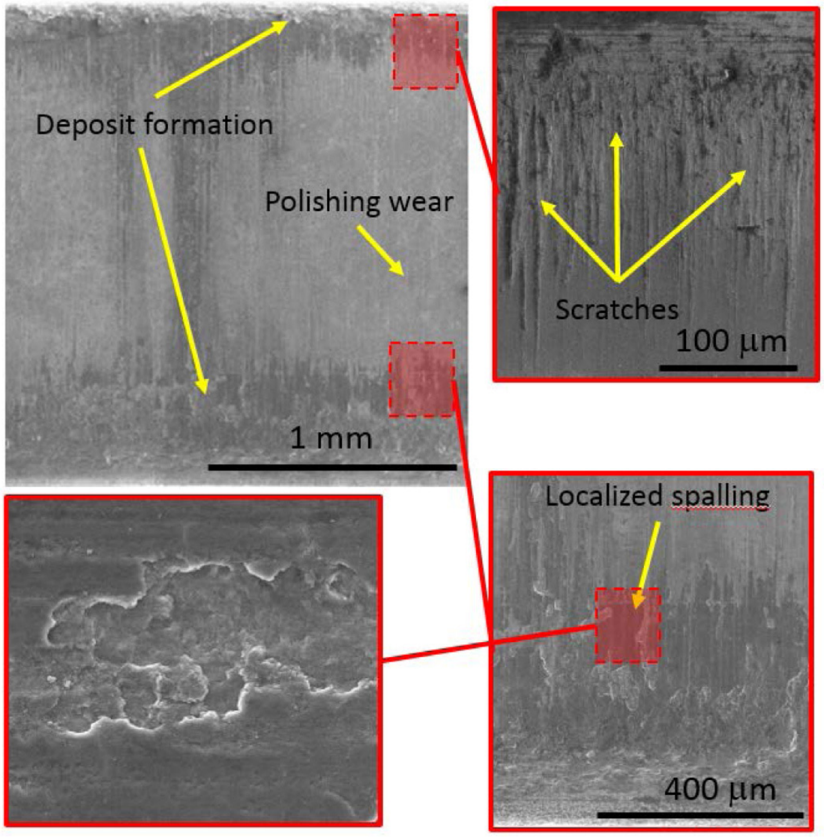

**FIGURE 3.** SEM Images of the Top Compression Ring

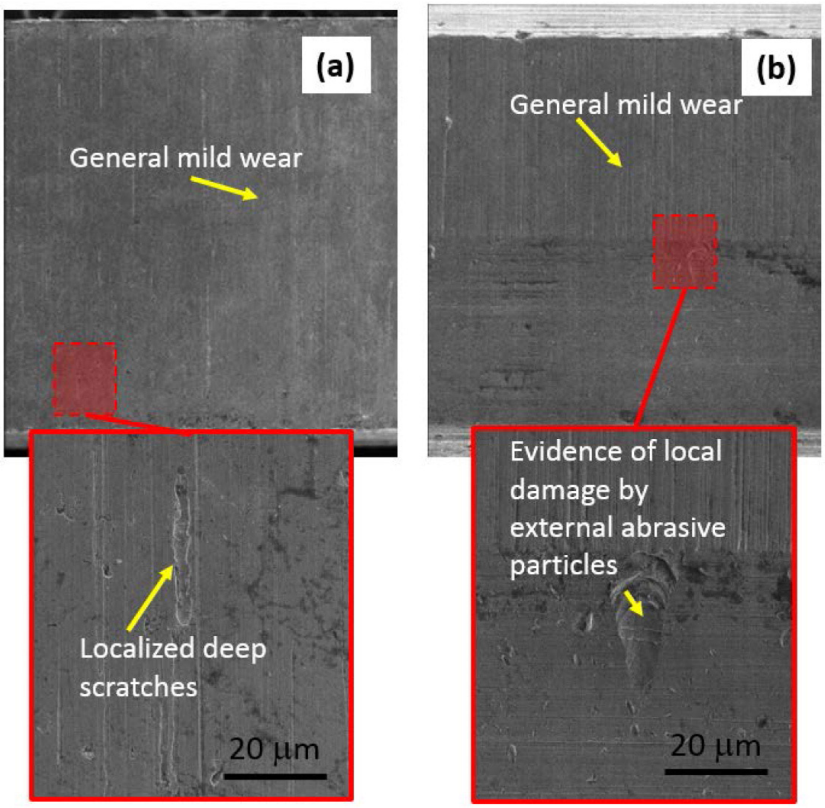

**FIGURE 4.** SEM Images of (a) Second Ring and (b) Oil-Control Ring

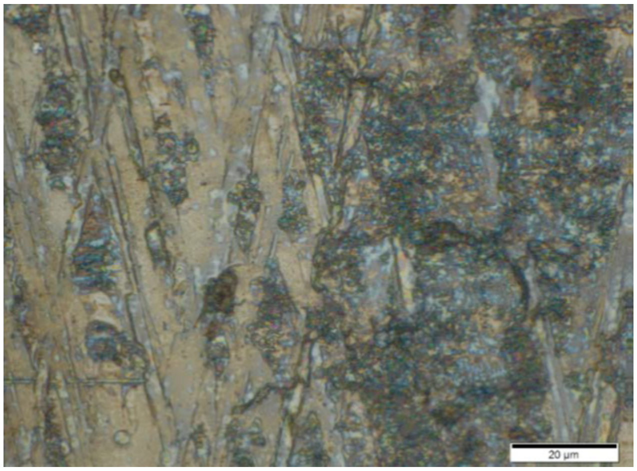

**FIGURE 5.** Optical Micrograph of a Cylinder Liner near TDC showing the Formation of a Tribofilm

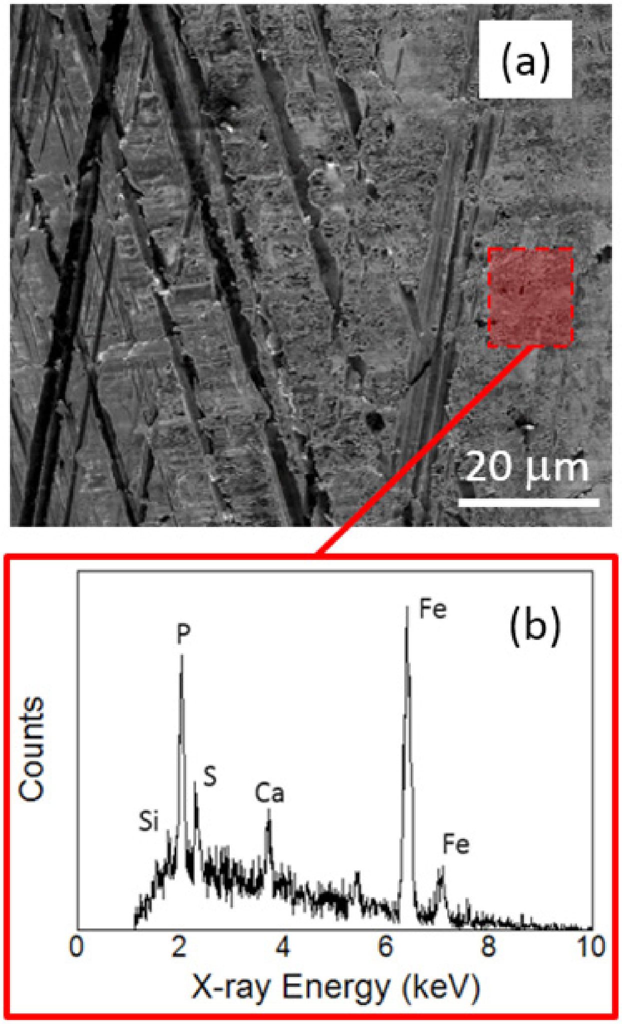

**FIGURE 6.** (a) SEM Image showing Tribofilm near TDC and (b) EDSX Examination

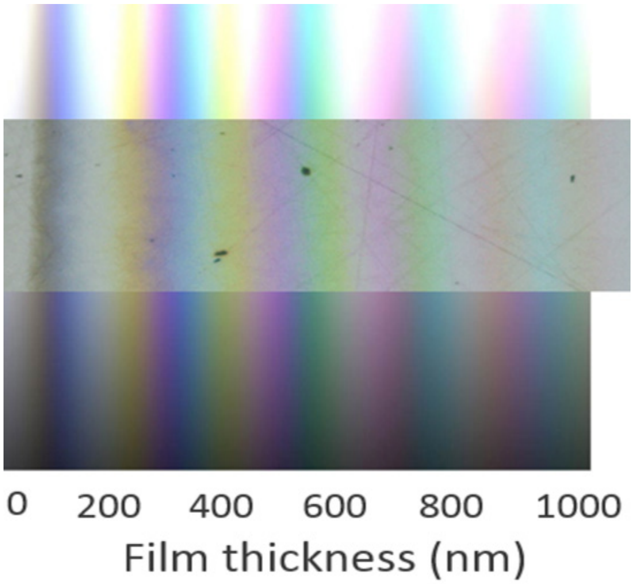

**FIGURE 7.** A smooth 52100 steel flat specimen with 15W40 oil placed on and allowed to drain under gravity for 12 hours. Color fringes can be matched to color-thickness chart.

smooth 52100 steel flat specimen after 15W40 oil had been placed on it and allowed to drain under gravity for 12 hours. Color fringes that can be matched to a color-thickness chart can be seen. When the colors disappear, the thickness is approximately 2 µm. We found that gravity drain produces films that are on the order of microns in thickness, but the process takes long and is not practical. Therefore, tilting our rig is not something we consider necessary at the moment. Use of a micro-pump to apply a small amount of oil was also examined. Due to the test setup, even minimal amounts of oil led to adequate lubrication; therefore, that did not become the focus of this study.

In order to apply a 4-µm-thick film, we deposited 0.025 ml of oil onto a liner segment. Then, the oil was smeared out thin, and 95% of it was removed (see Figure 8). The amount of oil present on the interface was assessed using the top compression ring, which gives momentary friction reduction ("cusps") at 23°C. When a micron-thick film was pre-deposited, the frictional sliding was hydrodynamic, but after about 15 cycles it became boundary lubricated. Momentary friction reductions can be seen in Figure 9 (i.e., 5,057-5,059 s), and transition into "starved" lubrication is evident by the square waveforms at 5,072-5,074 s. Friction data show that due to air blow-off, starved conditions can be seen in the laboratory. Air blow-off reduces the oil thickness to <2 µm to produce starved conditions.

Durability and reliability are major goals of the automotive industry. In particular, scuffing is a

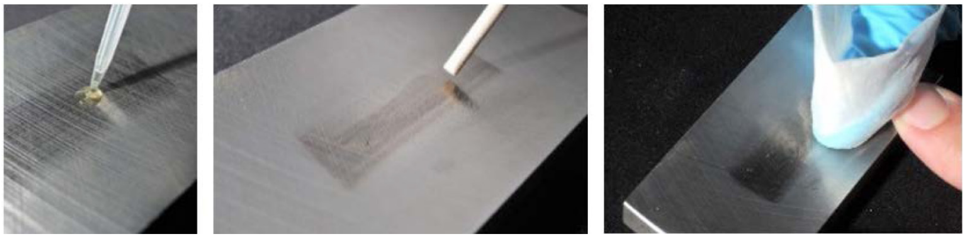

**FIGURE 8.** A series of photographs demonstrating the deposition of a 4-µm-thick oil film.

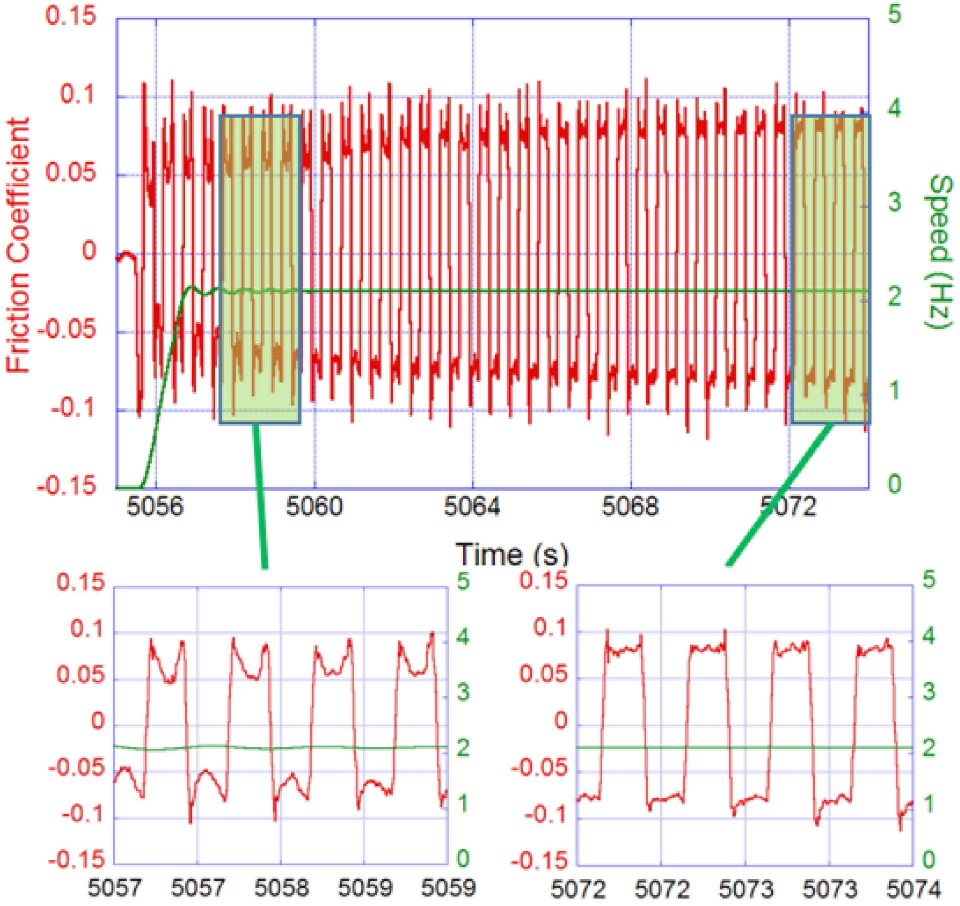

**FIGURE 9.** Transition into starved conditions (in 15 cycles) due to air blow-off.

catastrophic phenomenon that manufacturers would like to understand better and have expressed a need to replicate in the laboratory using a reciprocating test rig. Scuffing can be induced in the laboratory under certain test conditions, i.e., increase in speed or load in a step-wise fashion until the point of catastrophic failure beyond which the contact cannot recover. Under the Falex block-on-ring test configuration, scuffing can be routinely induced. However, developing a protocol for inducing scuffing in the laboratory on engine prototypic components is not trivial. The general approach of increasing speed/load was taken, but so far no evidence of scuffing was found. We will continue to work on a test protocol to induce scuffing.

As shown in Figure 10, oil is present before air blow-off and removed after air blow-off. The color of the oil film indicates the oil film thickness is the same as described previously. After discussions with an automotive manufacturer, we performed load–speed ramp tests in order to compare single-cylinder engine data with data acquired using the reciprocating test rig. An initial comparison was made on the basis of the Stribeck curve. A typical profile is shown in Figure 11.

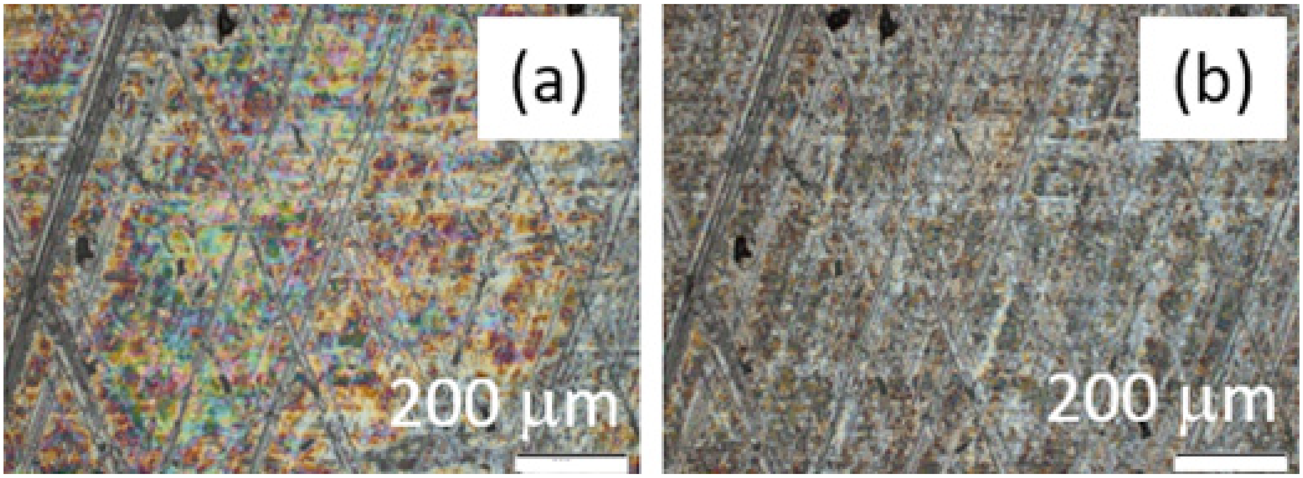

**FIGURE 10.** Micrographs showing that oil is (a) present before air blow-off and (b) removed after air blow-off.

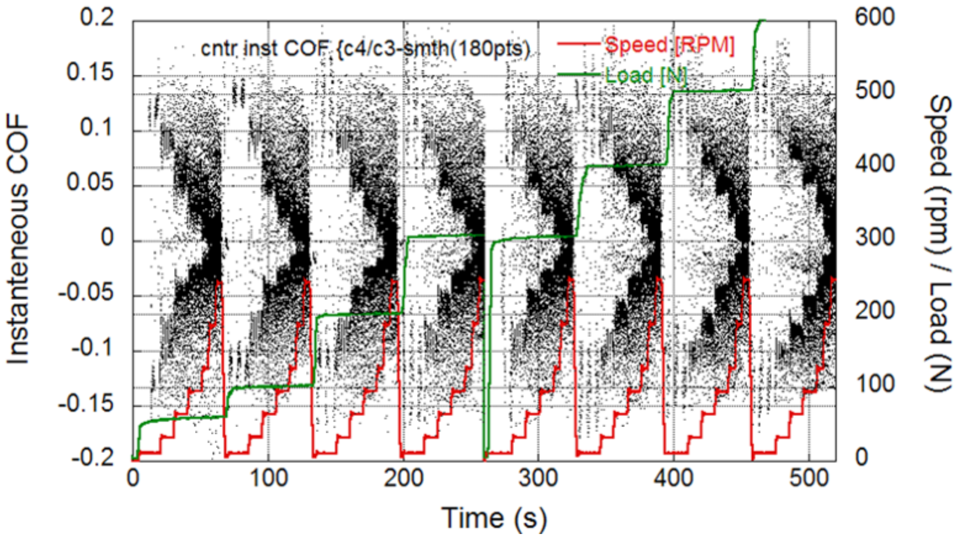

**FIGURE 11.** A typical load/speed ramp performed in the laboratory using the reciprocating rig.

In this particular case, the speeds varied from 10 rpm to 300 rpm (5 Hz), and the load was increased from 50 N to 600 N. Higher loads resulted in changes of the contact patch, which, in turn, led to a reduction in contact pressure.

Processing the load–speed ramps of the previous plot, we obtained the Stribeck-like curve of Figure 12. The data resemble the form of the Stribeck curve [3]; however, the form of the Stribeck curve is for a confined geometry, such as a journal bearing or an actual engine. As a consequence, friction increases toward higher speeds, unlike the result shown in this particular case, where the contact between the ring and the liner in the reciprocating rig is not confined and oil shear dependence cannot

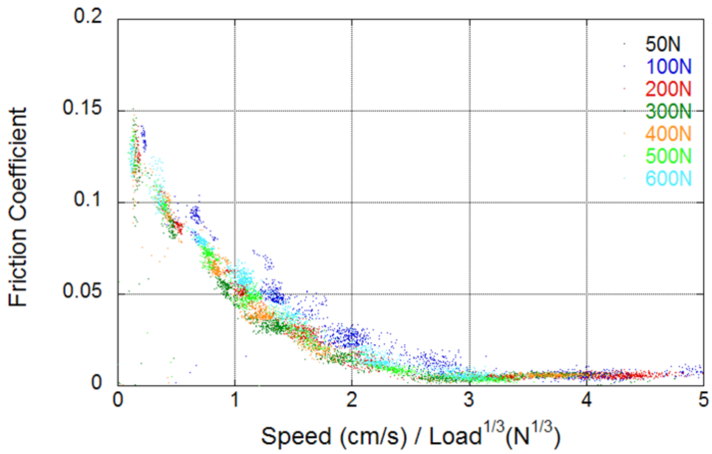

**FIGURE 12.** Stribeck-like curve for a test performed at room temperature using polyalphaolefin-10.

be observed. Figure 12 shows a near steady state was reached at 3 cm/s/N$^{1/3}$. Applying the previous speed-load profile, a test at 170°C shows that we are operating under the boundary regime, and the friction remains approximately constant at all speeds, as expected (Figure 13). We are currently working with our collaborators to obtain single-cylinder data that can be compared with data obtained from the reciprocating ring under a common set of conditions (oil, temperature, materials, and loads).

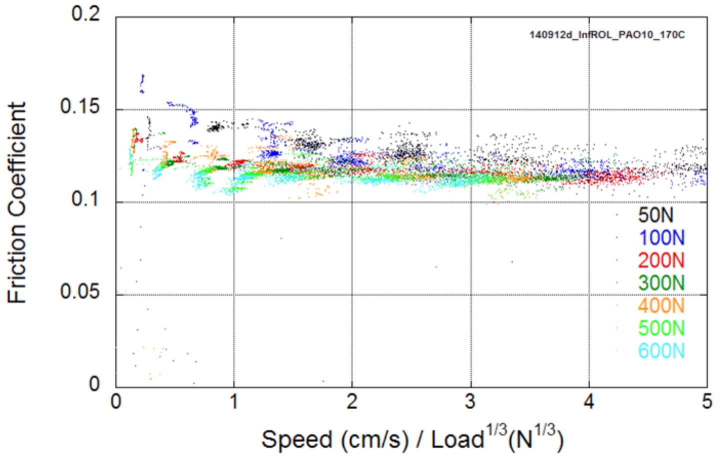

**FIGURE 13.** Stribeck-like curve for a test performed at 170°C using polyalphaolefin-10.

## CONCLUSIONS

- Tribochemical reactions are often driven or accelerated by temperature changes. Therefore, the boundary friction observed for the same lubricant at low temperatures (e.g. below 50°C) might be different from that at higher temperatures. Due to the formation of a tribofilm, the boundary friction can also vary significantly.
- The addition of nanoparticles can reduce the coefficient of friction of basestock oil and improve wear in most cases. However, the positive effect is not observed when nanoparticles are added to partially or fully-formulated oil. Furthermore, contact configuration is important when nanoparticles are being evaluated, because the rubbed surfaces experience mild-to-severe polishing using materials prototypical to an engine.
- The lubrication regimes encountered in the engine can be simulated in a well-controlled laboratory test setup using a reciprocating test rig, though such regimes are challenging to simulate and not very well controlled.
- Single-cylinder testing might be helpful in moving a step closer to actual engine operating conditions. Therefore, we are beginning to acquire data over a range of speeds and loads so that Stribeck curves can be constructed, and a comparison of data might be done on this basis.
- Durability and reliability are major goals of the industry. In particular, scuffing is a catastrophic phenomenon that manufacturers would like to understand better and have expressed a need to replicate in the laboratory using a reciprocating test rig. Therefore, we will continue our efforts in the examination of the various wear mechanisms of parts that have been in use and try to establish a protocol for inducing scuffing in the laboratory on prototypic engine components.

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# II.3 Advanced Lubrication Additives for Improved Fuel Efficiency

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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 both new and legacy vehicles.
- Conduct comprehensive tribological performance evaluation in terms of friction, wear, and scuffing for the new lubricant additive system(s).
- Develop mechanistic understanding of how the new additives function at the lubricated interface.
- Optimize the additive systems for different lubricated components and systems in transportation vehicles.
- Ultimately validate performance in both bench-top testing and engine environments.

## Fiscal Year (FY) 2014 Objectives

- Evaluate the impact of the encapsulating system on tribological performance and the time sensitivity of nano-additive systems.
- Assess the impact of concentration on the tribological performance of different viable nano-additive systems.
- Characterize surfaces lubricated by nano-additive systems for mechanistic understanding and eventual additive system optimization.

## FY 2014 Accomplishments

- Established the minimum concentration for friction reducing nano-additive systems to be about 0.1%. Higher concentration did not produce any further friction reduction.
- Determined that use of an appropriate encapsulator resulted in further enhancement of friction and wear performance.
- Established the anti-wear mechanism of the nano-additive system via the formation of nano-sized and structured surface tribo-films by the additives.
- Observed that under severe sliding contact conditions many nano-additives reduced wear compared to current state-of-the-art lubricants. Encapsulation with oleic acid further enhanced the wear reduction.

## Future Directions

- Refocus the project to the development of a colloidal additive system in order to address the stability issue with nano-additive systems.
- Develop and synthesize colloidal-based friction reducing, wear reducing, scuffing preventing, and thermal dissipating lubricant additives.
- Evaluate the scuffing performance of potential nano-additive and colloidal additive systems with standard block-on-ring test protocol.
- Analyze nano-structure of tribo-chemical films formed from nano-additive and colloidal systems using transmission electron microscopy (TEM) with focused ion beam.
- Evaluate the thermal properties and behavior of colloidal lubricant additive systems.
- Measure nanoscale mechanical properties of the tribo-chemical films formed from particulate colloidal additive systems.

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## 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 the U.S. roads. At present, there are an estimated 250 million vehicles on the U.S. roads, and less than 10 million of them are flex-fuel models. About 95% of fuels for these vehicles comes from petroleum; as much as 70% is imported. Thus, any meaningful petroleum-based fuel savings will result in reduction of oil importation and increase in national energy security. The DOE Vehicles Technologies Office 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 also 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 in both new and legacy vehicles 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 a lubricant that can protect the engine components from expected accelerated wear. Thus, substantial reduction of petroleum for transportation can be achieved in the near term with legacy vehicles by developing engine lubricants for friction reduction below the current levels and by protection of engine component surfaces from accelerated wear when higher levels of bio-based fuels are used. From the long-term perspective, lubricant additives that can reduce friction and ensure reliability and durability in the new vehicles being developed by various original equipment manufacturers are needed. The current project seeks to develop lubricant additives that can reduce friction and enable the use of higher levels of bio-derived fuels in legacy vehicles and can reduce friction without compromising reliability and durability in new 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 and new 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 legacy vehicles as well as the ever-increasing more severe operating conditions in new engines.

The new additive systems will be based on a nano-technology platform, invoking both physical and chemical mechanisms for their tribological performance attributes. Compared to the chemically based state-of-the-art lubricant additive systems, which are designed and optimized for ferrous materials, the versatility of the new additive systems will make them applicable to non-ferrous materials and coatings that are increasingly being used in engines. Thus, in the present effort, nano-particles will be specifically designed and functionalized to reduce friction, protect surfaces against wear and scuffing, especially at high temperatures, 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. Additives systems will also be designed and synthesized to reduce wear and prevent scuffing. 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 byproducts accumulate in the engine oil, the shell layer will be removed, making available the core to neutralize the acid. Again, these additives will be activated only when functionally needed. Formulating engine oils with these engineered nano-particulate additives will enable sustained friction reduction, prevent wear and scuffing, and facilitate the use of higher levels of bio-based (ethanol) fuels in 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 the tribological contact interface.

## RESULTS

In the previous year, efforts were devoted to establishment of a tribological performance benchmark for the new additive system. This was done by determining the friction coefficient wear rates for five state-of-the-art engine oils. Similarly, several nano-particulate additives with different attributes of friction reduction, wear reduction, and scuffing prevention were evaluated with and without encapsulation with organic molecules. Many of the candidate nano-additives showed tribological performance comparable and often superior to the benchmark performance requirements. Of course, the performance of some additives was worse than that of the benchmark.

Efforts during this reporting period were devoted to investigating the effect that concentration of several candidate additives has on friction and wear performance. Performance of the additives under severe contact conditions was also evaluated, as was the nano-structure of several tribo-chemical surface films formed from the additive systems.

Figure 1 shows the friction coefficient variation with time for one of the friction-reducing additives at different concentrations. At a concentration of 0.01%, the average friction coefficient was about 0.12, which is about the same as that of the base stock (Figure 1a). With a concentration of 0.1%, the friction coefficient was substantially reduced, to 0.06 (Figure 1b). At much higher concentration of 1%, no further reduction was observed, as Figure 1c shows. For this particular additive ($CaCO_3$), 0.1% concentration is adequate to reduce the friction by a factor of 2. The impact of concentration on frictional behavior is, however, dependent on the function of the additive in question. As an illustration, Figure 2 shows the average friction coefficient for different additives at different concentrations. For the additive that provided anti-wear attributes ($SiO_2$), the average friction appears to increase with increasing concentrations. Note that anti-wear chemical additives are also known to increase friction. Another friction-reducing additive (Cu) showed similar behavior as $CaCO_3$, with a significant friction reduction at a concentration of 0.1% with not much change at higher concentrations. A clear implication of the concentration effect on friction behavior is needed to optimize the additive content for low-friction performance.

In terms of wear under severe contact condition of four-ball testing with the standard ASTM D4172 protocol, no clear trend can be discerned on the effect of concentration (Figure 3). Compared to the project baseline of fully-formulated, state-of-art, commercially available engine oil (indicated by dashed line in Figure 3), the nano-additives substantially reduced the amount of wear in the stationary balls. Note the log scale for the wear axis in Figure 3. The wear reduction by the additives was further enhanced when the particles were encapsulated with oleic acid. This improvement is attributed, in part, to better dispersion of the particles, which enables entrainment of an adequate amount of particles to form a surface-protecting tribo-film at the contact interface.

Efforts were also devoted to the nano-structural characterization of tribo-films formed from various nano-additive systems. In many systems, but not all, a well-bonded tribo-film with thicknesses in the range of 50-150 nm is formed at the lubricated surfaces. Encapsulation can result in significant modification of the nano-structure of the tribo-films. The micrographs in Figure 4 were obtained by cross-sectional TEM of the tribo-film formed from Cu nano-particles with and without encapsulation. The films formed by Cu nano-additives without encapsulation consist of nano-crystalline material of about 5-nm particle size and disordered grain boundary region (Figure 4a). The Cu grain size in the tribo-film is substantially smaller than the original size of 20-25 nm. This finding suggests grain size reduction

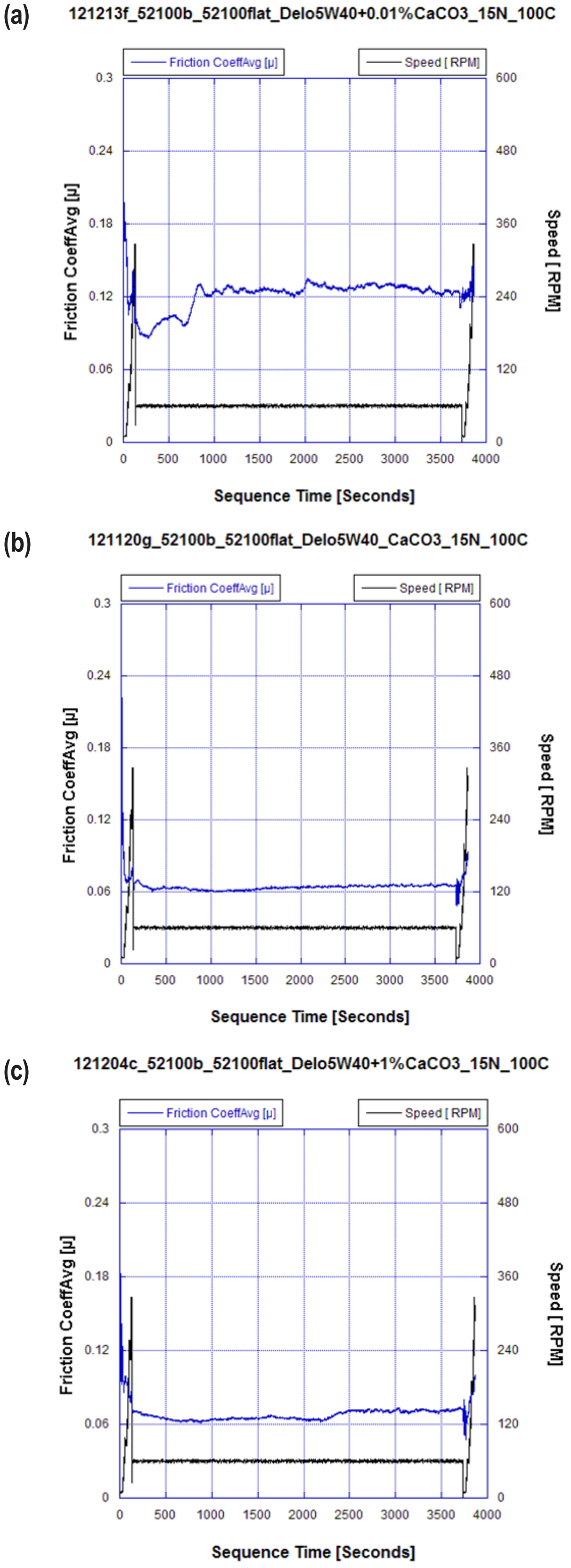


**FIGURE 1.** Variation of friction coefficients with time for friction-reducing nano-additive at concentrations of (a) 0.01%, (b) 0.1%, and (c) 1%.

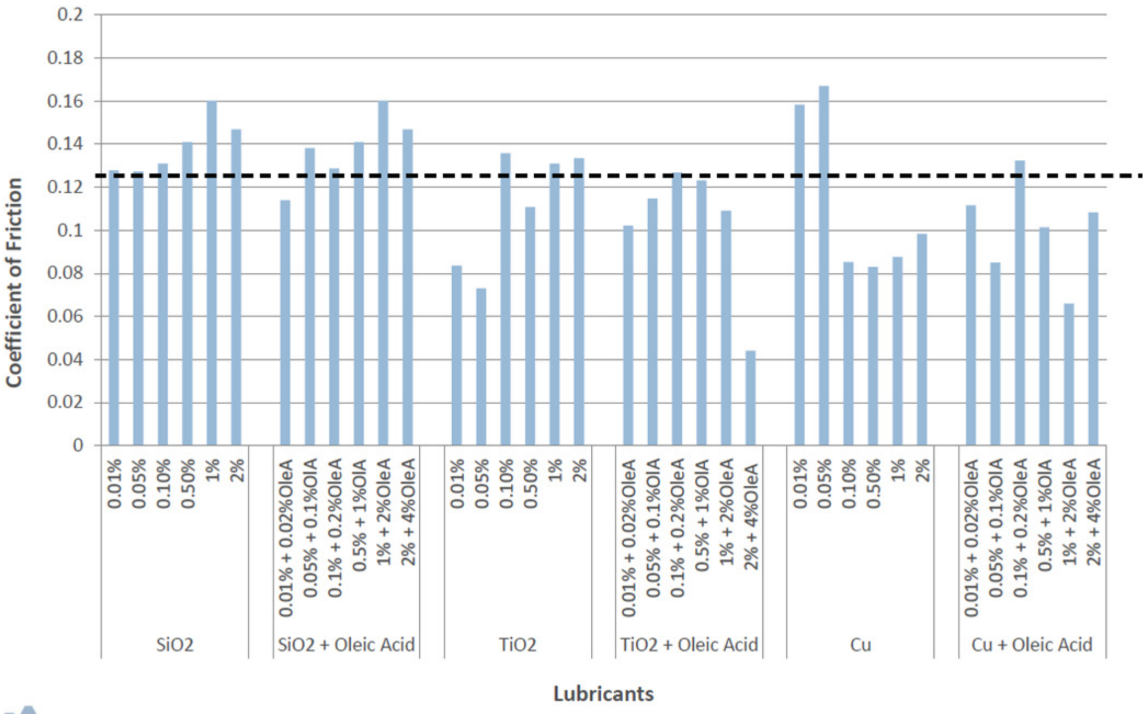


**FIGURE 2.** Average friction coefficients for several friction-reducing and anti-wear additives at different concentrations in comparison with the project baseline – horizontal dashed line.

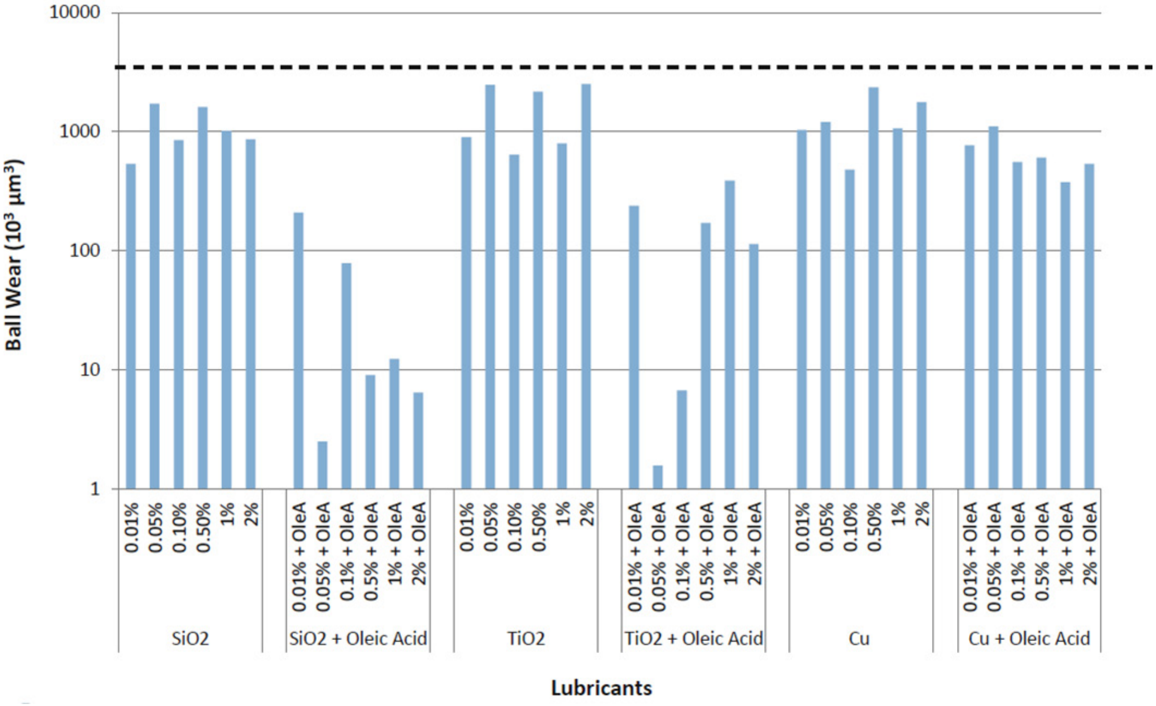
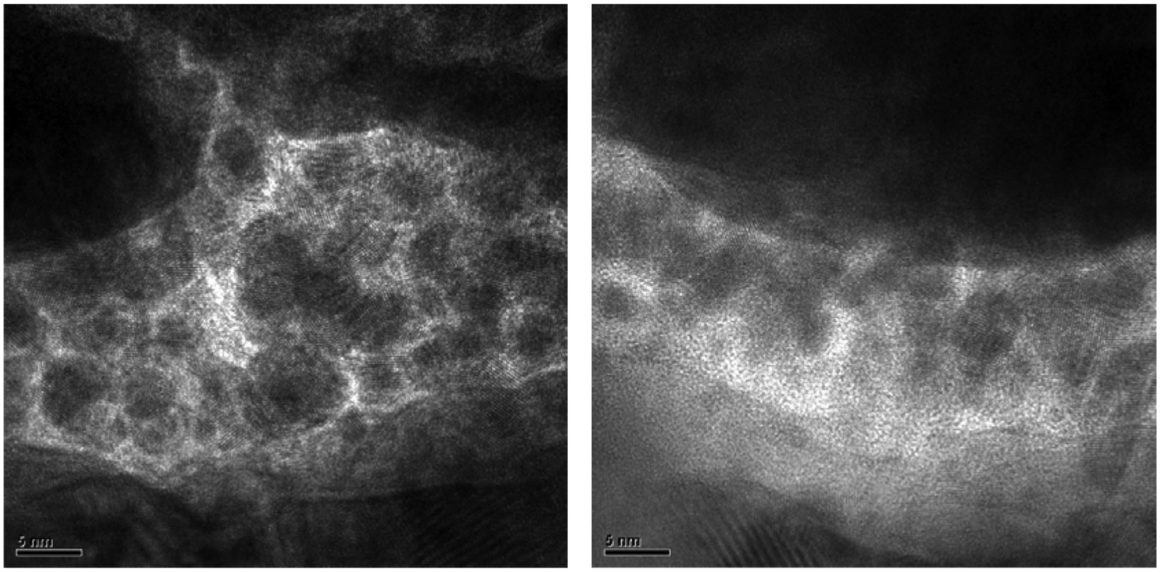


**FIGURE 3.** Average wear volume in four-ball test of different additives at different concentrations with and without encapsulation with oleic acid.



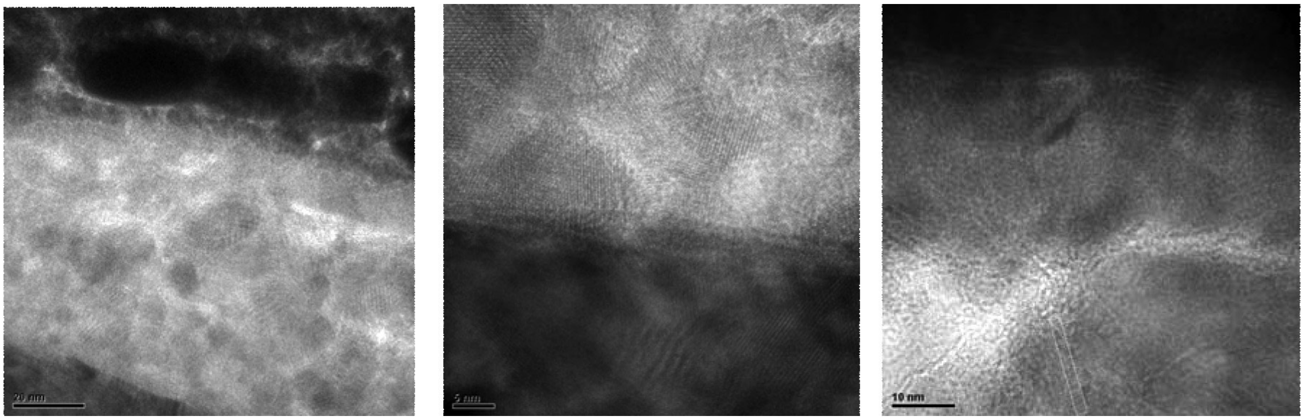
(a) (b)

**FIGURE 4.** Cross-sectional TEM micrograph of tribo-films formed from Cu nano-additive (a) without encapsulation and (b) with oleic acid encapsulation.

of the particles during tribological contact—a form of tribo-commutation. With encapsulation, the tribo-film consists of a mixture of amorphous and nano-crystalline phase, as shown in Figure 4b. The grain size of the crystalline phase was also about 5 nm. In both cases of encapsulation and no encapsulation, the tribo-films are well bonded to the steel substrate material. Analysis of the tribo-film formed from carbon nano-tubes (CNTs), which are functionalized with -COOH group, also showed excellent bonding to the surface (Figure 5). The films are mostly crystalline, as indicated by the prominence of Moiré's lattice fringes in Figure 5b. Although individual CNTs can be identified as indicated in Figure 5c, it appears some morphological changes have taken place during tribo-contact.

## CONCLUSIONS

Results of the tribological performance evaluation of several friction-reducing and anti-wear nano-additives showed there is an optimum concentration. For several friction-reducing additives, a concentration of about 0.1% was sufficient for a factor of two reduction in friction. Anti-wear nano-additives increased the friction, which is consistent with observations based on chemical anti-wear additives, such as zinc dialyldithiophosphate. Under



(a) (b) (c)

**FIGURE 5.** Cross-sectional TEM micrograph of tribo-films formed from -COOH functionalized carbon nano-tubes (CNT-COOH): (a) overview, (b) tribo-film-substrate interface, and (c) intact CNT within the tribo-film.

severe contact conditions of the standard four-ball test, all nano-additives substantially reduced wear compared to the commercially available engine oil. Encapsulation of the additives with oleic acid further enhanced the wear reduction. Initial characterization of the nano-structure of tribo-films formed by nano-additives indicates possible occurrence of tribo-commutation. The structure of the film is also influenced by encapsulation, changing from a crystalline phase to a mixture of amorphous and crystalline phases—with implications for tribological performance.

## FY 2014 PUBLICATIONS/PRESENTATIONS

**1.** O.O. Ajayi, C. Lorenzo-Martin, D. Singh, and G.R. Fenske, "Fuel Efficient Lubricants for Legacy Vehicles," FY 2012 Annual Progress Report, DOE Office of Vehicles Technologies, Fuels & Lubricant Program, II-21-23 (2013).

**2.** C. Lorenzo-Martin, O.O. Ajayi, R.A. Erck, G.R. Fenske, "Effect of Concentration on Friction and Wear Behavior of Oxide Nano-Additives" 69th Annual Meeting and Exhibition STLE 2014, May 18–22, 2014, Lake Buena Vista, Florida, USA.

# II.4 Phenomenological Modeling of Lubricant Film Formation and Performance

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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 base-stock oil.
- Determine and develop model for the failure mechanisms in lubricated systems in engine.
- Validate performance in both bench-top testing and engine environments.

## Fiscal Year (FY) 2014 Objectives

- 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.
- Determine the mechanical durability of tribochemical surface films with different structures.

## FY 2014 Accomplishments

- Determined the thermal limit of tribochemical films from several commercially available lubricants to be in the range of 220°C to 250°C.
- Identified the failure modes of tribochemical films under thermal loads to be sudden film removal by increased shear stress or extensive oxidation.
- Observed a peculiar effect of base-oil viscosity on boundary-lubrication friction behavior.
- Analyzed tribochemical films by X-ray absorption near edge structure at the Advanced Photon Source.
- 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

- Conduct tribological performance evaluation in terms of scuffing and wear under severe contact conditions for additives that produce low-friction tribochemical films.
- Evaluate the basic mechanisms of scuffing in engine components.
- Determine and formulate constitutive equations to enable friction prediction and modeling at the lubricated interface.
- Develop empirical relationship between base-fluid viscosity and boundary-regime frictional behavior.

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## 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 are 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. Another goal of this project is the study of the basic mechanisms of failure, especially scuffing in engine components, and the development of a predictive model for such failures.

## APPROACH

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 with low friction to the point of commercialization. This effort will involve development of a controlled method of production, characterization of tribological properties, and performance optimization for 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 (“tribo-film”) and (2) the validation of its performance through engine testing at Massachusetts Institute of Technology. Based on input from engine manufacturers, an additional component of this project is the study of basic mechanisms and the development of predictive model for piston ring and liner systems of internal combustion engines. Briefly, this will involve the following tasks:

- Develop a technique for low-friction tribo-film deposition,
- Characterize the composition and structure of the film using various analytical techniques,
- Characterize the nano-mechanical properties of the films,
- Evaluate the film by bench-top friction and wear testing, and
- Study mechanisms and develop scuffing model for engine piston ring/cylinder liner.

## RESULTS

There are two primary driving forces for failure in lubricated interfaces: mechanical and thermal loads. The durability and ability of the tribochemical surface films to maintain friction reduction and protect surfaces of interest can be diminished by either of the two driving forces or a combination of both. During FY 2013, results were given for the mechanical durability of tribochemical films with different structures. Films with crystalline phase or a mixture of crystalline and amorphous phases were found to exhibit very high load-carrying capacity. These films can sustain a 3-GPa contact pressure under reciprocating sliding contact without failure. Films with all-amorphous phase are less durable mechanically.

During FY 2014, we evaluated the thermal capacity of tribochemical films formed from several commercially available lubricants. This evaluation was conducted with a line contact configuration consisting of a hardened 4340 steel roller in reciprocating sliding against hardened 4140 steel flat. The tests were conducted with a normal load of 150 N, which imposes a Hertzian contact pressure of about 0.5 GPa, reciprocating frequency of 0.5 Hz, and stroke length of 10 mm, translating to an average sliding velocity of 1 cm/sec. Tests were conducted for a total of 180 min (3 hours). At the start of each test, adequate lubricant was applied to the contact to ensure no starvation. Four drops was established to be adequate to create a flooded contact. Starting at room temperature (25°C), the temperature was increased at a constant rate of about 1.6°C/min until 300°C. The friction coefficient was continuously monitored throughout the test. The thermal limit of the tribo-film was determined by the temperature at which friction showed a sudden irreversible rise or the frictional behavior became unstable. Either of the frictional behaviors will result in noise or vibration in the contact, indicative of failure. For each lubricant evaluated, three tests were conducted to ascertain the repeatability of the behavior and their thermal limits.

Two thermal failure modes were observed in all the lubricants tested. One mode consists of a sudden increase in the friction coefficient at a particular temperature, as shown in Figure 1. The figure also shows that the failure mode is repeatable, as the plots of the two tests are almost identical. For the lubricant in Figure 1, the thermal limit was about 250°C. The second failure mode consists of an occurrence of frictional instability at a particular temperature, as illustrated in Figure 2. In the figure, the instability occurred at a temperature of about 220°C.

Analysis of the failed specimen’s surface showed that the two observed failure modes occurred by two mechanisms. Failure by sudden increase in friction and the consequent increase in noise and vibration coincided

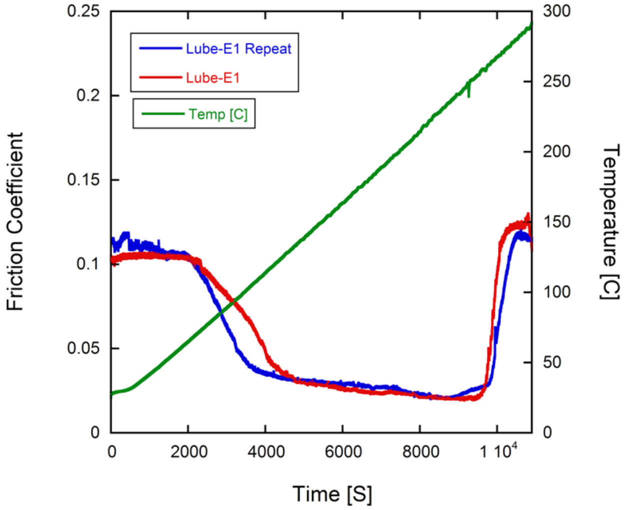


**FIGURE 1.** Friction variation with time and temperature during thermal limit testing of tribo-film showing failure mode by sudden increase in friction.

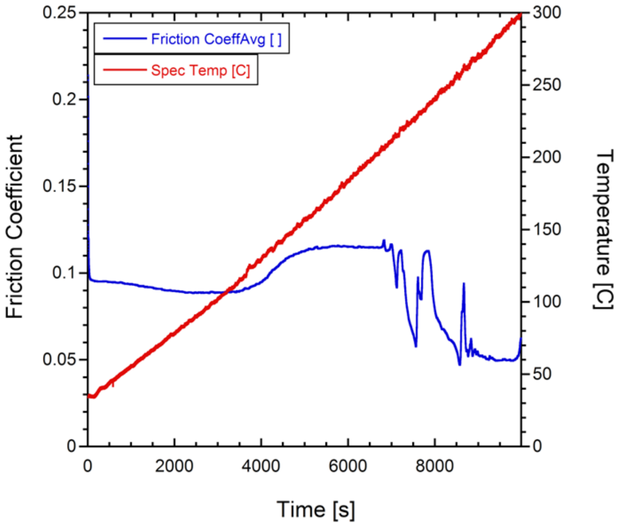
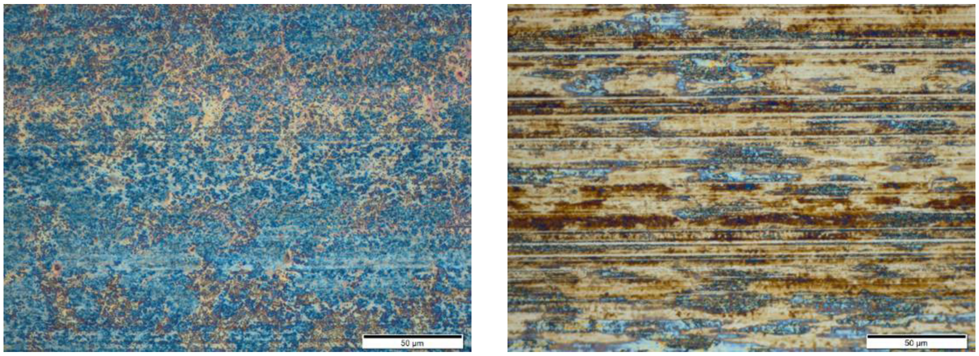
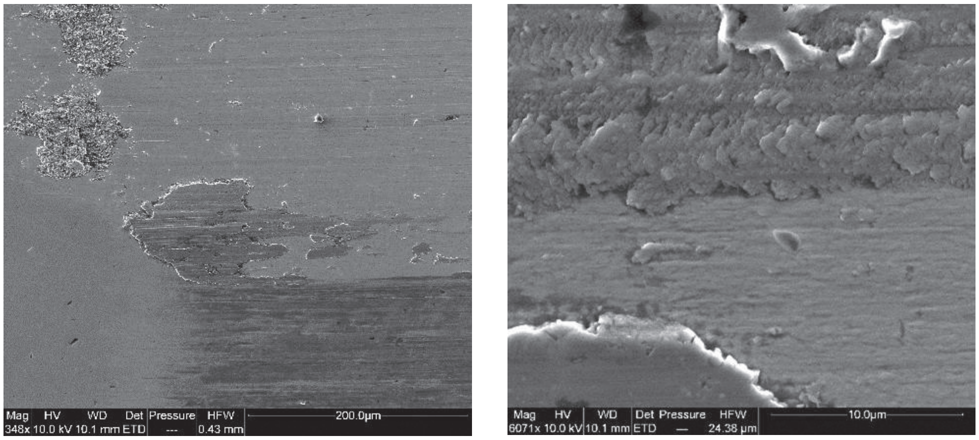


**FIGURE 2.** Friction variation with time and temperature during thermal limit testing of tribo-film showing failure mode by frictional instability.



(a) Optical image of tribo-film before failure

(b) Optical image of film removal after failure



(c) SEM micrograph of debris at end of travel

(d) SEM micrographs of shear serration in film

**FIGURE 3.** Optical and SEM micrograph of failure mechanism of tribochemical film removal in failure mode involving sudden friction increase.

with the removal of the surface tribochemical film, as illustrated in Figure 3. Optical microscopy showed the presence of a patchy tribochemical surface film prior to failure (Figure 3a). After failure, there was clear evidence of surface film removal and perhaps some abrasive wear, as indicated by the prominence of scratches in the direction of sliding (Figure 3b). Scanning electron microscopy (SEM) analysis showed that the removed tribo-films accumulated at the edge of contact end of travel (Figure 3c). The presence of shear serration in patches of the tribo-film, as shown in Figure 3d, suggests that the thermal failure by film removal involves shearing. In the films that failed by frictional instability as shown in Figure 2, surface analysis indicated that failure occurred by an oxidation mechanism, as shown in Figure 4. Optical micrographs show a prominent reddish color in the contact area, indicative of the formation of $Fe_2O_3$ – iron oxide (Figure 4a). Little or no scratches were observed on the track.

One of the strategies to improve fuel economy in transportation vehicles is the use of lower viscosity engine oil. Thus, a preliminary evaluation of the effect of base-fluid viscosity on the frictional behavior of tribochemical films was conducted. The study was conducted by adding a model performance additive package consisting of an anti-wear agent (zinc dialkyldithiophosphates) and an organo-metallic friction modifier agent (molybdenum dithiocarbamate) into a synthetic poly-alpha-olefin (PAO) base stock with different viscosities (PAO2, PAO4, PAO10, and PAO21). The lubricants were evaluated with a roller-on-flat contact configuration using 52100 steel. Tests were conducted at a normal load of 150 N and reciprocating frequency of 1 Hz. Starting at room temperature, the temperature was increased at a rate of about 1.5°C/min until a maximum of 160°C. The friction coefficient was continuously monitored. Figure 5 shows the variation of the friction coefficient with time and temperature. A peculiar dependence of the frictional behavior on viscosity was observed. The shape of the frictional curve is indicative of fundamental mechanisms yet to be understood. Certainly more work is needed to further elucidate this peculiar observation. Nonetheless, the frictional increase in the mid-temperature range as the base oil viscosity decreases may have significant implications for tribological failure mechanisms in such temperature ranges.

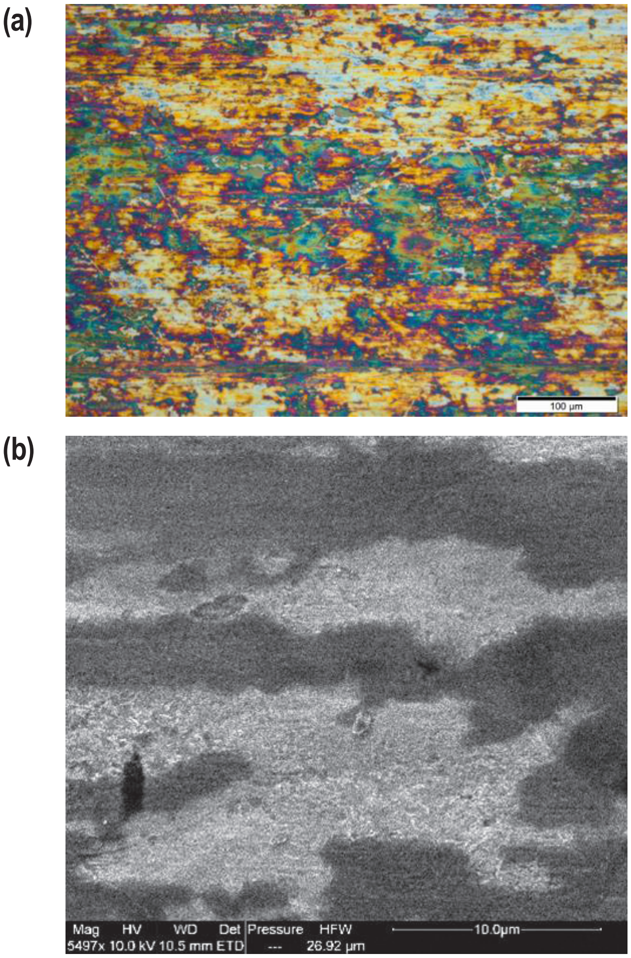


**FIGURE 4.** (a) Optical and (b) SEM micrograph of failure mechanism of tribochemical film by oxidation in failure mode involving frictional instability.

## CONCLUSIONS

This report presents results of experimental studies of the thermal limit of tribochemical surface films. Using several commercially available fully formulated lubricants, the thermal limit was established to be between 220 and 250°C. Two distinctive thermally driven failure modes and corresponding mechanisms were observed for the group of lubricants studied. One failure mode consisted of a sudden and irreversible rise

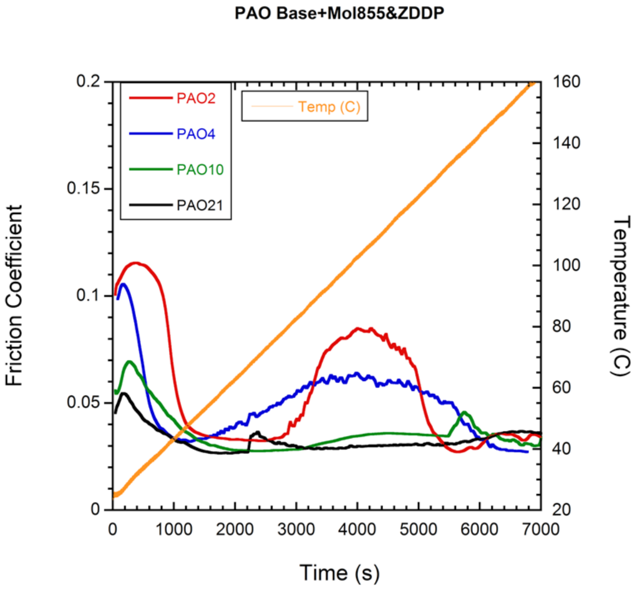


**FIGURE 5.** Variation of friction coefficient with time and temperature for different viscosity PAO base fluid containing the same performance additives.

in friction at a particular temperature. This failure mode was due to shear removal of the tribochemical surface films. The second failure mode was the onset of frictional instability at a given temperature. Surface analysis showed that this failure mode is due to oxidation. The impact of base-fluid viscosity on the frictional behavior of the tribochemical film was also evaluated. Test results showed a peculiar behavior indicative of a yet to be understood mechanism. This observation requires further study and elucidation, in view of the increasing desire to use lower viscosity oils in engines.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

**1.** O.O. Ajayi, C. Lorenzo-Martin, and G.R. Fenske, "A Tribochemical Synthesis Method for Producing Low-Friction Surface Film Coatings," U.S. Patent application (Pending).

# II.5 Lubricant Formulations to Enhance Engine Efficiency in Modern Internal Combustion Engines

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## Overall Objectives

- Identify the best lubricant formulations for individual engine subsystems
- Identify the best composite lubricant formulation for the overall engine system
- Demonstrate mechanical efficiency improvement for optimized lubricant formulations via engine testing
- Develop in situ oil composition model and apply results to friction modeling for engine subsystems.

## Fiscal Year (FY) 2014 Objectives

- Identify optimal lubricant formulations for subsystems by developing and conducting friction and oil aging experiments on a diesel engine with the assistance of lubricant and engine industry partners.
- Identify opportunities for improved mechanical efficiency and lubricant performance resulting from segregating engine lubrication subsystems between the valvetrain and power cylinder.

## FY 2014 Accomplishments

- Demonstrated ability to maintain the wear protection performance of a 15W40 lubricant in the valvetrain while using a 5W20 lubricant in the power cylinder. A friction reduction of 9% was demonstrated in low-speed, low-load operating condition.
- Demonstrated additional 1% reduction in total engine friction using reduced antiwear additive in the power cylinder.
- Demonstrated contaminant protection of engine subsystems during a 250-hour oil aging test with a dual-loop lubricating system. Eliminated potential for soot related wear in the valvetrain.

## Future Directions

The project is scheduled to end in January 2015.

- Continue to develop advanced power cylinder friction models incorporating local oil composition changes.
- Experimentally investigate the effect of additive changes on valvetrain subsystem losses through parametric studies.
- Experimentally investigate the effect of oil aging in separate lubricant subsystems under different operating conditions and with different additive packages.
- Experimentally investigate opportunities for material selection in engine subsystems given the implementation of a dual-loop lubricating system.
- Further investigate the effect of oxidation in valvetrain lubricants.

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## INTRODUCTION

It is estimated that up to 15% of useful mechanical energy is lost to friction in modern diesel engines [1]. The environment in which the lubricant operates in an engine varies in space (location in the engine) and time (warm-up and degradation). Temperature, mechanical load, and shear rate vary widely in an engine, and therefore so does the degradation rate. The extent to which a lubricant/additive package can tailor to the local conditions determines the gains that can be achieved, in terms of friction, wear, and emissions [2-6]. Given modern fuel economy and emissions reduction goals, significant benefit may be derived from such a configuration.

## APPROACH

Significant R&D was completed in recent years for advanced chemistries for base oils, viscosity modifiers, and friction modifiers (anti-wear, low sulphated ash, phosphorus and sulphur (SAPS), or ashless agents, etc.) of various types. Their effectiveness depends strongly on the local environments (thermal, mechanical, shear, contamination, oxidation/degradation, depletion, replenishment, etc.) internal to the engine at which the lubricant/additives operate, which we still do not fully understand and on which we lack data and analyses. The overall approach in this study focuses on the 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 investigated using advanced computer modeling and practical engine laboratory tests. A diesel engine was modified to investigate friction and lubricant changes in the cylinder head/valvetrain subsystem and the power cylinder subsystem. With an advanced understanding of friction and composition changes in parts of the engine, and actual engine data, the proper lubricant base-oil and additive technologies were selected and methods proposed for optimizing the lubricant/additive package. The data and technology developed is available to the lubricant and engine industries at large (multiple beneficiaries) for further technology fine-tuning, and competitive production and commercialization, as appropriate.

## RESULTS

A 16-hp twin-cylinder diesel was instrumented for the measurement of indicated mean effective pressure, and valvetrain and crankshaft torque. The lubrication system was divided to allow different oils in the cylinder head and block. Parametric studies characterized optimal lubricants for each subsystem in actual fired engine tests. Figure 1 shows the resulting friction mean effective pressure (FMEP) at 1,800 rpm and 33% load. The "NEW40" consisted of a polyalphaolefin (PAO) formulation with the same kinematic viscosity, and additive package, as the 15W40. Motored valvetrain tests indicated an up to 25% reduction in valvetrain friction compared to the 15W40 case. A 9% total engine FMEP increase would be realized in a conventional system, making use of the lubricant impractical. The dual-loop configuration allowed use in the head without the overall friction detriment. The gains associated with different lubricants in the head were within the range of experimental uncertainty in fired engine tests

A dual-loop lubricating system facilitates improved mechanical efficiency and wear protection by allowing the use of higher viscosity lubricants in the valvetrain. The previously reported reduction in valvetrain friction indicates total engine friction benefits of up to 2% are possible. Higher viscosity valvetrain lubricants also remove a significant wear barrier to the adoption of lower viscosity lubricants in the power cylinder. Use of a 5W20 lubricant, in lieu of 15W40, in the power cylinder provided an 8% friction reduction in this study.

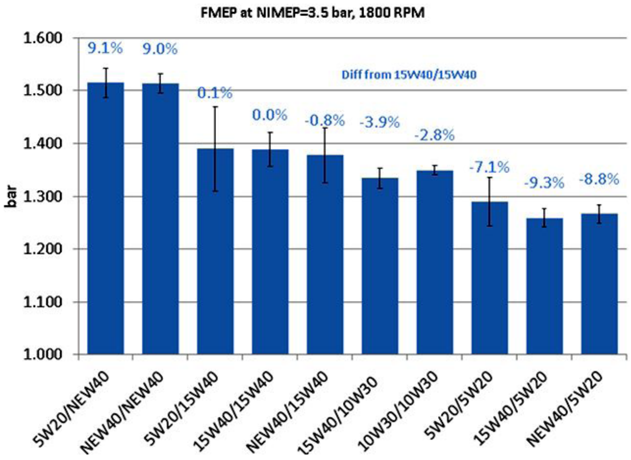


**FIGURE 1.** Comparisons of FMEP for various lubricant combinations in the head/power cylinder. Data labels provide the difference in FMEP from the baseline 15W40/15W40 case.

Additive optimization, resulting from decoupled functional requirements in a dual-loop system, provides additional opportunities. Segregation of subsystems allows the introduction of previously incompatible friction modifiers to the valvetrain due to reduced detergent interaction. Detergent and dispersant reduction may allow for additional optimization of zinc dialkyl-dithiophosphate (ZDDP) concentration. Overbased detergents have been shown to provide comparable wear protection, compared to ZDDP, under low load [7]. The use of low-SAPS lubricants in the power cylinder could provide considerable improvement in diesel engine aftertreatment system performance.

A prototype was developed to study aging effects as shown in Figure 2. A 250-hour test was conducted with the same 15W40 lubricant in each subsystem. Valvetrain and power cylinder sumps were 1.1 liter and 1.4 liter, respectively. The engine was operated at 1,800 rpm and 33% load over a three-week period. Oil samples were drawn at 50, 150, and 250 hours, to measure changes in total base number, total acid number (TAN), kinematic viscosity, high-temperature high-shear viscosity, and water, soot, and oxidation. The valvetrain operated at 65°C-75°C, while the main sump operated at 95°C -101°C. Water levels remained below 0.06% in each subsystem, although levels were higher in the valvetrain.

**FIGURE 2.** Prototype Engine

**FIGURE 3.** Lubrication oil; from left to right: fresh, head, power cylinder.

Significant fuel dilution affected valvetrain results as shown in Table 1. The cause was likely improper seal installation during engine modification. Oxidation in the valvetrain was higher according to Fourier transform infrared, while deposit formation tendency was lower according to Thermo-Oxidation Engine Oil Test - Moderately High Temperature test results. The valvetrain lubricant was effectively protected from soot contamination as shown in Figure 3, providing a significant wear benefit.

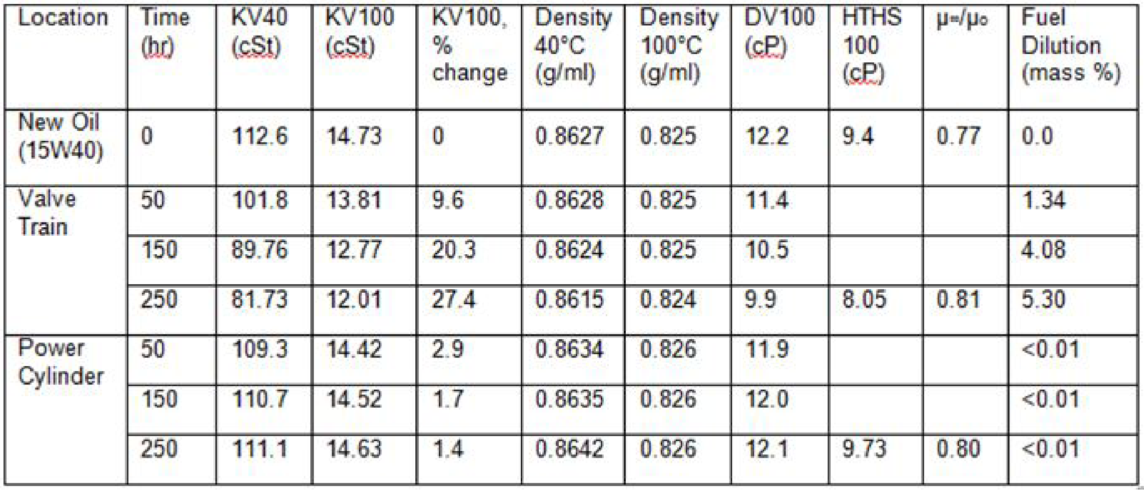
The valvetrain exhibited slightly lower TAN compared to the power cylinder after 250 hours. TAN and TBN remained relatively unchanged given the test duration and use of ultra-low sulfur diesel fuel. The valvetrain is expected to exhibit lower TAN increases as a result of lower oxidation, sulfur, and nitration, which could lower detergent additive costs. Additive concentration in the power cylinder indicated a greater decrease in the more volatile Zn and P than Mg and Ca as shown in Figure 4. This is consistent with studies in literature [8].

Additional opportunities, not investigated in this study, include selection of different engine materials and further additive optimization.

## CONCLUSIONS

- A dual-loop lubricating system facilitates an improvement in mechanical efficiency by allowing the use of higher viscosity lubricants, including PAO base oils, in the valvetrain. A total engine friction reduction of approximately 2% may be possible.
- A dual-loop lubricating system facilitates an improvement in wear protection by allowing for higher viscosity lubricants in the valvetrain, removing a significant barrier to the adoption of lower viscosity lubricants in the power cylinder.

**TABLE 1.**



| Location | Time (hr) | KV40 (cSt) | KV100 (cSt) | KV100, % change | Density 40°C (g/ml) | Density 100°C (g/ml) | DV100 (cP) | HTHS 100 (cP) | $\mu_{=}/\mu_{o}$ | Fuel Dilution (mass %) |
|---|---|---|---|---|---|---|---|---|---|---|
| New Oil (15W40) | 0 | 112.6 | 14.73 | 0 | 0.8627 | 0.825 | 12.2 | 9.4 | 0.77 | 0.0 |
| Valve Train | 50 | 101.8 | 13.81 | 9.6 | 0.8628 | 0.825 | 11.4 | | | 1.34 |
| | 150 | 89.76 | 12.77 | 20.3 | 0.8624 | 0.825 | 10.5 | | | 4.08 |
| | 250 | 81.73 | 12.01 | 27.4 | 0.8615 | 0.824 | 9.9 | 8.05 | 0.81 | 5.30 |
| Power Cylinder | 50 | 109.3 | 14.42 | 2.9 | 0.8634 | 0.826 | 11.9 | | | <0.01 |
| | 150 | 110.7 | 14.52 | 1.7 | 0.8635 | 0.826 | 12.0 | | | <0.01 |
| | 250 | 111.1 | 14.63 | 1.4 | 0.8642 | 0.826 | 12.1 | 9.73 | 0.80 | <0.01 |

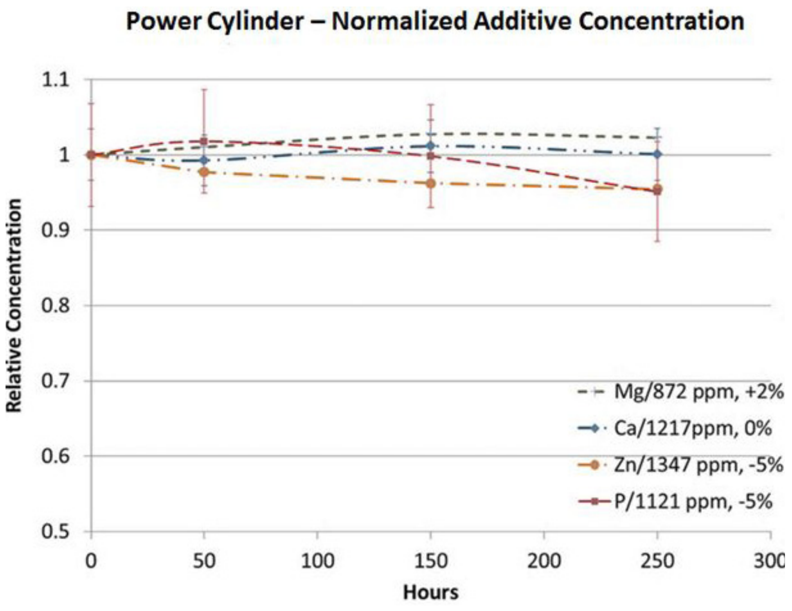


**FIGURE 4.** Relative additive concentration evolution over run time.

- The dual-loop lubricating system effectively protected each subsystem from contaminants present in other subsystems. The valvetrain was effectively protected from soot contamination, indicating the potential for reduced wear.
- The dual-loop lubrication system provides opportunity for emissions improvements by allowing use of low-SAPS lubricants in the power cylinder.

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**3.** Plumley, Wong. “Analysis of Shear-thinning on Engine Friction Using Mineral and PAO Base Oils”. Presentation. STLE 69th Annual Meeting and Exhibition, May 18–22, 2014, Orlando, FL.

**4.** Plumley, Wong. “Optimizing Base Oil Viscosity for Power Cylinder Friction Response Temperature Dependency” Presentation. STLE 69th Annual Meeting and Exhibition, May 18–22, 2014, Orlando, FL.

**5.** Martins, Plumley, Wong. “Engine Lubricant Viscosity Optimization for Valvetrain and Power Cylinder Systems”. Presentation. STLE 69th Annual Meeting and Exhibition, May 18–22, 2014, Orlando, FL.

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# II.6 High Compression Ratio Turbo Gasoline Engine Operation Using Alcohol Enhancement

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## 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 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 octane requirements and knock-suppressing characteristics of ethanol-gasoline, ethanol-water, methanol-gasoline fuel blends over the engine's operating map.
- 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.
- Quantify two practical approaches: two tanks, one each for gasoline and 85% ethanol and 15% gasoline (E85); onboard gasoline (which is 10% ethanol, aka E10) separation into high and low octane streams.

## Fiscal Year (FY) 2014 Objectives

- Complete set of performance maps for turbocharged spark-ignited (SI) engines with blends of gasoline with ethanol, defining the knock onset contours.
- Complete development of chemical-kinetic methodology that defines knock onset on these performance maps for gasoline-ethanol blends.
- Continue engine-in-vehicle simulations using the code Autonomie to assess fuel economy benefits and ethanol usage as a function of compression ratio, boost level, and extent of engine downsizing.
- Determine the octane requirements of a turbocharged engine over the full load and speed range.
- Explore the potential for membrane-based onboard gasoline (E10) separation into high and low octane streams.

## FY 2014 Accomplishments

- Finalized our set of simulation-based turbocharged SI engine performance maps for a range of different knock-suppressing fuels.
- Validated a fundamentally-based chemical-kinetic methodology for predicting knock onset at peak cylinder conditions for different fuels.
- Completed our light-duty engine-in-vehicle simulations, using Automonie, quantifying the significant fuel economy benefits that knock suppression provides.
- Initiated work on onboard fuel separation to produce the high octane ethanol stream this approach requires.

## Future Directions

- Complete our experiments that determine the octane requirements of our turbocharged 2-liter engine at mid and low loads to explore the application of onboard membrane fuel separation (pervaporation).
- Quantify the knock-suppressed turbocharged-engine fuel economy benefits in medium-duty vehicles.
- Analyze the single-cylinder SI engine data from Cummins; compare it with our performance maps.

- Develop a model of onboard fuel separation system for use with engine-in-vehicle simulations to explore benefits of onboard fuel separation.

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## INTRODUCTION

The objectives of this project are to quantify the potential for improving the performance and efficiency of gasoline engine technology through use of alcohols to suppress knock. Use of an “anti-knock” fuel such as ethanol, enables use of higher compression ratios, increased turbocharging, and significant engine downsizing.

## APPROACH

Our approach is to generate engine performance maps with compression ratios and boost levels significantly higher than current values, using knock suppressing fuels (such as ethanol) at high load to prevent the occurrence of knock with gasoline. Knock onset limits are defined experimentally and through induction-time integral and fundamental kinetic autoignition modeling. These performance maps are then used in engine-in-vehicle simulations (Autonomie) to quantify the reductions in vehicle gasoline consumption and the amount of the different knock-suppressing fuels required.

## RESULTS

Experimental work in our turbocharged direct-injection gasoline engine test facility has produced experimental engine performance maps with gasoline and other knock-suppressing fuels. The simulation tools for engine combustion analysis (GT-POWER), and knock-onset calculations (CHEMKIN™), have been used to interpret and expand this experimental database to higher compression ratios and boost levels.

Vehicle simulation results are summarized in Table 1. It shows the effects of engine downsizing and spark retard on average engine efficiency and miles per gallon for three driving cycles, for a 2.4-L naturally aspirated engine and 1.2-L boosted engine in a mid-size car. Downsizing and boosting results in significantly higher vehicle fuel economy (measured as miles per gallon, MPG) and brake engine efficiency, but requires higher ethanol consumption for knock suppression (shown as a percentage in the MPG columns). For urban driving, downsizing increased MPG and average engine efficiency by 30%: ethanol consumption increased from 1% to 12%. Spark retard reduces the ethanol consumption requirements.

As part of our study of onboard fuel separation into higher and lower octane streams, we have quantified our turbocharged engine’s octane requirements over its performance range. Figure 1 shows various fuels’ knock limits on the map. Primary reference fuel blends were tested on a General Motors Ecotec engine to establish knock limits in low load regions.

This octane requirement map with operating points obtained from the driving cycle simulation, yields the fuel octane requirement distribution. Figure 2 shows the Research Octane Number (RON) distribution in terms of fuel energy consumed. About 36% of fuel used was under 50 RON. The weighted average for fuels above 50 RON for urban driving is about 77 RON.

We used primary reference fuels (PRF), mixtures of iso-octane and n-heptane, to explore the chemistry-based nature of knock. Illustrative results are shown in Figure 3 for individual knocking cycles for engine operating conditions of 8.5 bar brake mean effective pressure (BMEP) and 1,500 rpm, at three spark timings. We compare the gas temperature at 25 crank angle

**TABLE 1.** Effect of Turbocharging and Engine Downsizing on MPG and Engine Efficiency*

| | Engine Displacement | UDDS | | HWFET | | US06 | |
|---|---|---|---|---|---|---|---|
| | | MPG (ethanol %) | Brake Efficiency (%) | MPG (ethanol %) | Brake Efficiency (%) | MPG (ethanol %) | Brake Efficiency (%) |
| **MBT** | **2.4-L** | 26.5 (1) | 21 | 37 (0.5) | 24.8 | 25.8 (5) | 29.2 |
| | **1.2-L** | 35.2 (12) | 28.7 | 48.5 (9) | 31.2 | 30.5 (38) | 34.5 |
| **5° max retard** | **2.4-L** | 26.2 (0.2) | 21 | 38 (0.1) | 24.5 | 25.7 (1.5) | 29 |
| | **1.2-L** | 35.5 (5) | 28.3 | 48.5 (3) | 31 | 29.8 (20) | 33.6 |
| **10° max retard** | **2.4-L** | 26.5 (0) | 21 | 38.7 (0) | 24.3 | 25.4 (0.5) | 28.8 |
| | **1.2-L** | 35 (2.5) | 28 | 48.5 (1) | 31 | 29.3 (12) | 33 |

*Drive cycles used: Urban Dynamometer Driving Schedule, UDDS; Highway Fuel Economy Test, HWFET; US06, high-speed aggressive driving cycle. MBT – minimum spark advance for best torque.

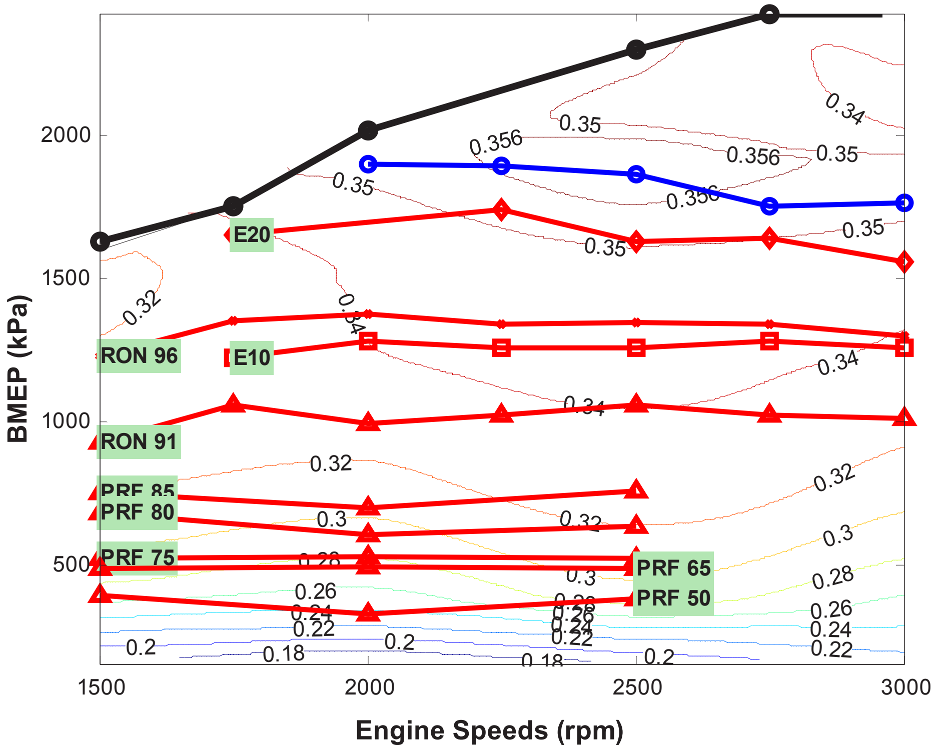

**FIGURE 1.** Fuel octane requirements superposed on turbocharged engine performance map. Engine peak pressure constraint (blue line), knock onset lines for fuels ranging from PRF 50 to 20% ethanol in gasoline (E20): at MBT spark timing, compression ratio 11.5.

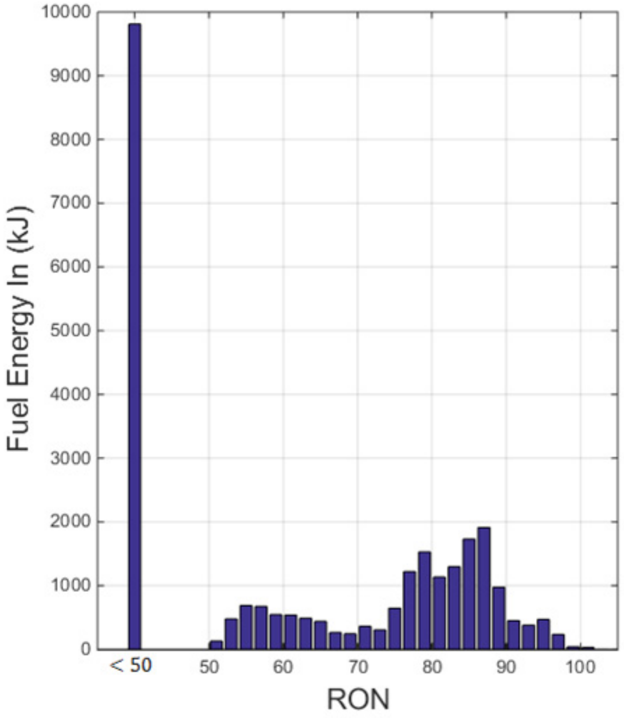

**FIGURE 2.** Gasoline (or PRF) RON distribution as a function of fuel energy for the UDDS driving cycle: turbocharged engine, 11.5 compression ratio, mid-size car, MBT spark timings.

before top-dead center (CA BTDC) determined from GT-POWER, to that determined from CHEMKIN that results in knocking. The horizontal scale shows the gas temperature estimated from GT-POWER. The vertical axis, $T_{Chemkin\_knock}$, shows the lowest temperature determined from CHEMKIN, that results in knocking. The results indicate that the model, with local end-gas temperatures about 25 K higher than the spatial average (at 25 CA BTDC) successfully predicts knock onset. Note that GT-POWER predicts the average end-gas temperature: our CHEMKIN methodology is based on the hottest local end-gas temperatures which are higher than the average.

## CONCLUSIONS

- Appropriate engine performance maps (BMEP vs. speed) embodying knock limits, for engine-in-vehicle drive cycle studies, can be generated through high-level engine simulation codes (such as GT-POWER). Critical questions are: turbocharger configuration and engine size scaling, effects of spark retard on knock onset for a given fuel, and maximum pressure constraints.

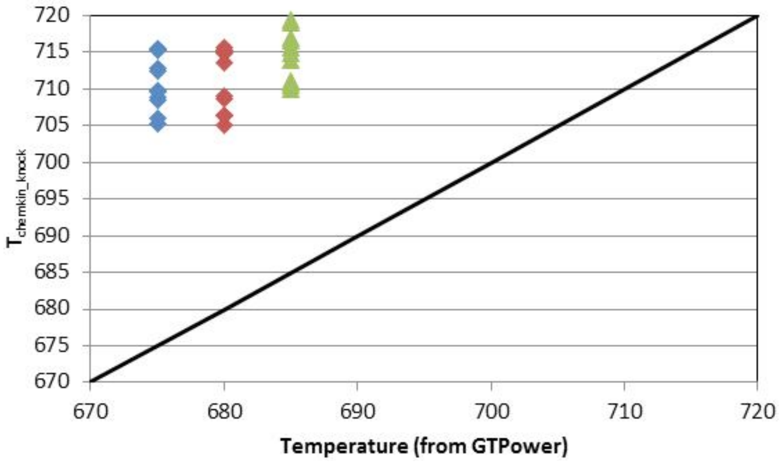

**FIGURE 3.** Knocking cycles: comparison between model (CHEMKIN-based) and engine model (GT-POWER), for engine operating conditions of 8.5 bar BMEP and 1,500 rpm, for three spark timings.

- Blends of gasoline with increasing amounts of ethanol, and also E85-water mixtures, substantially increase the knock-suppressing impact of the high-octane fuel.
- Chemical-kinetic-based knock onset prediction modeling in the engine's end gas can reliably predict autoignition. Empirical induction-time integral autoignition models can be calibrated to match experimental and chemical-kinetic based data.
- Measurements of engine octane requirement, high to mid to low load, show at least a factor of two reduction in RON required.
- Engine-in-vehicle simulations of various drive cycles in a mid-size car show that knock suppression with alcohol fuels enables an increase in compression ratio and boost level that, with engine downsizing, offers substantially higher engine efficiency and vehicle fuel economy.
- The amount of knock-suppressing fuel required can be significantly reduced with spark retard to 1% to 10%, relative to the (mostly) gasoline consumed, depending on driving cycle.

## FY 2014 PUBLICATIONS/PRESENTATIONS

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# II.7 Demonstration/Development of Reactivity Controlled Compression Ignition (RCCI) Combustion for High-Efficiency, Low-Emissions Vehicle Applications

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## 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) 2014 Objectives

- HD/LD computational fluid dynamics support/final combustion system specification.
- LD experiments with WERC piston bowl.
- HD experiments with dual-fuel direct injection.

## FY 2014 Accomplishments

- Novel two-zone piston bowl developed analytically.
- LD testing of analytically developed two-zone piston bowl with comparison to Open bowl.
- Demonstrated HD RCCI combustion at the rated power point (1,800 rpm, 21 bar indicated mean effective pressure). The data were acquired with a 12:1 compression ratio, but still had a 48% gross indicated efficiency with engine-out oxides of nitrogen (NOx) below 0.25 g/kg-f and peak pressure rise rates below 10 bar/deg.

## Future Directions

- Final reporting.
- Technical paper publication.

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## 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.

## APPROACH

For FY 2014, the LD engine experimental work was conducted at ORNL, while the HD engine testing was done at UW-ERC in collaboration with Caterpillar on a modern C15 single-cylinder engine. The HD work included installation of a dual-injector head to facilitate direct injection of both fuels, as well as quantifying performance with dual-fuel direct injection. The LD work was carried out on a General Motors 1.9-L multi-cylinder diesel engine and included testing with computationally derived WERC two-zone piston bowl design.

WERC used advanced computational fluid dynamics modeling tools to explore combustion system design and engine calibration with focus on extending the useful operating range with maximum efficiency. Focus was on investigating benefits of a unique analytically developed combustion chamber design.

## RESULTS

A novel two-zone piston bowl design (see Figure 1) was developed which addresses three of the major challenges associated with RCCI combustion, simultaneously: reduces peak heat release rate (HRR) and peak rate of pressure rise (RoPR), unburned hydrocarbon (UHC), and CO emissions. The strong flows developed between the two combustion zones result in enhanced mixing, which reduces the UHC and CO emissions. This allows later high reactivity fuel injection timings, which lowers the peak HRR and RoPR and also helps maintain control over combustion phasing. Therefore, the two-zone piston bowl design is a potential breakthrough towards the practical application of RCCI combustion. Bergin et al. [1] show the two-zone piston helps control RoPR and decreases unburned fuel emissions at high loads (9–18 bar brake mean effective pressure, BMEP) in both LD and HD engines.

The two-zone bowl was examined at medium load operation consistent with loads in the LD vehicle drive cycle (7.6 bar BMEP 2,600 rev/min). Experiments were performed in the multi-cylinder General Motors 1.9-L LD engine installed at ORNL. Three different configurations of testing were performed: Open bowl using RCCI injection strategy with early (~-55°) start of injection (SOI) timings, two-zone bowl with the RCCI strategy, two-zone bowl with late (~-11° SOI) or jet-ignition. For the two-zone jet-ignition cases, the load was increased in a stair step fashion from 7.8- 9.2 bar BMEP by increasing the amount of port fuel injection and adjusting the SOI for the diesel fuel to maintain phasing.

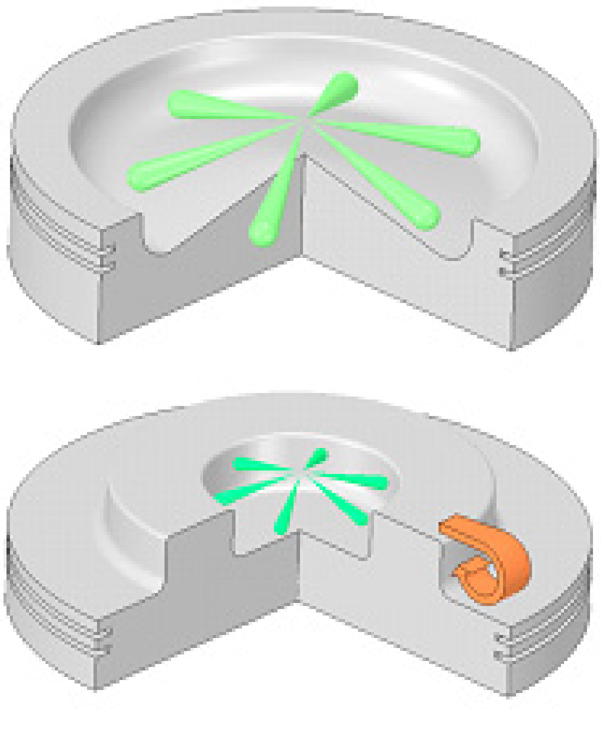

**FIGURE 1.** Two-Zone Geometry (bottom) and Generic Open Geometry (top) (Green shapes indicate fuel sprays. Orange arrow indicates hot combustion gases from inner volume entering outer volume.)

Figure 2 shows the pressure and heat release for all cases. The jet-ignition cases, mostly have lower maximum pressures compared to the Open bowl due to later heat release phasing, despite operating with a higher intake manifold pressure and higher compression ratio. All of the two-zone jet-ignition cases exhibit the same small initial heat release followed by a larger event when the outer volume ignites. The injections for the jet-ignition cases are very late (SOI -12.1 to -9.3) with high pre-mixed fuel fractions (~94%). The amount of direct injection fuel stays constant over the load range. The combustion phasing was positively correlated with the fuel injection timing. That is, if the injection was advanced then phasing was advanced and vice versa. The jet-ignition cases had low CO+UHC relative to the open piston case.

Figure 3 shows the CO+UHC versus NOx for all cases. The RCCI two-zone has the best emissions trade-off of any of the cases. An interesting trend can be seen with the jet-ignition cases in that the NOx emissions decrease as the load is increased because the direct injection timing could be retarded allowing less time for NOx formation. A modeling study [2] was performed

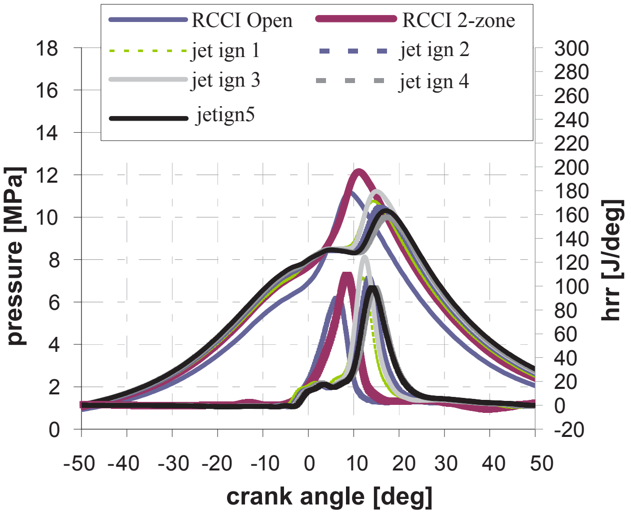

**FIGURE 2.** Experimental Pressure and Apparent Heat Release Rate for all Cases

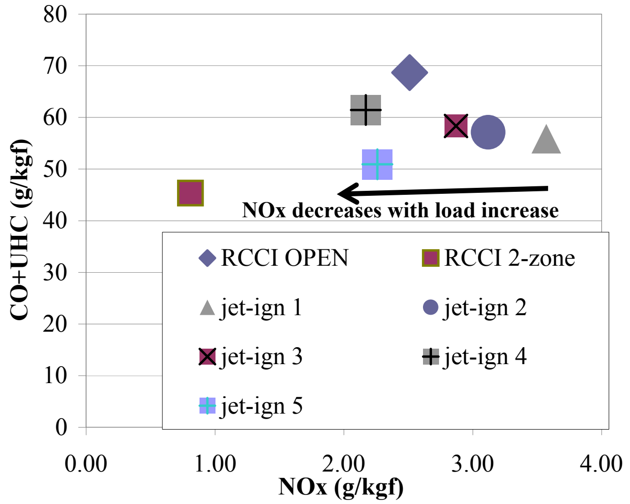

**FIGURE 3.** Experimental CO+UHC versus NOx for all Cases

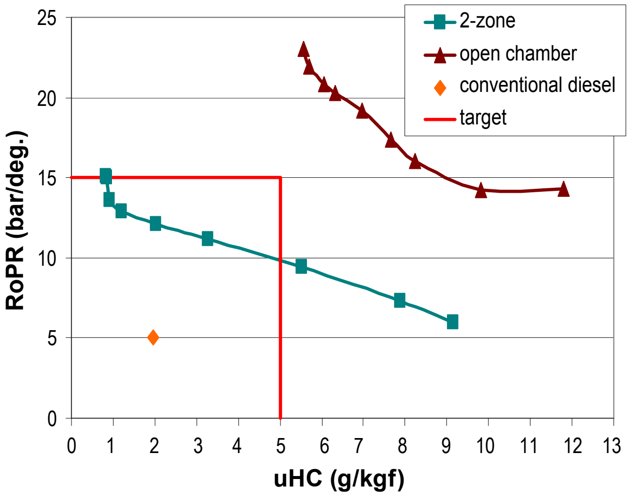

**FIGURE 4.** Peak Rate of Cylinder Pressure Rise vs. Unburned Hydrocarbon Emissions

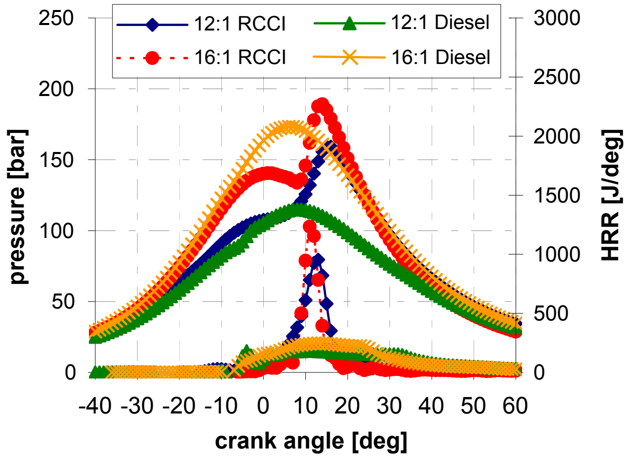

**FIGURE 5.** Cylinder Pressure and Heat Release Results for two Compression Ratios; Data were Acquired at the Rated Engine Power (see text for more details).

on the cases shown to provide insight into cycle-to-cycle variations seen with the jet-ignition cases. Fuel stratification of the pre-mixed fuel was shown to be a likely cause.

HD simulations performed were focused on optimizing the two-zone chamber volumes and squish height. The results shown in Figure 4 indicate a near optimal volume split between the combustion zones of 60/40 (outer/inner) and a clearance height (squish) of approximately 1 mm. The results also emphasize the importance of minimizing the top ring land crevice region of the piston. Increased crevice volumes result in increased unburned hydrocarbon emissions when using premixed low reactivity fuels.

HD engine experiments were performed to compare the performance characteristics of RCCI and conventional diesel combustion at rated operating condition (1,800 rpm, max load). Data were acquired for two engine geometries: the stock piston with a 16:1 compression ratio, and an Open bowl with a 12:1 compression ratio. Cylinder pressure and HRR results for these tests can be found in Figure 5. The high compression ratio RCCI data gave the highest gross indicated efficiency of 53%, but the load was constrained to 17 bar by the high RoPR (approaching 20 bar/deg). This, along with the high peak cylinder pressure, led to the investigation of the lower compression ratio piston. The 12:1 RCCI data shown in Figure 5 were acquired at 20 bar indicated mean effective pressure, and had a 47% gross indicated efficiency, which was comparable to the 16:1 conventional diesel combustion result in spite of the low compression ratio. The RCCI cases had low engine-out emission levels. All of the tests were performed using a 93 Research Octane Number gasoline and a 45 Cetane Number diesel fuel. Additionally, a dual-injector head was tested. There was a slight detriment of performance seen with dual-fuel direct injection in terms of increased CO, UHC and soot.

## CONCLUSIONS

- A novel two-zone piston bowl design was developed, which addresses three of the major challenges associated with RCCI combustion, simultaneously. The new bowl design reduces the peak HRR, peak RoPR, as well as uHC and CO emissions.
- LD experiments were planned to demonstrate the potential of the two-zone piston concept to extend RCCI's operating range.

- The two-zone pistons were installed in the ORNL LD engine and it was found that:
    - Higher loads could be achieved relative to the standard Open bowl piston geometry (using engine noise or pressure rise rate as the limiting factor).
    - The two-zone pistons operated at a lower maximum pressure despite having more boost and a higher compression ratio (15.1 for the open and 15.5 for the 2-zone).
    - The already low NOx emissions decreased with increasing load.
- High-load (20 bar) operation of RCCI was demonstrated in the HD engine with an acceptable peak pressure rise rate and moderate peak in-cylinder pressure using a 12:1 compression ratio; gross indicated efficiency was comparable to the stock engine's gross indicated efficiency at the same condition.
- Direct injection of the less reactive fuel (gasoline) for RCCI was not found to extend the load range of the engine when using the stock reactive fuel (diesel) injection timings.

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## FY 2014 PUBLICATIONS/PRESENTATIONS

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**2.** Bergin, M. J., et al., "Load Limit Extension in Pre-Mixed Compression Ignition Using the 2-zone Combustion System," SAE Technical Paper Submission, 15PFL-0317.

**3.** Storey, S., et al., "The Contribution of Lubricant to the Formation of Particulate Matter with Reactivity Controlled Compression Ignition in Light-Duty Diesel Engines," *Emiss. Control Sci. Technol.*, Article in Press, DOI 10.1007/s40825-014-0007-2.

# II.8 Hybrid Base-Stock Fluids for Fuel Efficient Lubricants

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## Overall Objectives

- Develop hybrid base-stock fluids as lubricants to minimize viscosity and thus improve fuel economy.
- Conduct comprehensive characterization of the rheological properties of hybrid fluid systems.
- Evaluate tribological performance of the hybrid base stocks and optimize blend mixtures to minimize friction and wear in tribological contacts.
- Assess the impact of conventional lubricant additives on the tribological performance of fluid mixtures.

## Fiscal Year (FY) 2014 Objectives

- Formulate polyalphaolefin (PAO)-ester blends with various ratios.
- Characterize rheological properties of PAO-ester fluid mixtures.
- Evaluate friction and wear performance of PAO-ester fluid mixtures.

## FY 2014 Accomplishments

- Formulated hybrid base-stock mixtures with different PAO-ester ratios.
- Measured rheological properties for hybrid base-stock blends. Various PAO-ester ratios showed substantially lower viscosity than mineral-based lubricants (over two-times reduction at both low and high temperature).
- Evaluated traction coefficient under slide/roll contact for different PAO-ester ratios. All blended mixtures showed lower traction coefficient compared to pure PAO.
- Determined that friction and wear performance of all PAO-ester mixtures under sliding contact was superior to that of PAO alone. Up to 50% friction reduction and up to six times less wear were determined for the hybrid mixtures compared to PAO of similar viscosity.

## Future Directions

- Develop a thermodynamic model to predict rheological properties of binary and ternary fluid mixtures.
- Conduct comprehensive characterization of rheological properties of additional hybrid base stocks produced from different chemistries and viscosities.
- Evaluate friction and wear performance of fluid mixtures with optimized rheological properties.
- Evaluate the effect of model additives on friction and wear behavior of base-stock fluid mixtures.

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## INTRODUCTION

Different engine components and systems operate in various lubrication regimes. For overall engine friction reduction, the oil should exhibit low viscous shear losses in the hydrodynamic and elasto-hydrodynamic regimes. A problem arises when low viscosity oils are used in the boundary regime, as oil viscosity reductions also translate into reduction in fluid film thickness and hence an increase in friction, wear, and reliability concerns in components. For this reason, low-viscosity mineral oils are usually loaded with high levels of additives—mostly low-friction, antiwear, and extreme pressure additives—for adequate performance under the boundary regime. Nevertheless, numerous problems are associated with excessive use of additives [1]. Another problem with low-viscosity mineral oils is the increased evaporation rate. The development of a synthetic, low-viscosity hybrid base-stock provides a potential pathway to practical and commercial use of a low-viscosity lubricant. The rheological properties of base-stock fluid can be optimized for reducing friction in the hydrodynamic regime without compromising performance in the boundary regime. This engineering will enable both fuel economy and reliability of engine components with the beneficial aspect of the reduced evaporation rate.

## APPROACH

Base-stock fluids for engine oil formulations are usually based on mineral oil or synthetic fluid. These fluids usually have a homogeneous composition and rheological properties. When different base fluids are mixed, however, the rheological properties of the fluid mixture can be substantially different from those of the constituent fluids [2]. Ester is the most widely used base stock in extreme applications, such as aerospace, because of its desirable properties such as stability over a wide temperature range, low volatility, and inherent lubricity and wear protection, but it is too expensive for vehicle lubrication. PAO is the main synthetic base-stock used in engine oils for its good performance at a relatively low cost. A fluid mixture of PAO and ester can provide a cost-effective composite base stock for new-generation engine oil formulations.

The project proposes to develop a composite base-stock consisting of the two fluids in order to minimize viscous shear losses. The approach will involve the mixture of low-viscosity PAO fluids (PAO-4 and PAO-2) and different low-viscosity ester fluids. The rheological properties of the blend mixtures and the pure fluids will be measured. Also, friction, wear, and scuffing performance will be determined for all mixtures. The same attributes will be also evaluated for the hybrid base-stock fluids in the presence of conventional model additives to lubricants.

## RESULTS

During the first year of this project, the hybrid base-stock fluids were formulated by mixing different ratios of polyol ester in PAO-4 (0, 30, 40, 50, 60, 70, and 100 wt%), both with similar viscosities. Comprehensive characterization of the rheological properties of the hybrid basestock composites was conducted over a wide range of temperatures.

**Rheological Properties:** Kinematic viscosity and the viscosity index were measured with a Koehler capillary viscometer at constant temperature (40°C and 100°C). In addition, a cold-crank viscosity simulator was used to measure the viscosities of the test fluids between -20°C and -40°C, and high-temperature high-shear (HTHS) viscosities were measured at 150°C with the Tannas HTHS viscometer. The kinematic and cold crank viscosity values are summarized in Table 1.

Figure 1a shows the cold crank viscosity as a function of temperature for the pure PAO, ester base-stock, and mineral oil base-stock. Values for all the blended mixtures (Table 1) fall between the PAO and ester values, and are considerably lower than those for the reference mineral oil. This difference is more pronounced at the lowest temperatures (-35°C and -40°C), where the viscosity values for the mineral oil drastically increases compared to the almost constant values for the synthetic fluids. Similar behavior was found for the HTHS viscosity measurements, with all synthetic fluids exhibiting considerably lower viscosity than that of the reference mineral oil (Figure 1b). In both cases, the pure ester exhibited slightly higher viscosity than the fluid mixtures and PAO alone, although this difference was negligible compared to that of the mineral oil values.

The traction coefficient under slide/roll contact was also evaluated for the mixed base stocks and pure constituents. A PCS Instruments traction machine was used to measure traction coefficient (see test conditions summarized in Figure 2). Comparison of the traction properties for the different mixtures and their pure constituents showed noticeable lower traction coefficients for the mixtures. Since the traction coefficient is a direct measurement of the viscous shear resistance of the fluid, this lower traction coefficient translates to lower viscous losses.

**Tribological Evaluation**: The friction and wear attributes of the hybrid base-stock were assessed under

**TABLE 1.** Kinematic and Cold Crank Viscosities for Hybrid Base-Stock Mixtures, as well as Pure Ester and Pure PAO-4

| %Ester | Kinematic Viscosity (cSt) | | | Cold Crank Viscosity (cP) | | | | |
|---|---|---|---|---|---|---|---|---|
| | 40°C | 100°C | VI | -20°C | -25°C | -30°C | -35°C | -40°C |
| 0 | 17.8 | 4 | 124 | 306 | 563 | 846 | 1,453 | 2,489 |
| 30 | 17.8 | 4.06 | 130 | 319 | 572 | 862 | 1,490 | 2,575 |
| 40 | 17.9 | 3.95 | 117 | 302 | 572 | 866 | 1,511 | 2,635 |
| 50 | 17.9 | 4.01 | 123 | 331 | 601 | 925 | 1,588 | 2,784 |
| 60 | 18.3 | 4.16 | 133 | 337 | 609 | 928 | 1,630 | 2,874 |
| 70 | 18.4 | 4.34 | 150 | 350 | 639 | 994 | 1,722 | 3,060 |
| 100 | 19.6 | 4.33 | 132 | 439 | 770 | 1,219 | 3,414 | 5,410 |

VI – viscosity index

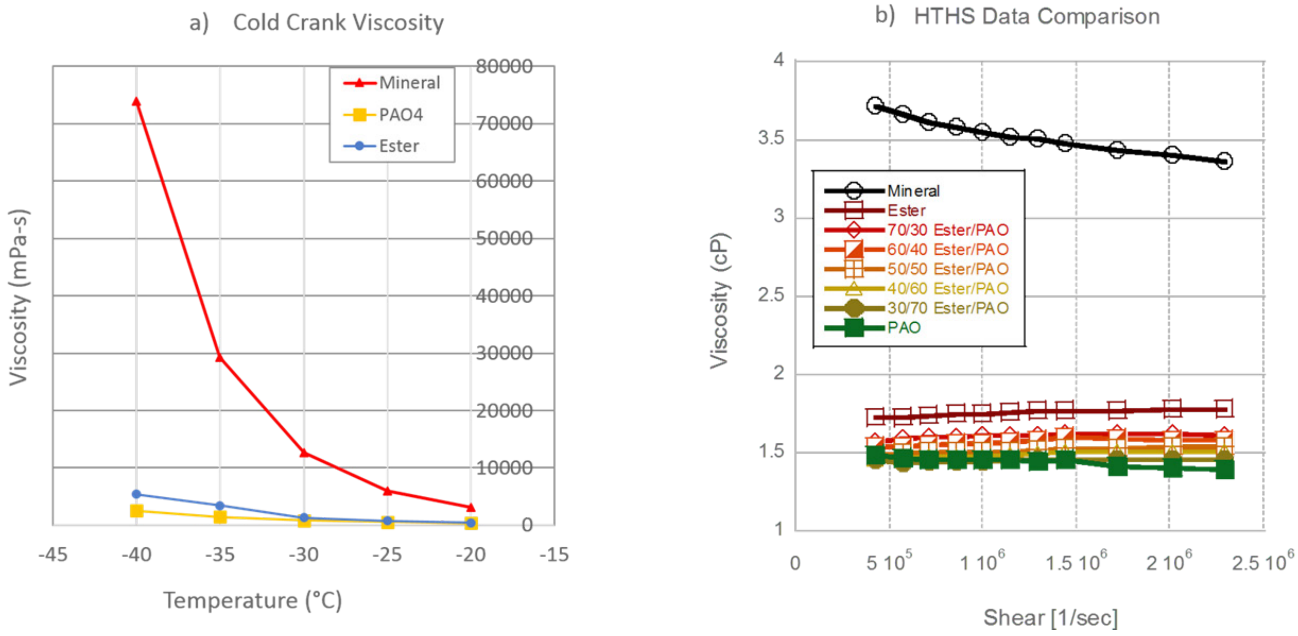
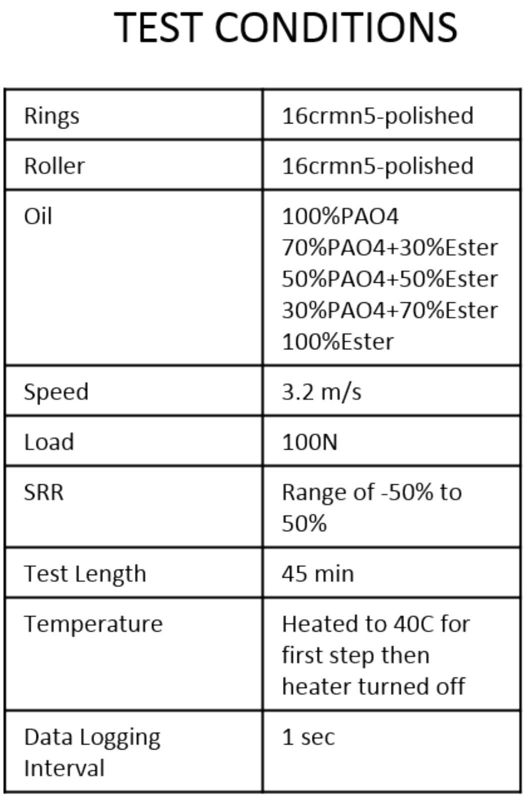


**FIGURE 1.** (a) Cold crank viscosity as a function of temperature for PAO-4, reference mineral oil, and reference ester and (b) HTHS viscosity as a function of shear rate for hybrid base-stock mixtures, as well as pure ester and pure PAO-4.



TEST CONDITIONS

| | |
|---|---|
| Rings | 16crmn5-polished |
| Roller | 16crmn5-polished |
| Oil | 100%PAO4<br>70%PAO4+30%Ester<br>50%PAO4+50%Ester<br>30%PAO4+70%Ester<br>100%Ester |
| Speed | 3.2 m/s |
| Load | 100N |
| SRR | Range of -50% to 50% |
| Test Length | 45 min |
| Temperature | Heated to 40C for first step then heater turned off |
| Data Logging Interval | 1 sec |

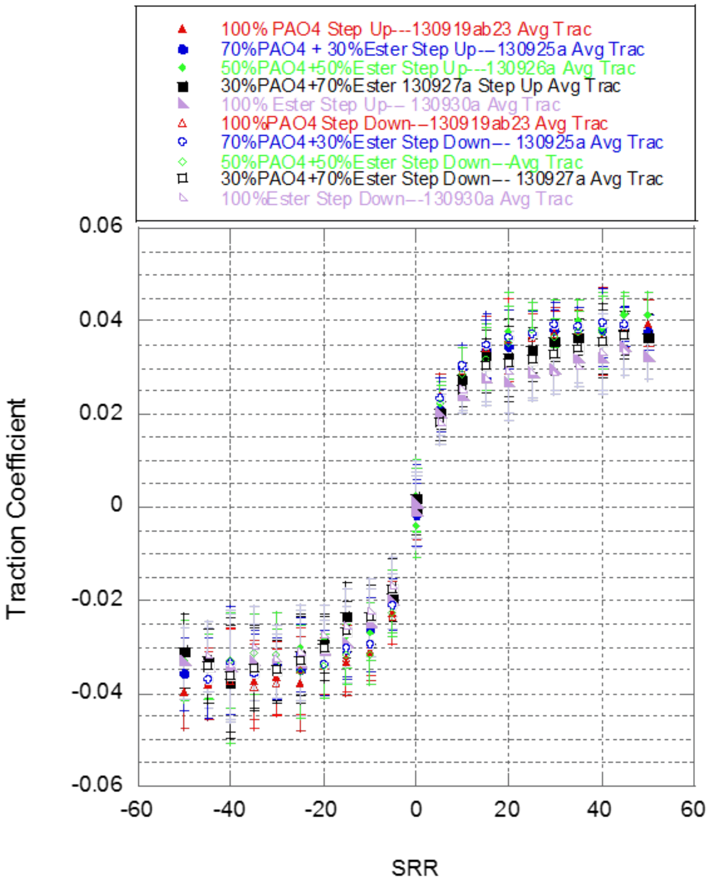


**FIGURE 2.** Traction coefficient as a function of slide-to-roll ratio (SRR) for hybrid base-stock mixtures, as well as pure ester and pure PAO-4.

both reciprocating and unidirectional sliding contacts using a ball-on-flat configuration, in which a 52100 steel ball and flat were lubricated with the blend mixtures and tested at 100°C. A normal load of 15.6 N (~1 GPa Hertzian contact pressure) was applied for two types of test: reciprocating sliding at 1 Hz with a maximum speed of 1 cm/s and unidirectional sliding at 1 cm/s. Both test types were run for an hour. A minimum of two tests for each fluid was performed to ensure repeatability. Figure 3 shows the average friction coefficient for all the fluids evaluated. These results show that for both types of tests, the addition of any amount of ester ≥30 wt% to the PAO base stock reduced the friction coefficient by at least 50%. For reciprocating sliding, the friction coefficient was reduced from ~0.16 to ~0.10 for all ratios of ester evaluated. Similarly, for unidirectional sliding, the friction coefficient dropped from ~0.17 to ~0.12 for all mixtures.

After testing, wear tracks of both counterface materials, flats and balls, were characterized by optical microscopy and white light profilometry in order to assess the wear mechanism and estimate the total wear volume. Figure 4 summarizes the average wear volume measured in the steel flat in both types of tribological tests. It is worth noting that only PAO produced a wear scar with material removal (positive wear) in contrast to all the other fluids, in which a protective tribofilm was formed or grown on the surface (negative wear). This trend is even more significant when it is taken into consideration that the lowest amount of ester (30 wt%) produced the thickest protective film in all hybrid mixtures evaluated.

Wear volume produced in the steel ball counterface for all the fluids tested was also measured and averaged among repeat tests. As shown in Figure 5, ball wear was significantly reduced by the addition of any amount of ester to the PAO. The strongest effect occurred under reciprocating sliding, with a wear reduction of six times greater than that of pure PAO. The lowest wear was observed at 40-60 wt% ester in PAO, but even the smallest amount of ester yielded a wear reduction of three times. Under unidirectional sliding, we observed the same trend of ball wear reduction with addition of ester, but this trend was more gradual and directly related to the amount of ester in the fluid. Over 70 wt% of ester

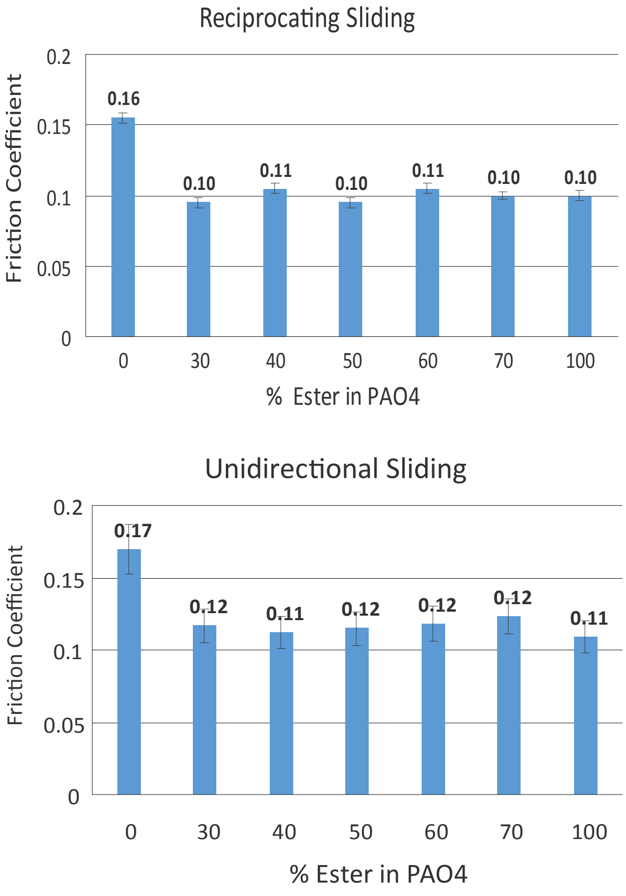


**FIGURE 3.** Friction coefficient under reciprocating and unidirectional sliding for hybrid base-stock mixtures, as well as pure ester and pure PAO-4.

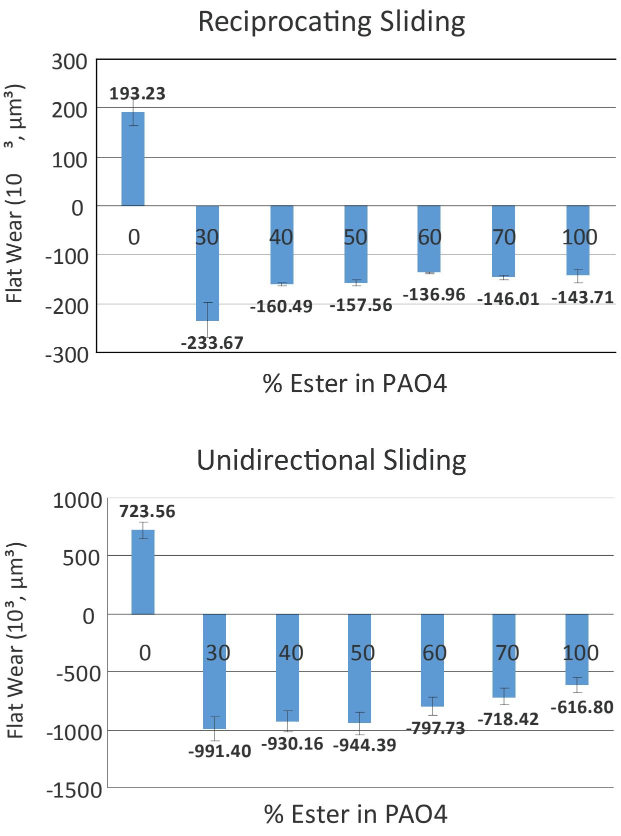


**FIGURE 4.** Flat wear volume under reciprocating and unidirectional sliding for hybrid base-stock mixtures, as well as pure ester and pure PAO-4.

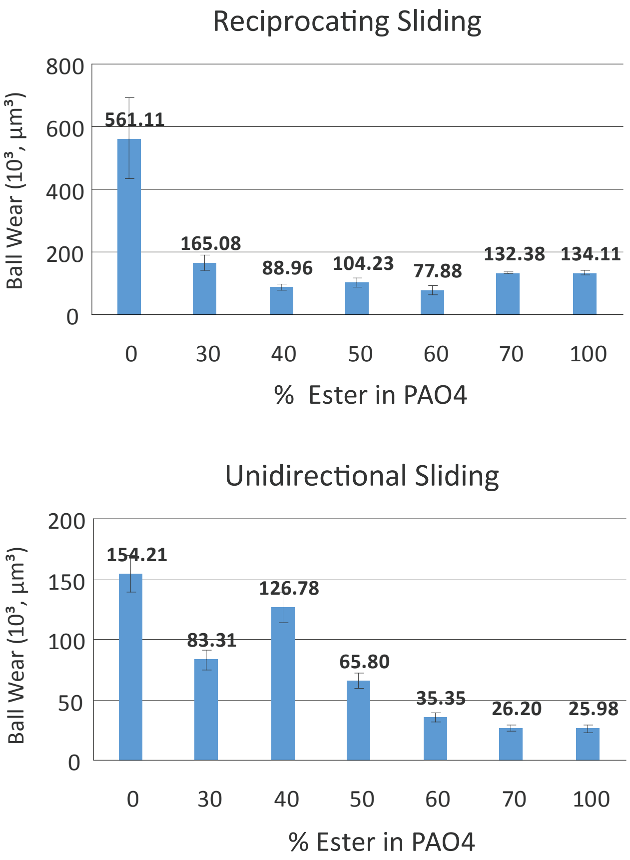


**FIGURE 5.** Ball wear volume under reciprocating and unidirectional sliding for hybrid base-stock mixtures, as well as pure ester and pure PAO-4.

produced the least amount of wear, with a reduction of six times compared to that of the pure PAO base-stock.

These results clearly indicate that any amount of ester ≥30 wt% added to the PAO drastically improved tribological performance overall, with significant wear reduction in both ball and flat, as well as reduction in friction coefficient by 50% compared to that of pure PAO.

## CONCLUSIONS

We concluded from a comprehensive evaluation of the rheological properties for hybrid base-stock fluids that:

- Viscosity measurements of the all hybrid base-stock fluids evaluated are about the same.
- All synthetic hybrid base-stock mixtures showed substantially lower cold temperature viscosity and HTHS viscosity values compared to mineral oil-based lubricants (over two times).

We also concluded that under slide/roll contacts, the mixture fluids showed noticeably lower traction coefficients.

The tribological performance of all hybrid base-stock fluids was significantly improved compared to pure PAO under both unidirectional and reciprocating sliding:

- Friction coefficient was reduced by 50%.
- Wear in the ball counterface was reduced by six times.
- Wear in flat specimens was unmeasurable as a protective surface film was produced with the use of hybrid base-stock mixtures.

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# II.9 Optimization of Non-Ferrous Coatings for Improved Lubricant Performance

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## Overall Objectives

- Identify and incorporate catalytically active non-ferrous metallic and ceramic ingredients in a nanocomposite coating that can derive carbon-based boundary films from long-chain hydrocarbon molecules of lubricating oils.
- Using a commercial-scale CemeCon (Model: CC800/9XL) deposition system, produce and optimize the structure and chemical composition of the nanocomposite coatings at large scales and reasonable costs.
- Characterize the structural, mechanical, adhesion, and tribological properties afforded by carbon-based boundary films and elucidate their unique lubrication mechanisms.
- Explore the viability of the large-scale applications of optimized coatings in next-generation engine components that will operate under increasingly harsh conditions so that their performance, efficiency, and durability are maximized.
- Demonstrate viability of the novel coatings under actual (motored/fired) engine conditions and transfer technology to industry.

## Fiscal Year (FY) 2014 Objectives

- Identify and procure sputtering targets that are suitable for catalytically active non-ferrous coating deposition.
- Develop reliable/repeatable deposition protocols to optimize these coatings.
- Characterize their structural, mechanical, and tribological properties.
- Perform post-test surface analysis to understand their friction and wear mechanisms.
- Demonstrate the viability of the optimized coatings under harsh tribological conditions.

## FY 2014 Accomplishments

- During FY 2014, we ordered a number of non-ferrous sputtering targets and commenced our systematic studies to confirm their viability for the development of non-ferrous coatings. Initial trials with V and Cu worked quite well. We achieved a 2.2 µm-thick coating with very strong adhesion and confirmed a very smooth surface finish. The deposition parameters (e.g., bias voltage, substrate temperature, and deposition chamber pressure) were optimized during the deposition trials of these coatings. The microhardness of the coating was about 23 GPa. We are currently performing scanning electron microscopy and X-ray diffraction to determine the structural and chemical nature of this coating.
- We have run many coating trials to further optimize the physical vapor deposition conditions in a commercial-scale coating unit and successfully produced a range of non-ferrous coatings on test samples for tribological evaluation.
- We optimized the bonding, thickness, and surface finish of these coatings by effectively controlling the deposition parameters.
- During FY 2014, we also procured the sputtering targets for the synthesis of other non-ferrous coatings (NbN-Ni, NbN-Cu, WN-Ni, WN-Cu, MoN-Ni, etc.).
- Several engine and lubricant companies have showed strong interest in testing the performance of these coatings on sliding and rolling engine components.

## Future Directions

- Develop and optimize non-ferrous coatings in nanocomposite form from V, Nb, W, Ni, Cu, and Ag.
- Optimize coating microstructure, adhesion, hardness, surface roughness, and chemistry.
- Perform detailed characterization of chemistry and structure of the coatings using both surface and structure-sensitive techniques.

- Evaluate effects of coating composition on tribological behavior under boundary-lubricated sliding regimes.
- Using a pin-on-disk and a reciprocating test machine, perform endurance test on these coatings under severe boundary-lubricated sliding conditions with poly-alpha-olefin (PAO) base oil and assessing its ability to derive a boundary film from the lubricating oil that is similar to that of diamond-like carbon (DLC).
- Characterize boundary films and elucidate lubrication mechanism using surface sensitive techniques.
- Perform long duration friction and wear tests using a bench tribological test machines and demonstrate superior performance under conditions that are typical of actual engine components (load, speed, and temperature).
- Evaluate effect of oil type (synthetic, mineral, vegetable, and additized) on friction and wear performance of non-ferrous coated surfaces.
- Explore other promising coatings systems incorporating, Pt, Pd, Ir, etc. (other than the current ones). Continue to test the friction and wear performance of these new coatings with bench-top ring-liner and block-on-ring test machines.
- Collaborate with industry and establish test programs for more engine-specific applications.

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## INTRODUCTION

During the past two decades, public awareness for more fuel-efficient engine systems has increased considerably, mainly because of the diminishing oil reserves and skyrocketing fuel prices. As a rule of thumb, the fuel economy, durability, and environmental compatibility of all moving mechanical systems (including those in engines) are closely related to the performance and effectiveness of the lubricants being used on the rubbing, rolling, rotating, and reciprocating surfaces. Poor or inefficient lubrication can always result in higher friction and wear losses, which can, in turn, impair the efficiency and durability of these systems. On average, engine and drive-train friction accounts for 10-15% of the national transportation fuel consumption in the U.S., and this translates to about 1.5 to 2 million barrels of petroleum per day lost to friction alone. Accordingly, in recent years, a great deal of effort has been devoted to the development of low-friction materials and lubrication technologies that reduce energy losses in engines and thus boost the fuel economy. On the materials side, several tribological coatings, such as DLC, CrN, etc., have been developed in recent years and used to reduce friction and wear of various engine parts [1]. These coatings appear to function the best in the presence of certain additives; otherwise, their friction coefficients under boundary-lubricated sliding conditions are comparable to conventional engine materials. In the case of DLCs, low friction is only achieved with the use of specialty additives (such as glycerol) in lubricating oils with hydrogen-free DLC coatings [2]. When hydrogenated DLCs were used with anti-wear and -friction additives in oils, adverse tribochemical effects or reactions were detected, and the rapid wear of such coatings has been reported [3].

What would be most desirable is that the lubricants used in engines contain little or no harmful additives yet provide equally good or even better friction and wear performance than those of the current approaches. In this project, we are pursuing a novel approach that focuses on the design and development of unique catalytically active non-ferrous coatings that provide much superior lubrication and lifetime, even with the use of base oils. The transformational nature of this novel concept comes from the fact that these coatings essentially are made of catalytically active hard nitrides of such non-ferrous metals as V, W, Mo, Ta, Hf, and Re as the major phases and soft non-ferrous metals such as Ni, Ag, Pt, Co, Ru, Cu, Pd, and Ir as the minor catalytic phases (at 1-5 at% concentrations). We discovered that such composite non-ferrous coating systems are able to catalytically crack or split long-chain hydrocarbon molecules of lubricating oils into carbon dimers and trimers and then deposit them on rubbing surfaces as low-shear, carbon-based boundary films. With this novel approach, we aim to drastically reduce the uses of harmful additives from lubricating oils, yet still achieve and maintain low friction and wear through the formation of a carbon-rich boundary film. Undoubtedly, if realized at industrial scales, this approach will help achieve a sustainable transportation future in an efficient, clean, and cost-effective manner. These higher performance coatings can also help in achieving higher power density in engines by downsizing. Accordingly, the major goals of this project are to design, develop, and optimize novel non-ferrous coatings for use in critical engine parts and components that are subject to harsh operating conditions so that they will be protected against wear. Another important goal is to optimize and implement these coatings in engines to improve their performance, efficiency, and durability even under stringent operating conditions.

## APPROACH

### Design and Synthesis of Non-ferrous Coatings

The non-ferrous coatings used in our experiments were synthesized in a commercial-scale dual magnetron sputtering system (CemeCon, Model # CC800/9XL) in the high-power impulse magnetron sputtering mode. These coatings were designed to consist of catalytically active non-ferrous metallic and ceramic ingredients in the resultant coating that will derive carbon-based boundary films from the lubricating oils. Accordingly, we strategically selected and combined hard nitride phases of V, Nb, Mo, and W with known catalyst metals like Ni, Cu, Co, Ag, and Pt at optimal concentrations (typically 1-3 wt%) so that the resultant coatings not only would have high hardness (and, hence, high wear resistance) but also would trigger catalytic effects to fragment the hydrocarbon molecules of lubricating oils to result in carbon-rich boundary films on sliding surfaces. Specifically, we obtained sputtering targets made out of the elements cited above, and using the CemeCon magnetron sputter deposition system, we synthesized a series of non-ferrous coatings made of distinct nitride phases of V, Nb, Mo, etc., and catalyst metals such as Ni, Cu, Ag, and Co. Again, the choice of these phases was very strategic in that they are all expected to trigger high catalytic effects on sliding surfaces to produce a carbon-rich boundary film that can provide low friction and wear. While designing these coatings, we had to pay special attention to the proportion of hard and soft metallic phases so that the resultant coatings would have sufficient hardness for wear protection while at the same time affording low friction. The sputter deposition system used in our studies consisted of two sputtering targets: one made of catalyst metal (i.e., Ni, Cu, or Co), and the other made of hard nitride formers with high catalytically active V, Mo, Nb, etc. In our deposition runs, we were careful to apply the right level of power to both targets to achieve the exact proportions needed between the metallic and nitride phases. Metal catalysts were selected based on their strong affinity and catalytic reactivity toward the long-chain hydrocarbon molecules in oils and thus result in a carbon-based boundary film that has low friction and high scuff resistance when in sliding contacts. During our deposition runs, we tried a wide range of metal catalyst (Ni, Cu, Co, etc.) concentrations, ranging from below 1 wt% to 10 wt% in the final non-ferrous coatings. Depending on the concentration, we were able to produce films with hardness values as low as 20 GPa and as high as 30 GPa. To improve coating adhesion to the steel substrates, we had to remove organic contaminants from the surfaces by means of chemical solvents in an ultrasonic bath. After loading these ultrasonically cleaned substrates into the deposition chamber, we performed an Ar ion etching step to remove remaining contaminants, followed by metal ion etching using the high-power impulse magnetron sputtering feature of the deposition system. To further help improve adhesion and reduce the deleterious effect of internal stresses, we always deposited a pure V, Mo, or Nb bond or transition layer, which provided a smooth transition from the base steel to the top non-ferrous coating. Finally, the appropriate plasma deposition conditions were established, and the deposition of non-ferrous coatings on steel substrates was started. In most cases, the coating thickness ranged from 2 µm to 3 µm, and the surface roughness was below 0.1 root mean square.

### Tribological Tests

Tribological testing of non-ferrous coatings was carried out with a reciprocating cylinder on a flat test machine. All of the tests were performed under severe contact pressures (1 GPa) and relatively low sliding velocities (0.05 m/s) to create a boundary-lubricated sliding regime where direct metal-to-metal contacts occur. Most tests were performed at 100ºC to confirm that the sliding surfaces were under the severe boundary regime. The lubricant used was PAO 10 base oil. These test conditions were applied to all the coated and uncoated surfaces. In the following, we concentrate more on the VN-Cu coatings as an example, but we have also produced and tested many other coatings made out of non-ferrous composites of Mo, V, Cu, Ni, and Co.

## RESULTS

### Tribological Performance

Figure 1 compares the typical friction coefficients of control and non-ferrous-coated test pairs under boundary-lubricated sliding conditions. The specific non-ferrous coating in this case was made of VN and Cu phases. The majority of the coating phase (more than 95 wt%) was made of VN, while Cu was present in only a small amount (i.e., ≈5 wt%). As evident in Figure 1, after the initial low-friction run-in period, the friction coefficient of the control test pair increases rapidly and stabilizes at around 0.12. The friction coefficient of the non-ferrous coated test pair is initially about 0.08 but decreases steadily to less than 0.07 after about 30 minutes of sliding.

Figure 2 shows the wear performance of the same test pairs. The uncoated 52100 pin and flat suffer significant wear losses, as is evident from the deep scratch marks on the flat side and a flat wear scar on the pin side. However, for the coated surfaces, it was hard to discern any wear damage on both the pin and flat surfaces, despite very severe sliding conditions.

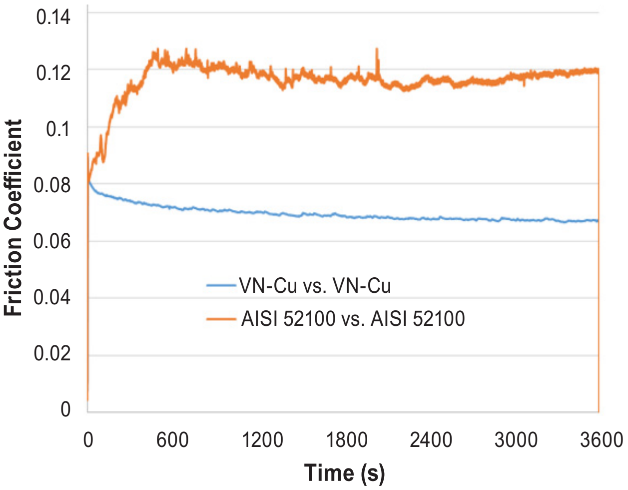

**FIGURE 1.** Typical friction coefficients of uncoated (control) and non-ferrous-coated AISI 52100 steel test samples under boundary-lubricated sliding conditions.

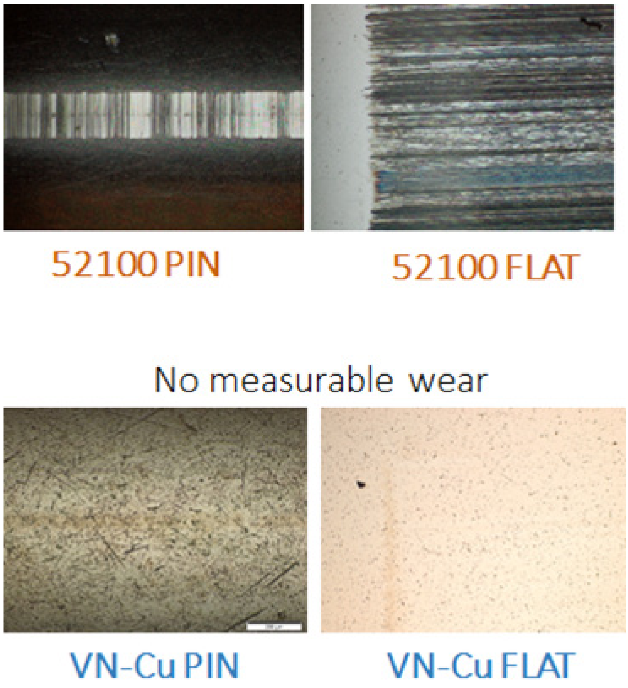

**FIGURE 2.** Wear performance of uncoated (top) and non-ferrous VN-Cu coated pin and flat samples (bottom). Uncoated steel samples show severe wear losses, while the coated samples shown no discernible wear.

Figure 3 shows the friction and wear performance of an uncoated 52100 steel pin against the non-ferrous VN-Cu-coated 52100 steel flat under the same test conditions as the previous tests. As is clear, the friction coefficient of the test pair is around 0.05 and quite steady throughout the test. By contrast, the wear of the uncoated 52100 steel pin is very difficult to quantify. A black tribofilm had formed on its rubbing surface, and this film was apparently protecting it from wear.

## Chemical and Structural Studies

During FY 2014, we also conducted surface and structure analytical studies on the sliding surfaces of non-ferrous coated test samples. The main motivation was to determine whether the coatings were made of the specific phases that we desired and to elucidate the fundamental tribological mechanisms controlling the friction and wear behavior of these coatings. The tool we used for the chemical characterization of the bulk coating was grazing-incidence X-ray diffraction, which is well-known for its effectiveness in thin film chemical analysis (capable of providing chemical information from the coating itself but not from the substrate). Figure 4 shows that the peaks in the grazing-incidence X-ray diffraction spectrum of the VN-Cu-coated sample corresponds to VN, and a Cu peak is not evident.

Preliminary characterization using Raman spectroscopy was conducted with the boundary films

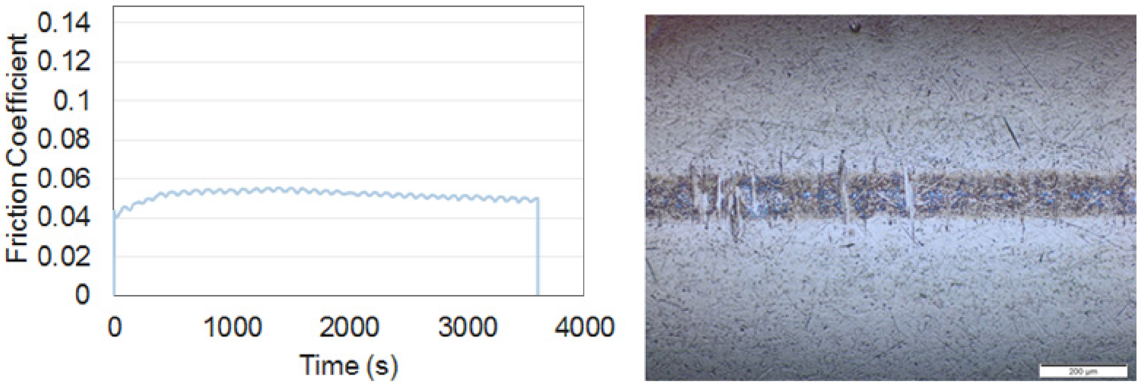

**FIGURE 3.** (a) Friction coefficient of an uncoated 52100 steel pin against non-ferrous VN-Cu-coated 52100 flat and (b) the physical condition of the pin surface after sliding test showing little or no wear.

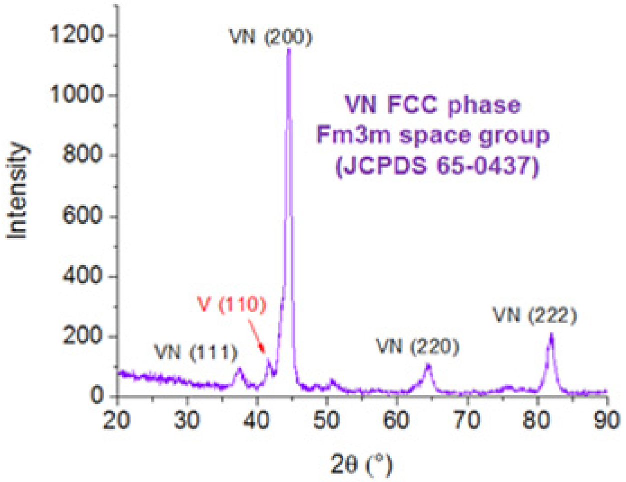

**FIGURE 4.** Grazing-angle X-ray diffraction of non-ferrous VN-Cu-coated test sample showing mostly peaks corresponding to a VN phase. The Cu phase (due to its much lower concentration) could not be resolved by this technique; X-ray photoelectron spectroscopy is more appropriate and will be applied in the near future.

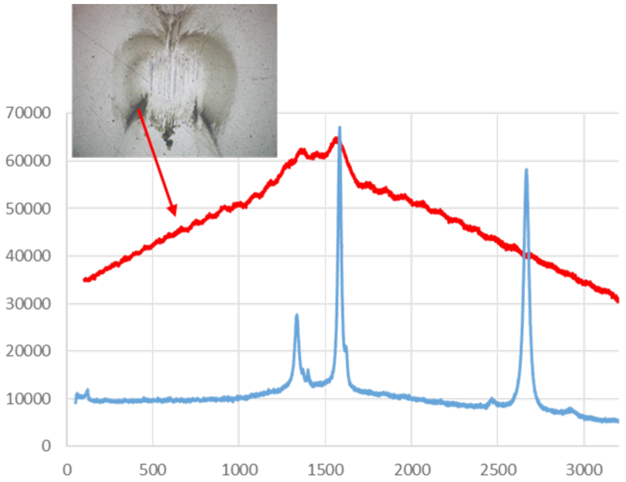

**FIGURE 5.** Typical Raman spectrum of the carbon-rich boundary film detected on rubbing ball surface (VN-Cu vs. VN-Cu). Red spectrum is from black carbon formation on lower left corner of the wear scar; locations of broad D and G bands correspond to those of graphite's characteristic D and G bands (blue spectrum), which was used as a reference. Inset shows a scanning electron microscope image of carbon-rich tribofilm.

that were formed on rubbing surfaces of pins and balls. As shown in Figure 5, the blackish deposit or boundary film found in and around the rubbing surface of a steel ball displays very clear D and G peaks that are typical of graphite (which was also used as a standard in the Raman studies). Overall, these tribological and surface analytical studies have increased our confidence that the original concept of extracting carbon-rich boundary films from lubricating oils is working. These films were able to reduce friction by more than 40% and bring wear to some unmeasurable levels.

## CONCLUSIONS

During FY 2014, we successfully produced a series of non-ferrous coatings on test samples using a commercial-size CemeCon magnetron sputtering system. We performed systematic tribological studies on these coatings to evaluate their friction and wear performance. These tests confirmed that as much as 50% reduction in friction is feasible with uncoated 52100 pins against VN-Cu-coated flats in pure PAO oil. The wear of coated against coated, and coated against uncoated, test pairs was reduced to unmeasurable levels, while the wear of uncoated against uncoated test pairs was severe. Overall, these novel coatings drastically improved the resistance of steel samples to wear and also reduced friction.

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# II.10 Advanced Nanolubricants for Improved Energy Efficiency and Reduced Emissions in Engines

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## Overall Objectives

- Develop, optimize, and implement novel boron-based lubricant formulations to achieve higher fuel economy, longer durability, and better environmental compatibility in engines in order to reduce dependence on imported oil.
- Demonstrate friction reduction by at least 10% compared to current lubricant technology without compromising wear and durability.
- Demonstrate scalability, lubricant compatibility, and commercial viability.

## Fiscal Year (FY) 2014 Objectives

- Demonstration of larger-scale production/lubricant formulation.
- Completion of lubricant optimization and bench tribology studies.
- Preliminary screening tests in engines.

## FY 2014 Accomplishments

- Completed compatibility studies of surfactant functionalized nanolubricant with base and fully formulated engine oils.
- Optimized lubricant formulations based on boron chemistries.
- Completed bench tribology studies of optimized lubricants, showing as much as 80% reduction in friction and more than two orders of magnitude reduction in wear.
- Completed scuffing studies, showing 30 to 40% increase in scuffing load of formulated engine oils.
- Completed surface analytical studies, revealing a boron-rich boundary film on rubbing surfaces.
- Completed friction, wear, and scuffing studies with conventional and PC-11 type diesel oils, showing 50% reduction in friction, as well as 30 to 40% improvement in wear rates and scuffing loads.
- Completed initial engine tests, showing as much as 2.5% fuel economy improvements under regimes where boundary and mixed lubrication prevail.

## Future Directions

Based on the very encouraging results from rigorous bench and limited engine studies, more comprehensive engine and valve-train tests should be conducted on the optimized lubricant formulations to determine their long-term engine-specific efficiency and durability benefits. Of particular interest in these tests will be the long-term additive–lubricant interactions (if any) and their impact on engine performance and efficiency.

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## INTRODUCTION

Growing concerns over dependence on imported oil and the adverse environmental impact of greenhouse gas emissions are calling for the development of more fuel efficient and environmentally friendly engine technologies. Engine friction still consumes 10 to 15% of the fuel energy with current engine technology, and as a whole, the transportation sector is a major contributor to greenhouse gases [1]. In fact, in most current engine systems, more energy is consumed by friction than that delivered to the wheels to move the vehicles. Accordingly, in recent years, significant efforts have been directed toward bringing friction and wear losses in engines down to the lowest possible levels. However, dramatic reduction of friction and wear in engines has been rather difficult to achieve by employing traditional means. Consequently, more advanced and effective friction control technologies (low-friction coatings, surface texturing, and low-friction additives such as ionic liquids, organic friction modifiers, nano-colloidal particles, polymeric brushes, etc.) have been developed and offered as more advanced solutions. In particular, the use of nanoparticles of certain solids in lubricants has gained considerable momentum in recent years [2].

Accordingly, this project is directed toward the development of a new lubricant technology that can help reduce fuel consumption and carbon emissions of advanced transportation vehicles by minimizing friction and wear losses in engines. The proposed lubrication technology is innovative and based on the use of boron-ester nano-colloidal lubricant formulations, which were proven to provide more than 50% reduction in mechanical friction when tested in bench-top friction and wear machines. The main emphasis is on further development and optimization of these formulations to achieve marked improvements in the fuel economy of future engine systems. Our target was to cut down boundary friction by half, thus achieving at least 2-3% improvements in fuel economy of fired engine systems. Overall, less friction and wear mean less energy consumption and longer durability, as well as lower greenhouse gas emissions to the environment.

## APPROACH

In this project, we mainly concentrated on the development and optimization of boron-ester nano-colloidal lubrication additives for use in fully formulated engine oils. Using a variety of bench-scale tribological test machines, we performed numerous tests to confirm the superior performance characteristics of these new formulations. With the help of our industrial partners, we performed more engine-specific or relevant tests to further demonstrate the fuel economy benefits of our technology under a wide range of operating conditions. Specific steps followed in our lubricant optimization studies included the determination of additive-lubricant compatibility or any adverse interactions between boron and other additives in formulated oils. Optimization of boron-additive concentration with respect to friction and wear performance was also an important element of our test program, as was an assessment of the long-term stability of boron ester nano-colloidal lubricant formulations.

At Argonne, we have unique tribological test capabilities, including a number of pin-on-disc and reciprocating test machines as well as block-on-ring, ring-on-liner, and four-ball test machines. All these machines are computerized and have proven to give very good repeatability and reproducibility in measured friction and wear values. They are used primarily for screening and product optimization studies using some of the most popular fully formulated engine oils as benchmarks and then using our boron additives at different concentrations to confirm the beneficial effect. After the tribological tests, extensive microscopy and surface analytical studies were performed on sliding surfaces to determine the nature of specific boundary films that resulted from the use of boron-based additives. In particular, X-ray photo-electron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF/SIMS) were used to obtain chemical information that can help explain the fundamental mechanisms associated with the formation of low-friction, low-wear tribofilms on rubbing surfaces. A three-dimensional optical interferometry microscope was used to generate three-dimensional images of sliding surfaces and to determine various surface roughness parameters. Knowledge gained from these studies can help close the gap in better understanding those key barriers to developing more advanced lubricant formulations affording superior performance in actual engine applications.

## RESULTS

Figure 1 shows the friction- and wear-reducing capacity of a highly optimized boron-based additive under severe boundary-lubricated sliding condition when

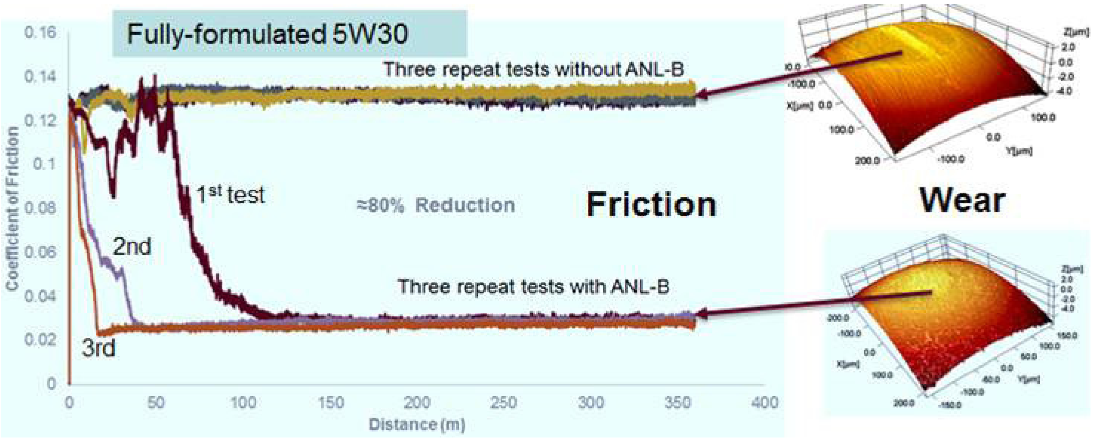


**FIGURE 1.** Friction and wear in pin-on-disk experiment of fully formulated gasoline engine oil 5W30 with and without boron additive.

mixed with a 5W30 gasoline engine oil. For comparison, the friction and wear performance of 5W30 oil without boron is also included. In this test protocol, we used a ball-on-disk test machine. Both the balls and the disks were made of fully hardened American Iron and Steel Institute 52100 steel, and they were polished to a surface finish of better than 0.1 µm root mean square surface roughness. The test load (10 N) created about 1 GPa peak hertz pressure while the sliding speed was kept constant at 0.1 m/s, and the test temperature was 100°C. In this experiment, we performed three repeat tests with and without the boron additive to confirm reproducibility of the test results. As is clear from Figure 1, the friction coefficients of oils with and without boron additive are quite reproducible (especially under the steady-state portion of the tests). For those test pairs evaluated in 5W30 oil, the friction coefficient is about 0.13; while for those that were tested in boron-additized 5W30, the friction coefficients were about 0.03, which indicates about 80% reduction in friction when boron additive is present. As for the wear performance, the sliding ball surface in 5W30 oil shows a very obvious flat wear scar, while the ball tested in boron-additized oil shows a wear mark without an obvious wear flat; in fact, the original spherical shape of the ball appears to have been largely preserved.

We also performed extensive tests with fully formulated diesel engine oils. When boron additives were mixed with a 15W40 diesel oil, the reduction in friction was more than 65% below what was feasible with unadditized 15W40 oil (e.g., 0.12 for 15W40 versus 0.04 for boron-additized 15W40 oil), while the wear scar diameter was reduced by more than 17%. For achieving better fuel economy and performance characteristics, PC-11 diesel oils are being developed and will be used in future diesel engines. These oils are much lower in viscosity, and the additive packages in them contain a suite of chemicals which are meant to reduce emissions and other unwanted effects. As part of our test projects, we included a PC-11 diesel oil to see if the boron additives would also have a positive effect on the friction and wear performance of this oil. Figure 2 shows the ball-on-disk test results from as-received and boron-additized PC-11 oil. As is clear with the use of boron additive, friction is reduced by more than 60% below what (i.e., 0.13) is feasible with PC-11 oil alone, while the wear scar diameter is also markedly reduced.

Figure 3 shows the scuffing performance of PC-11 with and without boron additive. These tests are run in a block-on-ring machine where the contact load (or pressure) is increased stepwise at 2-min intervals until the test pairs scuff and the friction rises sharply. The PC-11 alone shows evidence of micro-scuffing at around 1,100 N, but the catastrophic scuffing takes place at a

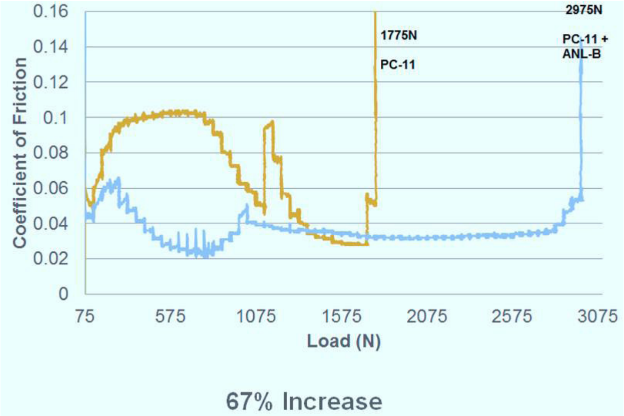


**FIGURE 3.** Scuffing load by block-on-ring experiment for additized and unadditized PC-11 diesel engine oil.

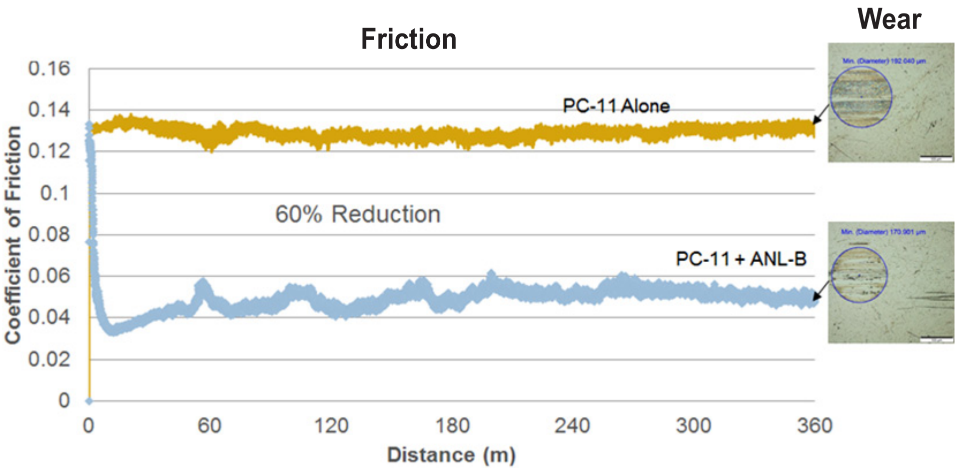


**FIGURE 2.** Friction and wear in pin-on-disk experiment of fully formulated diesel engine oil PC-11 with and without additive.

load of 1,775 N. When the same test is repeated with boron-additized PC-11, the friction remains fairly steady and low, and the final scuffing does not occur until reaching a load of almost 3,000 N. These results indicate more than 65% increase in scuffing load.

Figure 4 shows the variation of friction with respect to sliding speed for PC-11 with and without boron additive. At the lowest sliding velocity of about 0.0001 m/s (which corresponds to very severe boundary condition), the friction coefficient of the steel test pairs is nearly 0.16 for as-received PC-11. In the case of boron-additized PC-11, the friction coefficient is about 0.1. However, as the sliding speed is increased, the reduction in friction coefficient of test pairs in PC-11 alone is marginal, while in PC-11 with boron additive, it is very substantial, declining to a friction coefficient of 0.04. When similar tests were performed with fully formulated 5W30 gasoline engine oil, the reduction in friction due to boron additives ranged from 60% to more than 80%, depending on the sliding regime or velocity.

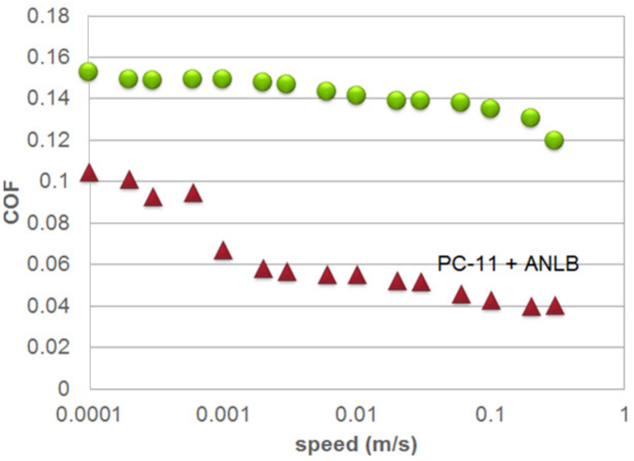
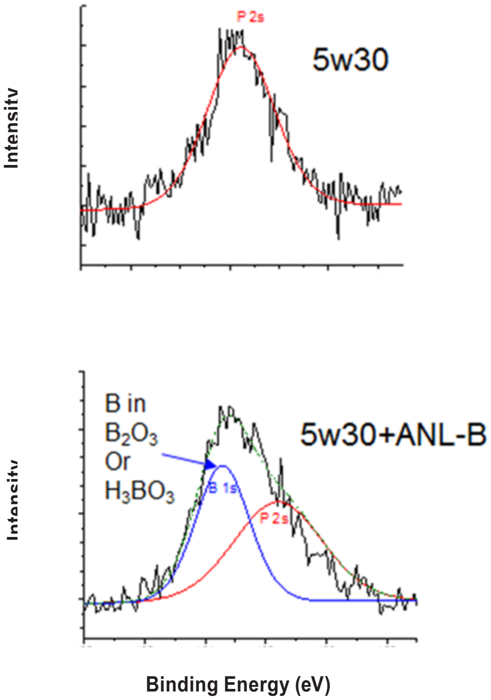


**FIGURE 4.** Stribeck curve for additized and unadditized PC-11 diesel engine oil.

Surface analytical studies of the boundary films resulting from boron were performed by XPS and TOF-SIMS. Figure 5 shows the high resolution spectra of peak regions for boron (which happens to somewhat overlap with that of phosphorous whose XPS is also provided). As is known, phosphorous in boundary film comes from the zinc dialkyl-dithiophosphate anti-wear additive and XPS clearly confirms its presence in the analyzed tribofilm in the amount of 12.64 at% along with sulfur, oxygen, zinc and calcium. In the case of boron-additized 5W30 oil, the shape of XPS spectrum has the same peak shape but the peak position is shifted to higher binding energy levels which suggest that the overall peak may be the result of more than one type of chemical compound. For this, we have attempted to distinguish the contribution of somewhat overlapping boron and phosphorous compounds by means of deconvolution. As is clear from the bottom XPS spectrum, in addition to P2s, we can also detect B1s corresponding to either $B_2O_3$ or $H_3BO_3$ both of which will be feasible with the boron-additive used in the oil. The table to the spectra confirms



| Element | At.% FFO 5w30 | At.% FFO 5w30+ANLB |
|---|---|---|
| O | 44.24 | 54.40 |
| Fe | 2.56 | 1.33 |
| Ca | 31.23 | 15.10 |
| Zn | 4.26 | 2.28 |
| P | 12.64 | 6.98 |
| S | 5.07 | - |
| B | - | 19.90 |

FFO - fully formulated oil

**FIGURE 5.** X-ray photoelectron spectroscopy of tribofilms generated by 5W30 gasoline engine oil and 5W30 additized with boron.

the presence of boron in analyzed boundary film region by nearly 20 at%. We believe that very impressive friction and wear results reported in Figures 1-4 may have been due to the formation of a boron-rich boundary film on the rubbing surfaces.

In support of the XPS results, we further conducted time-of-flight secondary ion mass spectrometry of the boundary film that resulted from the boron-additized 5W30 oil. As shown in Figure 6, the boron is present in the boundary film in the form of both BO and $BO_2$ along with phosphorous and sulfur which are consistent with the XPS and chemical analysis data presented in Figure 5. Overall, the boron-additives used in our tribological tests have shown strong tendency to tribochemically react with the sliding contact surfaces and form a boron-rich boundary film which appears to be very effective in reducing friction and wear as well as increasing resistance to scuffing.

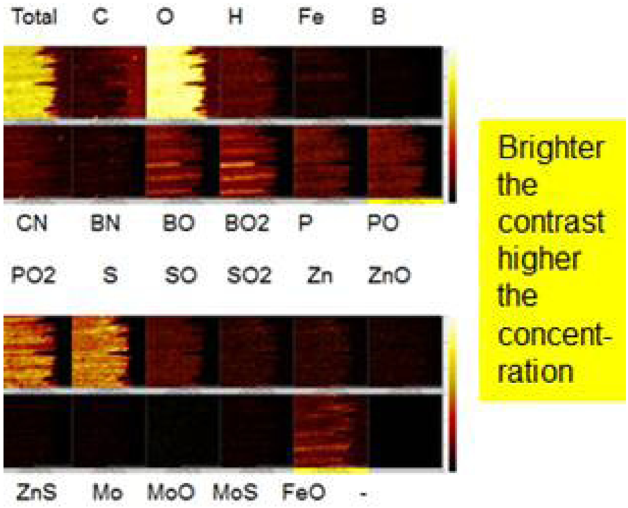


**FIGURE 6.** Chemical mapping of the boron-rich tribofilm by time-of-flight secondary ion mass spectrometry.

## CONCLUSIONS

Consistent with the tasks/milestones of our project, we have made remarkable progress in developing novel boron-based nanolubrication additives that can:

- Reduce friction by as much as 80% under severe boundary conditions.
- Increase resistance to wear and scuffing.
- Improve fuel economy (under engine running conditions involving mixed/boundary regime).

The much improved tribological performance is related to the formation of a slick and highly protective boron-rich boundary film, as confirmed by XPS and TOF-SIMS data.

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# II.11 ORNL-Shell: Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency

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## 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) 2014 Objectives

- Seek synergistic effects between ILs and the most common anti-wear additive zinc dialkyldithiophosphate (ZDDP)
- Conduct standard additive evaluation for the top candidate ILs
- Investigate the compatibility of the top candidate IL with other engine oil additives

## FY 2014 Accomplishments

- The team received a 2014 R&D 100 Award
- A new U.S. patent application was filed
- A journal paper has been accepted; results were presented at multiple technical conferences including three invited talks
- Synergistic effects on friction and wear reductions were discovered when combining phosphonium-phosphate ILs with ZDDP, while such synergy was not observed for other groups of ILs
- Mechanistic understanding is being achieved for the IL+ZDDP synergism
- Top candidate ILs have passed the standard no harm storage and elastomer compatibility tests, as required for automotive engine oil additives
- The compatibility of the top-performing IL [$P_{8888}$][DEHP] with other additives in the engine oil formulation is currently being investigated

## Future Directions

- Formulate a low-viscosity engine oil using [$P_{8888}$][DEHP]+ZDDP as anti-wear additives
- Conduct Sequence VID/VIE engine dynamometer tests on the formulated IL-additized engine oil to demonstrate improved engine mechanical efficiency
- Investigate the effects of an IL-ZDDP combination on three-way catalysts using an accelerated small engine test
- Gain further fundamental understanding of the synergism between ILs and ZDDP

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## INTRODUCTION

For an internal combustion engine, 10~15% of the energy generated in automobile engines is lost to friction. Developing effective additive packages in combination with a balancing lubricant viscosity has proven to be the most successful and cost-effective route for lowering engine friction. This project proposes to develop ILs as a new class of lubricant additives to improve the engine mechanical efficiency.

## APPROACH

Work scope 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) Investigation of ILs' compatibility with other additives in engine oil formulation; (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

Four oil-miscible ILs from three groups, phosphonium-organophosphate, phosphonium-phosphinate, ammonium-phosphate, were investigated for potential synergism with ZDDP. They are: $[P_{66614}]$[DEHP] (IL-A), $[P_{66614}]$[BTMPP] (IL-B), $[P_{8888}]$[DEHP] (IL-C), and $[N_{888}H]$[DEHP] (IL-D). As shown in Table 1, they are combined with ZDDP in the gas-to-liquid (GTL) base oil GTL 4 cSt at the same total phosphorus level of 800 ppm (upper limit of ILSAC GF-5/6).

The friction and wear performance of the lubricants in boundary lubrication were evaluated using a ball-on-flat reciprocating sliding bench test. Tests were carried out under a 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 1,000 m sliding with at least three repeats for each lubricant. As shown in Table 1 and Figure 1, results suggested strong synergistic effects between the phosphonium-organophosphate ILs (IL-A and IL-C) and ZDDP with significantly reduced friction and wear compared to either the IL or ZDDP alone. Similar synergistic effects were observed at both ORNL and Shell. In contrast, no such synergy was observed for the phosphonium-phosphinate (IL-B) or ammonium-phosphate (IL-D) when combined with ZDDP. This is quite interesting given IL-A and IL-B, have the same phosphonium cation and IL-A, IL-C, and IL-D share the identical organophosphate anion. Evidently, both cation and anion chemistry seem critical in generating the synergy with ZDDP.

Figure 2 shows the cross-sectional transmission electron microscopy image and energy-dispersive X-ray spectroscopy element maps of the tribofilm formed on the cast iron flat lubricated by GTL+0.4%ZDDP+0.52%IL-C. Similar to those formed by the IL or ZDDP alone, this tribofilm is also amorphous-based with a thickness up to 200 nm. The strong signals of Zn and P detected by energy-dispersive X-ray spectroscopy suggest involvement of both ZDDP and IL-C in the tribofilm formation.

Stribeck scans were conducted using rolling-sliding at Shell to explore the impact on friction behavior in mixed lubrication. As shown in the bottom chart in Figure 1, IL-C either by itself or combined with ZDDP at different ratios, demonstrated significant friction reduction compared to ZDDP alone. The surface roughness of wear scars correlates well with the friction performance: the introduction of IL-C mitigates the contact surface roughening and leads to a higher lambda ratio (lubricant film thickness/roughness) for a lower friction.

Further X-ray photoelectron spectroscopy chemical analysis revealed interesting similarities and distinctions in the compositions among the tribofilms generated by different IL+ZDDP combinations. As summarized in Table 2, all three ILs, when combined with ZDDP,

**TABLE 1.** Oil-Additive Blends and their Boundary Lubricating Performance

| Test Lubricant (additive in wt%) | P Content (wt%) | P(ZDDP):P(IL) | Zn Content (wt%) | Friction Coefficient | Wear vol. ($\times10^{+8}\mu m^3$) |
|---|---|---|---|---|---|
| GTL+0.8%ZDDP | 0.08 | 100:0 | 0.088 | 0.114 | 1.38 |
| GTL+1.04%IL-A | 0.08 | 0:100 | 0 | 0.112 | 1.79 |
| GTL+1.0%IL-B | 0.08 | 0:100 | 0 | 0.120 | 0.98 |
| GTL+1.04%IL-C | 0.08 | 0:100 | 0 | 0.115 | 1.05 |
| GTL+1.74%IL-D | 0.08 | 0:100 | 0 | 0.108 | 0.43 |
| GTL+0.4%ZDDP+0.52%IL-A | 0.08 | 50:50 | 0.044 | 0.084 | 0.34 |
| GTL+0.4%ZDDP+0.5%IL-B | 0.08 | 50:50 | 0.044 | 0.121 | 1.30 |
| GTL+0.6%ZDDP+0.26%IL-C | 0.08 | 75:25 | 0.066 | 0.092 | 0.82 |
| GTL+0.4%ZDDP+0.52%IL-C | 0.08 | 50:50 | 0.044 | 0.079 | 0.33 |
| GTL+0.4%ZDDP+0.87%IL-D | 0.08 | 50:50 | 0.044 | 0.123 | 0.66 |

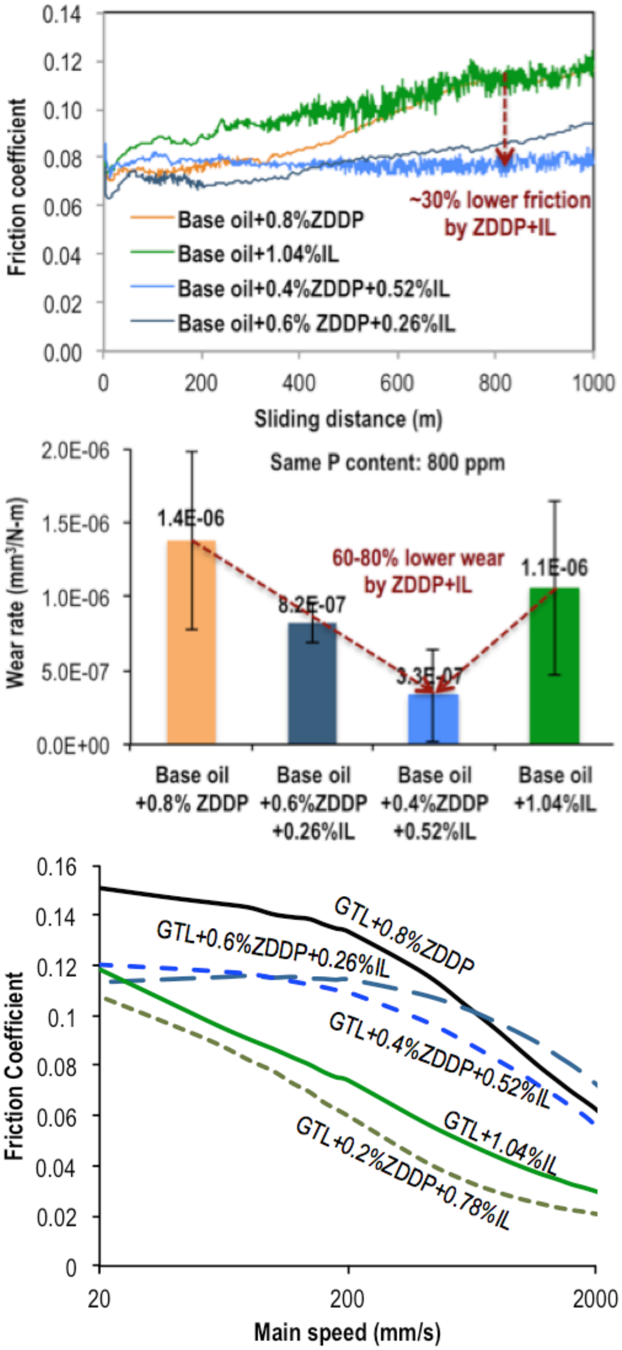

**FIGURE 1.** Synergistic effects of combining [$P_{8888}$][DEHP] and ZDDP (with the same 800 ppm of phosphorus in oil). Top two charts: boundary lubrication; bottom chart: Stribeck curves.

significantly reduce the sulfur contents in the tribofilm. On the other hand, IL-C promotes zinc compounds and metal-phosphates but reduces metal-oxides, while IL-B and IL-D preserve more metallic iron (wear debris) but reduce zinc compounds and metal-phosphates. Such distinctions may explain why synergistic effects were observed for ZDDP+IL-C, but not for ZDDP+IL-B or ZDDP+IL-D.

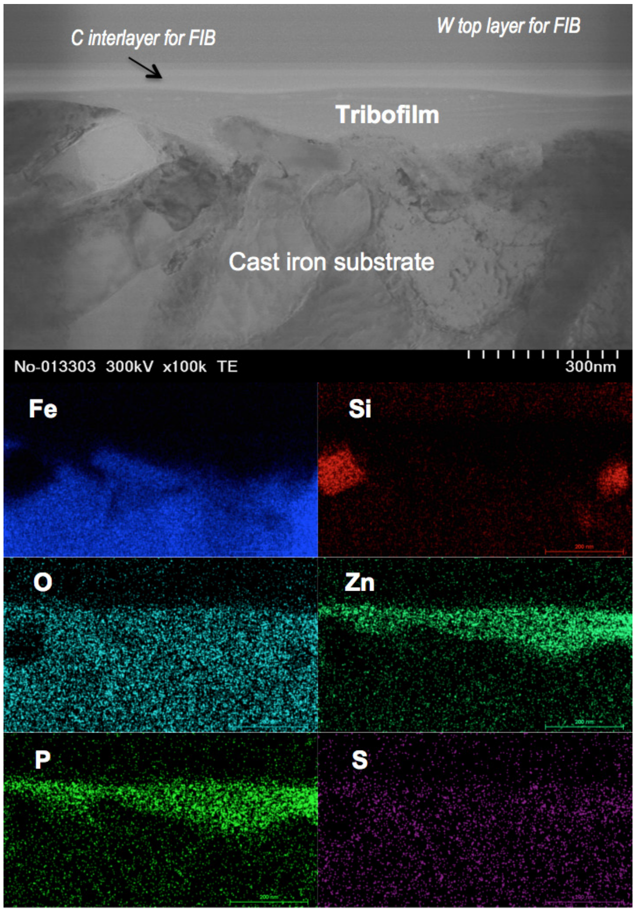

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**FIGURE 2.** Cross-sectional transmission electron microscopy image and energy-dispersive X-ray spectroscopy elemental maps of the anti-wear tribofilm formed on a cast iron surface lubricated by GTL+0.4%ZDDP+0.52%[$P_{8888}$][DEHP].

IL-C and IL-D top-treated fully formulated engine oils were evaluated in no harm storage tests at 0, 25, and 60°C for three months, elastomer (seal) compatibility tests, and high temperature (135°C) corrosion tests with tin, copper, and lead. Results are summarized in Table 3. Both lubricants passed the no harm storage and elastomer compatibility tests. No corrosion issue for tin but increased corrosion rates for copper and lead were observed, which is partially caused by the higher-than-normal phosphorus content in the top-treated oils. Note that the high temperature corrosion test is required for diesel engine oils only.

The IL-C ([$P_{8888}$][DEHP]) has been identified for engine oil formulation because of its strong synergism with ZDDP. It is important to understand its compatibility with other oil additives. Figure 3 shows the latest wear results when combining IL-C with common detergents (calcium salicylate, sulfonate, and phenate) and dispersants (low molecular weight), high molecular weight, and polyisobutylene succinimide) at

**TABLE 2.** X-Ray Photoelectron Spectroscopy Data—Compositions of Tribofilms formed by ZDDP, IL, and ZDDP+IL

| (at%) | C | Fe (metal) | Fe (ion) | O (oxide) | O (O-P) | P | S | Zn | N |
|---|---|---|---|---|---|---|---|---|---|
| GTL+0.8%ZDDP | 5 | <1 | 14 | 12 | 42 | 10 | 10 | 7 | 0 |
| GTL+1.0%IL-B | 14 | 7 | 24 | 32 | 20 | 3 | 0 | 0 | <0.5 |
| GTL+1.04%IL-C | 6 | <1 | 18 | 27 | 38 | 11 | 0 | 0 | <0.5 |
| GTL+1.74%IL-D | 16 | 12 | 11 | 23 | 30 | 8 | 0 | 0 | <0.5 |
| GTL+0.4%ZDDP+0.5%IL-B | 7.5 | 11 | 23 | 43 | 12 | 1.5 | 1.5 | 0.5 | <0.5 |
| GTL+0.4%ZDDP+0.52%IL-C | 7 | <1 | 13 | **4** | **52** | **13** | 1 | **10** | <0.5 |
| GTL+0.4%ZDDP+0.87%IL-D | 10 | 8 | 22 | 13 | 36 | 7.5 | 2 | 1.5 | <0.5 |

**TABLE 3.** Results of Standard Lubricant Additive Tests for IL-C and IL-D

| | No harm storage (°C) | | | Elastomer compatibility (change in %) | | | | High-temp corrosion (ppm) | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 25 | 60 | Volume [-2.13, 5.13] | Hardness [-6,8] | Tensile strength [-79.5,13.9] | Elongation [-79.9, 16.3] | Sn | Cu | Pb |
| Engine oil | Pass – no color change or precipitates | | | Not tested | | | | 0 | 11 | 138 |
| Engine oil + 1% IL-C | | | | 0.78 | 9 | -77.8 | -74.8 | 0 | 252 | 842 |
| Engine oil + 1% IL-D | | | | 0.98 | 2 | -65.8 | -60.2 | 0 | 254 | 467 |

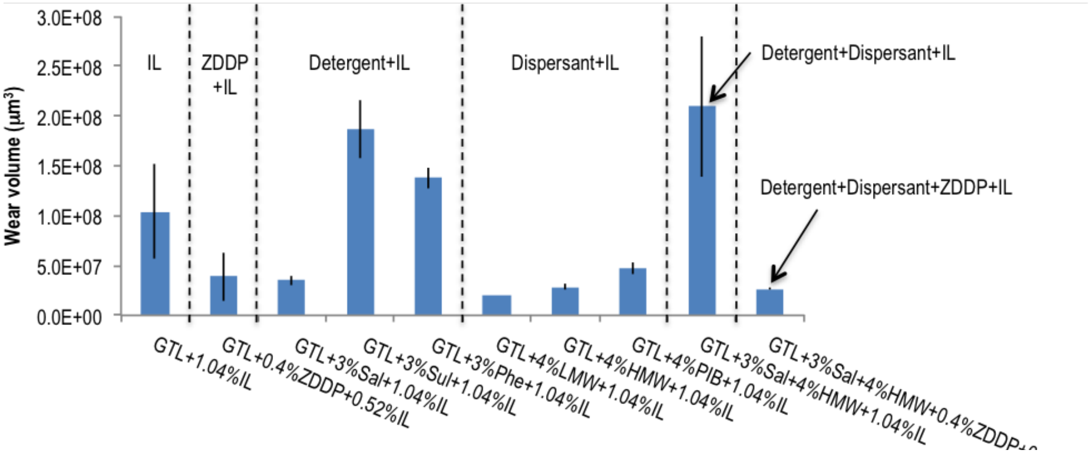

**FIGURE 3.** Compatibility of [$P_{8888}$][DEHP] with common engine oil detergents and dispersants.

realistic proportions in the GTL base oil. Individually, calcium salicylate worked well with IL-C while the other two detergents did not, and all dispersants showed no problems. However, when IL-C was mixed together with both the salicylate detergent and the high molecular weight (or low molecular weight) dispersant, a much increased wear rate occurred. Interestingly, the combined IL-C and ZDDP provided the best wear protection even with detergent and dispersant present in the oil!

## CONCLUSIONS

In FY 2014, the ORNL-Shell team discovered synergism between phosphonium-phosphate ILs and ZDDP, which allows potential further improved engine efficiency at a reduced cost. Comprehensive tribofilm characterization is revealing the mechanism behind. $P_{8888}$][DEHP] has passed the standard additive tests and its compatibility with other oil additives is currently being investigated. A prototype low-viscosity engine oil using IL+ZDDP will be formulated for engine dynamometer tests in FY 2015.

## FY 2014 PUBLICATIONS/PRESENTATIONS

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**2.** J. Qu, "Ionic liquids as next generation anti-wear additives: molecular design to engine dynamometer testing," *38th Automotive/Petroleum Industry Forum (Detroit Advisory Panel)*, Dearborn, April 16, 2014. (Invited talk)

**3.** J. Qu, "Ionic liquid-additized engine oil for improved fuel efficiency," *SAE 2014 High Efficiency IC Engine Symposium*, Detroit, April 6–7, 2014. (Invited talk)

**4.** J. Qu, "Oil-miscible ionic liquids as lubricant additives" in Panel Discussion: Ionic Liquids for Lubrication, *STLE 69th Annual Meeting*, Orlando, May 18–22, 2014. (Invited talk)

**5.** J. Qu, B.L. Papke, W.C. Barnhill, B. Kheireddin, H. Luo, C. Chen, P.J. Blau, B.H. West, M. Richard, S. Mercer, S. Dai, "Ionic liquids as ashless oil additives: correlations between molecular structures and oil-solubility and lubricating characteristics," *STLE 69th Annual Meeting*, Orlando, May 18–22, 2014.

**6.** J. Qu, "Oil-soluble ionic liquids as next-generation lubricant anti-wear additives," *248th ACS National Meeting*, San Francisco, August 10–14, 2014.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

**1.** 2014 R&D 100 Award, jointly among ORNL, GM, Shell, and Lubrizol, Ionic liquid anti-wear additives for fuel-efficient engine lubricants.

**2.** J. Qu and H. Luo, "Ionic liquids containing symmetric quaternary phosphonium cations and phosphorus-containing anions, and their use as lubricant additives," U.S. Patent Application 14/184,754, filed on Feb. 20, 2014.

# II.12 Development of Modified Polyalkylene Glycol High VI High Fuel Efficient Lubricant for Light-Duty Vehicle Applications

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Subcontractors
- Argonne National Laboratory, Argonne, IL
- Dow Chemical Company, Midland, MI

## 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, 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
- Estimate vehicle fuel economy and potential impact on emissions

## Fiscal Year (FY) 2014 Objectives

- Analyze surface films formed at tribological contacts of existing and new oil formulations
- Initiate cam and tappet wear measurements using a motored single cam and bucket valvetrain rig
- Complete motored engine friction evaluation
- Continue friction evaluation in Sequence VID tests and wear evaluations in Sequence IIIG and Sequence IVA tests
- Initiate chassis roll dynamometer test for fuel economy evaluation

## FY 2014 Accomplishments

- Dow Chemical Company (Dow) formulated several PAG oils to support various laboratory bench rig tests, motored valvetrain, and engine tests, engine dyno tests, and chassis roll tests. Dow also completed TEOST 33C, and MHT-4 tests on one PAG oil formulation.
- Argonne National Laboratory (ANL) completed friction and wear evaluations on PAG base oil (x97011.00) with no additives and compared against GF-5 base oil. ANL also analyzed surface tribo-films to gain a better understanding of the friction reduction mechanism.
- Ford Motor Company (Ford) evaluated and compared various PAG oil formulations to the standard SAE 5W-20 oil. Efforts included valvetrain wear measurements, traction coefficient measurements with and without additives, motored engine friction evaluations, fired engine dyno tests for fuel economy (ASTM Sequence VID) and wear assessments (ASTM Sequence IIIG and Sequence IVA tests) and chassis roll dynamometer fuel economy tests.

## Future Directions

- Complete valvetrain wear measurements
- Complete analysis of tribo-films formed on contacting surfaces to understand friction reduction mechanism(s)
- Complete any additional ASTM Sequence tests to demonstrate fuel economy, anti-oxidation and wear protection capabilities
- Complete chassis roll dynamometer fuel economy and emission evaluations of fresh and aged oils.

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## INTRODUCTION

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

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

## APPROACH

The project team consists of technical personnel from Ford, Dow and ANL. The project is led by Arup Gangopadhyay (Ford), Mr. John Cuthbert (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 roll dynamometer tests. Engine component durability will also be demonstrated through ASTM Sequence IVA and ASTM IIIG tests.

## RESULTS

### Friction and Wear Evaluations

Figure 1 presents friction coefficient results obtained from high frequency reciprocating tests under boundary lubrication condition at 100°C for PAG base oil (x97011.00) and GF-5 base oil having the same kinematic viscosity of 5.6 cSt at 100°C. In this test a polished American Iron and Steel Institute (AISI) 52100 steel flat reciprocated at 5 Hz against a stationary 6-mm long AISI 52100 steel pin under a contact stress of 0.8 GPa. Although there were some differences in friction coefficients between the oils early in the test, no significant difference was observed at the end of test. Analysis of tribo-film formed on the steel flats using Raman spectroscopy primarily showed presence of iron oxide and amorphous carbon (commonly observed on lubricated surface) for both oils (Figure 2).

Traction measurements were conducted on both oils using a MiniTraction Machine at 150% slide to roll ratio

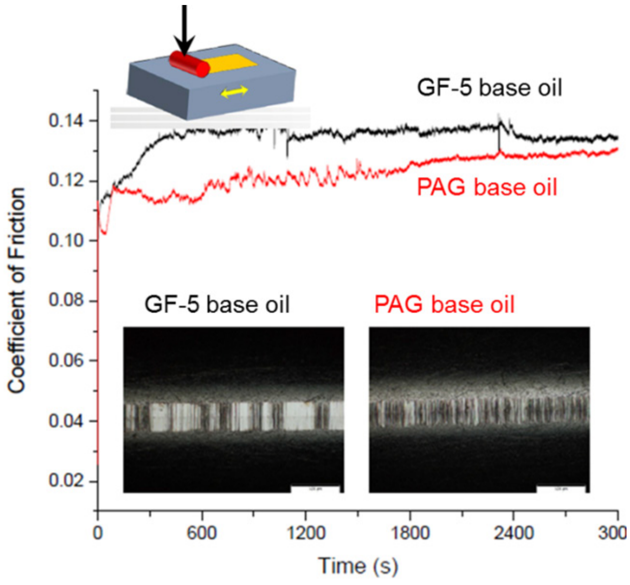

**FIGURE 1.** Coefficient of Friction at 100°C

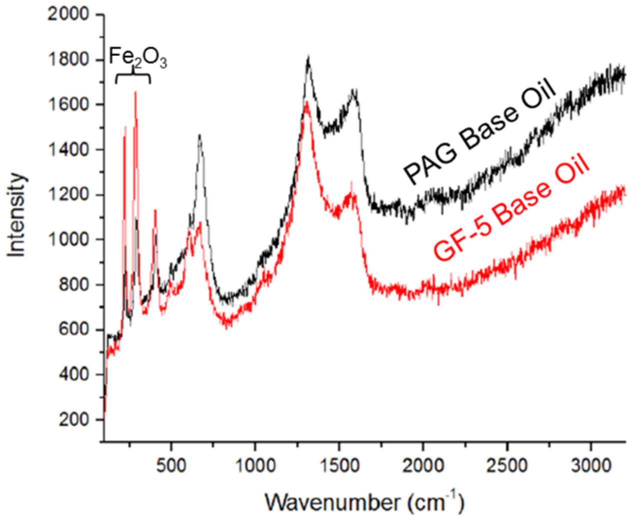

**FIGURE 2.** Raman Spectra of Tribo Films Formed with PAG and GF-5 Base Oils

at 100°C oil temperature and 50 N load. In this test a 19-mm diameter polished AISI 52100 steel ball rotated against a rotating polished AISI 52100 steel disk. Figure 3 results show substantial lower traction coefficient for PAG base oil compared to GF-5 base oil under mixed lubrication regime. Separate tests were run up to 20 mm/s (where significant separation exists between the two oils) and the steel disks are preserved for tribo-film analysis using multiple surface sensitive analytical techniques (Auger, X-ray photo-electron spectroscopy, and possibly time-of-flight secondary ion mass spectrometry).

### Motored Valvetrain Wear Evaluations

The wear of camlobe and tappet was measured simultaneously using a radiotracer method where the camlobe and the tappet were activated to $Co^{57}$ and $Co^{56}$ respectively. A single camlobe mounted on a shaft rotated against a tappet at 500, 1,000, and 1,500 RPM (camshaft) at 95°C oil temperature for 100 hours. The tappet was spring loaded as in an engine and all production engine parts were used. The measurement system allowed continuous wear monitoring throughout the test. Figure 4 compares the amount of wear at the end of the test between PAG oils and GF-5 SAE 5W-20 oil. All PAG oils have the same high-temperature high-shear viscosity (2.6 mPa.s) and additive pack but different base stock chemistry. The difference between PAG Oil 9-1 and PAG Oil 17-1 is the latter contains an additional antiwear boost. Results show the wear performance of PAG oils can be tailored by the choice of base stock chemistry and the antiwear boost on PAG Oil 17-1 was effective in improving wear performance.

### Motored Engine Friction Evaluations

Motored engine friction tests were conducted using an inline four cylinder engine with PAG and GF-5 oils at various oil temperatures and engine speeds. Five tests were conducted at each temperature with very good repeatability. The high-temperature high-shear viscosity of all oils was 2.6 mPa.s except PAG Oil 14-2 which was 2.4 mPa.s. Results in Figure 5 show either similar or lower friction torque for all PAG oils compared to GF-5 5W-20 oil. PAG Oil 15-1 showed the lowest friction torque. PAG Oil 14-2 showed the classical Stribeck hook at low engine speed due to its lower high-temperature high-shear viscosity value.

### ASTM Sequence Tests

ASTM Sequence tests are required performance tests for a passing GF-5 oil. ASTM Sequence VID test measures the fuel economy improvement over a baseline oil (20W-30) when fresh (FEI 1) and aged (FEI 2). The limits are based on FEI SUM (FEI 1 + FEI 2) and FEI 2. ASTM Sequence IIIG test measures oil oxidation

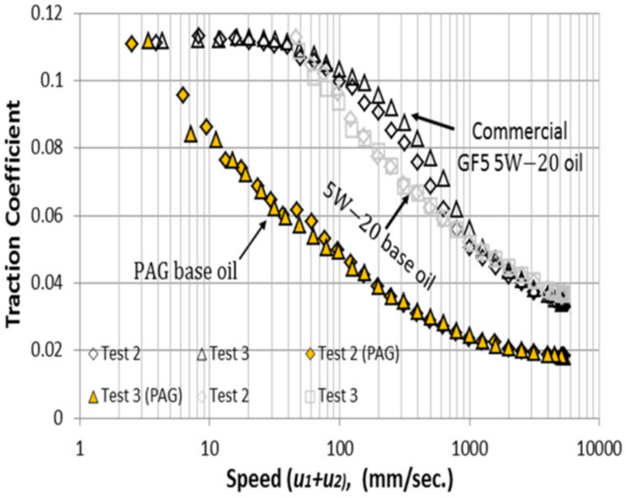

**FIGURE 3.** Traction Coefficients at 100°C as a Function of Sliding Speeds

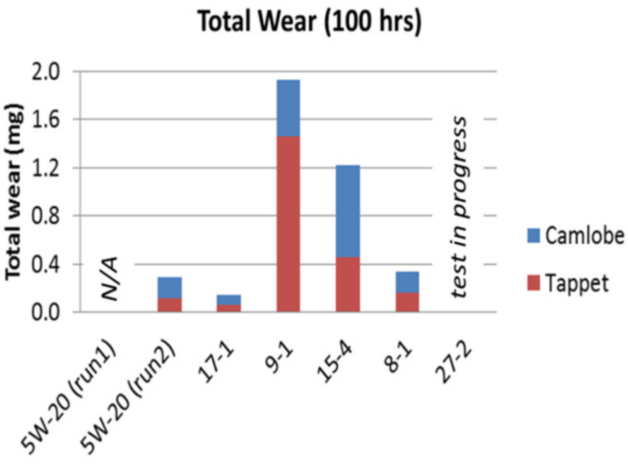

**FIGURE 4.** Motored Valvetrain Wear at 95°C Oil Temperature

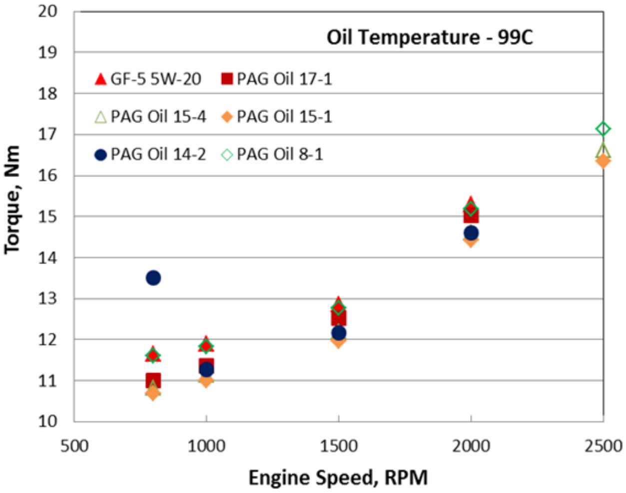

**FIGURE 5.** Motored Engine Friction at 99°C Oil Temperature

and camshaft and valve lifter wear. Sequence IVA measures camshaft and valve lifter wear at low engine oil temperatures (50°C and 60°C).

Two types of oil formulations were evaluated. PAG Oil 17-1 was evaluated in Sequence IVA. A fully formulated PAG oil (without the viscosity modifier) was evaluated in Sequence VID and Sequence IIIG tests. Formulation choice was limited by the solubility of different additive components in PAG base oil and does not represent an optimized formulation. Results in Table 1 show none of the formulations met the minimum GF-5 performance limits and highlight the need for additional development effort.

**TABLE 1.** Sequence Test Results

| Tests | Purpose | Results | GF-5 limits |
|---|---|---|---|
| **Sequence VID** | Fuel economy | FEI SUM – 1.24% | FEI SUM – 2.6% |
| | | FEI 2 – 0.43% | FEI 2 – 1.2% |
| **Sequence IIIG** | Oil oxidation, wear | Test terminated at 59 hour because of loss of load control due to low oil level | |
| **Sequence IVA** | Low temp. valvetrain wear | 1,037 µm | 90 µm (max.) |

FEI – fuel economy improvement

## CONCLUSIONS

- Motored valvetrain wear tests showed wear protection capability of PAG oils can be tailored by the choice of base oil chemistry and the antiwear boost can improve wear performance.
- Motored engine test results showed PAG Oil 15-1 reduced friction by over 8% at 99°C oil temperature compared to GF-5 5W-20 oil.
- ASTM Sequence test results highlighted the formulation challenges to meet the minimum GF-5 requirements.

# II.13 A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement

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## Overall Objectives

Novel lubricant formulations for improving vehicle fuel efficiency by at least 2% without adversely impacting vehicle performance or durability.

## Fiscal Year (FY) 2014 Objectives

- Initial design, synthesis, and characterization of a series of sulfur- and phosphorus-free heterocyclic additives for boundary lubrication (BL).
- Surface functionalization of solid-state-lubricating nanoparticles for friction reduction and scuffing prevention.
- Initial design and synthesis of a novel di-block copolymer-based viscosity modifier (VM) for low shear at high speed.
- Development of tribological tests in the BL regime similar to that of the powertrain components in a passenger vehicle; model of base fluids.

## FY 2014 Accomplishments

- Designed, synthesized, and characterized three major families of heterocyclic additives.
- Found excellent BL additives to reduce friction maximally by ~45% with the laboratory-scale tests.
- Obtained a visible lubrication enhancement and friction reduction in the BL regime using the as-synthesized additives in a fully formulated 5W30 engine oil.
- Conducted the first stage synthesis of a di-block PMMA-(LCB) polyalphaolefin (PAO) copolymer.
- Found organosilane functionalized nanoparticles reducing friction by forming significant tribo-layers.
- Developed a method for molecular dynamic (MD)-supported modeling of base fluids.
- Training of five graduate students and one undergraduate student. Three graduated, one with a Masters of Science and two (partially involved) with Ph.D.

## Future Directions

- Continue designing, synthesizing, and optimizing oil-soluble BL additives and the copolymer VM.
- Develop lubricant formulations using the optimized BL additives and the newly-synthesized copolymer VM.
- Conduct a comprehensive study on the tribological and rheological properties of the initial lubricant formulations.
- Conduct detailed physical/chemical investigations of surface functionalizations and additive-surface interactions.
- Develop MD simulations to visualize surface adsorptions of the additives and to predict molecular structure-viscosity relations. Investigate and model lubrication mechanisms.
- Transfer the successfully formulated lubricants from laboratory investigations to industrial tests.

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## INTRODUCTION

Achieving more than 2% fuel efficiency improvement of light- and medium-duty vehicles requires significant friction reduction in the powertrain and drivetrain systems; if by reducing boundary friction alone, this requires at least a 30% friction reduction [1]. Better BL additives are needed as a component to achieve this goal. The frictional loss due to high viscous shear at high speeds cannot be simply tackled by using oil of low viscosity because this will raise the friction at low speeds. We need a chemically and mechanically stable lubricant modifier that makes the lubricant less viscous only at high shear rates. Many lubricants undergo some shear-thinning in the contact interface, resulting in lower friction than expected from Newtonian flow assumptions [2-5]. A key problem to solve is to have a modified lubricant that only responds to high shear rate via molecular deformation, not scission. More friction reduction mechanisms should also be included, such as using nano-particles; hexagonal boron nitride (h-BN) (or α-BN) is a well-known solid lubricant, and its crystal structure is essentially the same as that of graphite [6], which can be an excellent choice.

## APPROACH

The fuel efficiency goal has to be accomplished by reducing friction in the entire operation regime, to lower friction in the boundary regime (low speed) via sulfur-and-phosphorus-free heterocyclic additives and nanosized h-BN particles, and in the hydrodynamic regime (high speed) via shear-thinning additives and nano-sized particles, which include synthesizing “designer” additives, characterizing their properties at conditions comparable to those in real-world applications, modeling the viscosity and frictional behaviors for design optimization, and testing their friction reduction capability. The present research is being conducted collaboratively by the NU-ANL team. All additives except nanoparticles were synthesized/prepared at the NU’s chemistry laboratory.

## RESULTS

**Synthesis of additives and surface functionalization of nanoparticles.** Three major families of heterocyclic additives synthesized and the di-block PMMA-(LCB) PAO copolymer process optimized. As listed in Figure 1a, hexahydrotriazines and their hybrids (TC12T, TC18T, TbenzylT, and TC12C18T), cyclen derivatives (C12cyc and C18cyc), and triazine compounds with (4C6Ptriaz and 4C12Ptriaz) or without (C6triaz and C12triaz) benzene spacers have been synthesized. The BL additives consist of side R groups and sulfur-and-phosphorus-free heterocyclic cores. The representative R groups are hydrocarbon chains with different length (i.e. C6, C12, and C18) or a small side group (i.e. benzyl substituent). Figure 1b shows a silanization process via attaching long alkyl chains to solid-state-lubricant nanoparticles (h-BN and $B_2O_3$). The surface functionalization leads to well suspended nanoparticles in a base oil (PAO4).

In order to synthesize the di-block PMMA-(LCB) PAO copolymer as new VM, poly-1-octene with a terminal olefin is highly sought after. The present catalyst has given a 50:50 mixture of the terminal and internal olefin. By optimizing the reaction conditions preference for the formation of the terminal olefin will be increased. In addition, via a hydroboration-bromination reaction, an achieve anti-markovnikov addition to the terminal olefin is being carried out to synthesize the new copolymer VM.

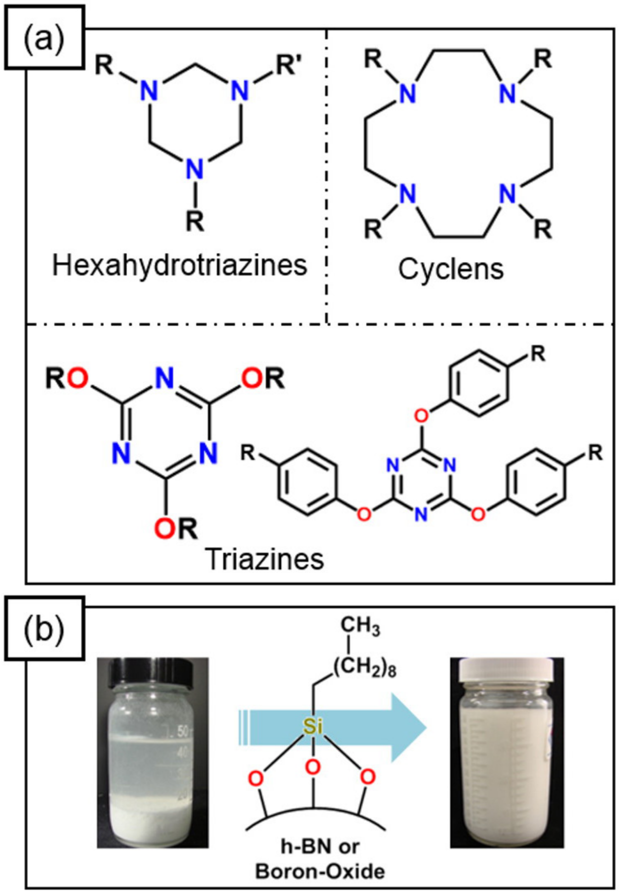

**FIGURE 1.** (a) Three types of heterocyclic additives synthesized. (b) Organosilane functionalized nanoparticles for their suspension in a PAO 4 oil.

**Low friction BL additives tested at room temperature**. Symmetrical hexahydrotriazine complexes shows a promising friction reducing functionality first. For Group II (Figure 2a), III (Figure 2b) and IV (Figure 2c) oils, the hexahydrotriazines with small side groups (TbenzylT) or short side chains (TC12T) show limited friction reductions. At different speeds, boundary friction was reduced by ~20% to ~30% using TC18T. TC12C18T2 with a high C18 ratio demonstrates ~15% to ~35% friction reduction with a good oil solubility. Post-test analyses also revealed that both wear volumes and wear coefficients were reduced by more than 95% using 5 wt% TC18T in Group II oil. Wear resistance is increased to be

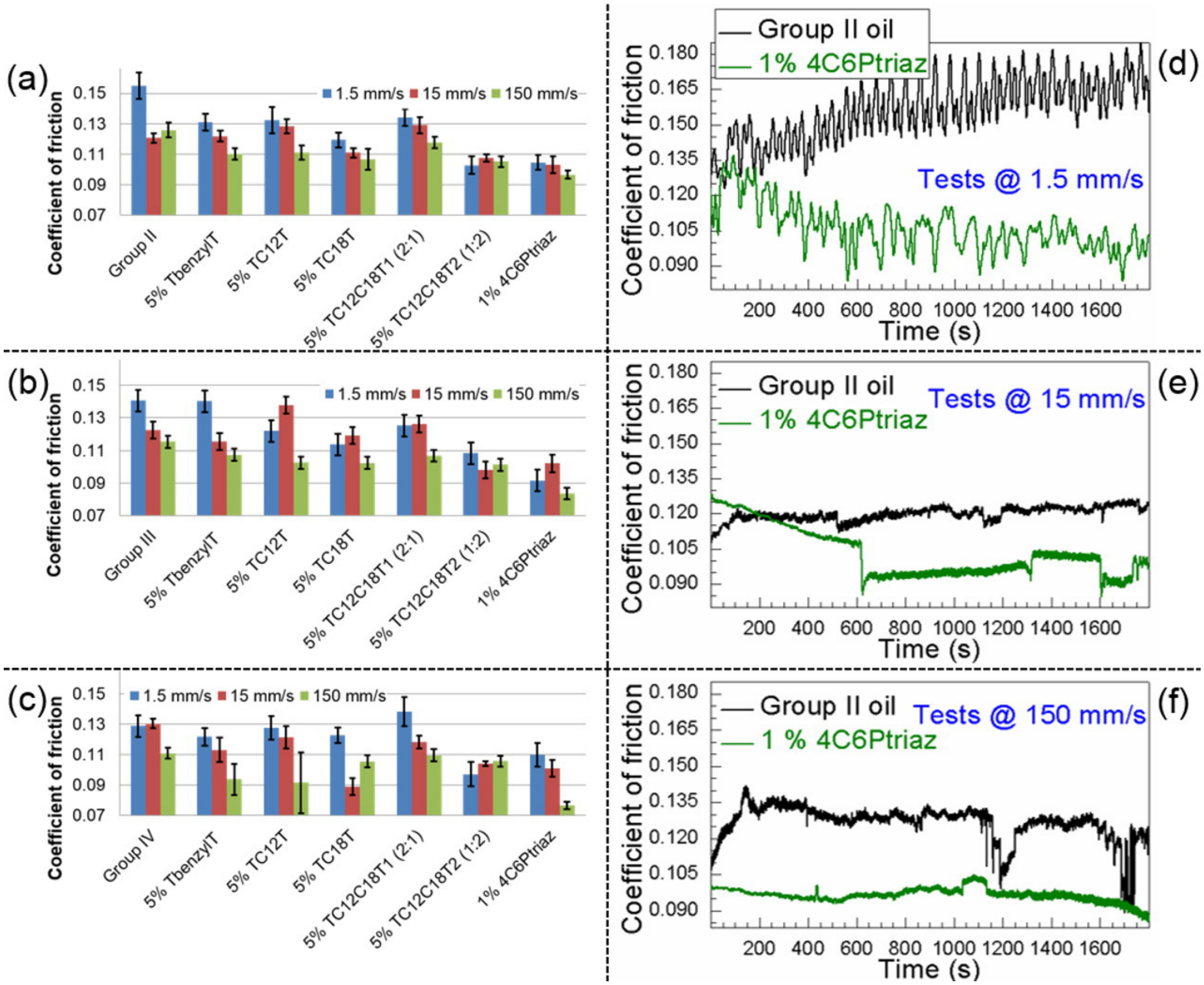

**FIGURE 2.** Comparison of average friction coefficients of representative additives in Group II (a), III (b), and IV (c) oils. Friction reduction examples of 4C6Ptriaz in Group II oil at 1.5 mm/s (d), 15 mm/s (e), and 150 mm/s (f).

comparable to that of zinc dialkyldithiophosphates but with the significant friction reduction.

Among all thermally stable additives, 4C6Ptriaz is found to be the best BL additive at room temperature. Only 1 wt% 4C6Ptriaz is able to reduce friction by ~20% to ~40% at different speeds (Figures 2a to 2c). Figures 2d through 2f are examples in Group II oil.

New additives were also investigated in a fully formulated 5W30 engine oil (Figure 3). Visible friction reductions are observed for C12triaz.

**Low friction BL additives tested at higher temperatures.** Both the triazine compounds and the cyclen derivatives have demonstrated good thermal stability already. More efforts are devoted to study their high temperature BL properties. Those results are shown in Figure 4. Overall, performances of the thermally stable additives are enhanced with elevated temperature, ranging from 25ºC to 200ºC. The C18cyc (purple plots in Figures 4a and 4b) is found to be the best BL additive in Group III oil with ~25% to ~45% improvement at high temperatures. High temperature investigations were also performed in the fully formulated 5W30 engine oil at 1.5 mm/s (Figure 4c). Synergetic effects of diverse additives in the formulated oil induce a great fluctuation of friction with temperature (the black plot in Figure 4c). On the contrary, with the presence of C12triaz, a continuous friction reduction along the heating process is obtained (the green plot in Figure 4c). At high temperatures, C12triaz is able to reduce friction by ~20% to ~35% in a 5W30 oil.

**Organosilane functionalized nanoparticles as anti-friction anti-scuffing additives.** Figures 5a and 5b are for friction comparisons with and without capped

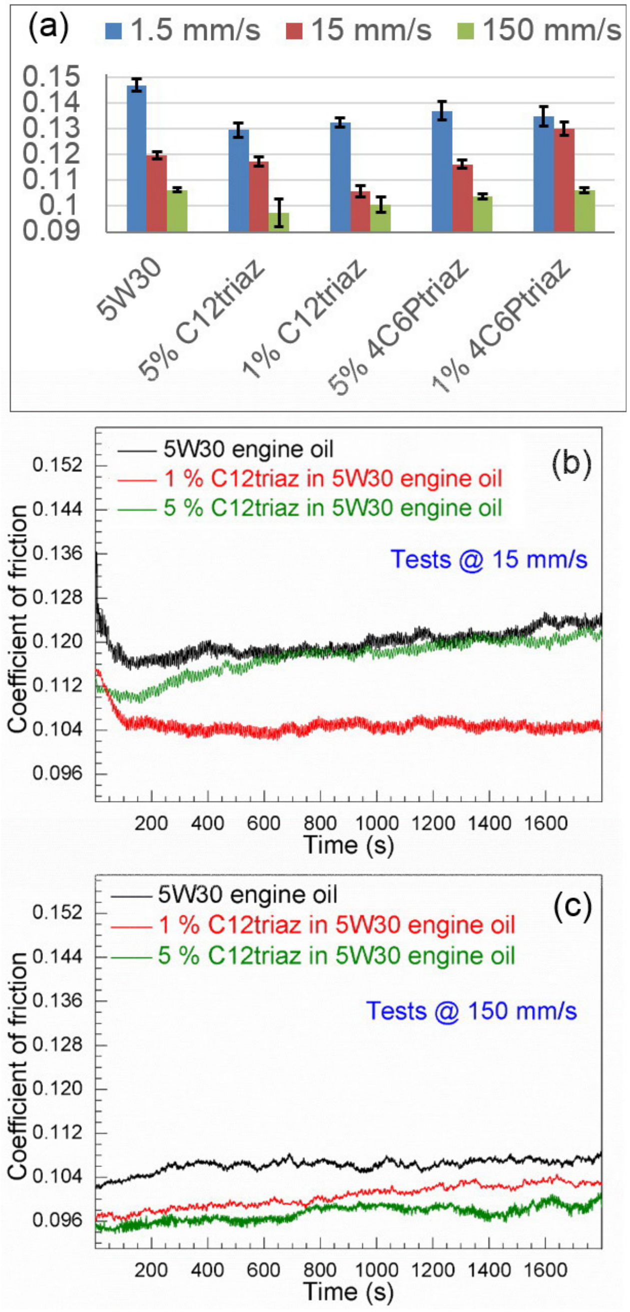

**FIGURE 3.** (a) Comparison of average friction coefficients of selected triazine compounds in 5W30 engine oil. Friction reduction examples of C12triaz in the engine oil at 15 mm/s (b) and 150 mm/s (c).

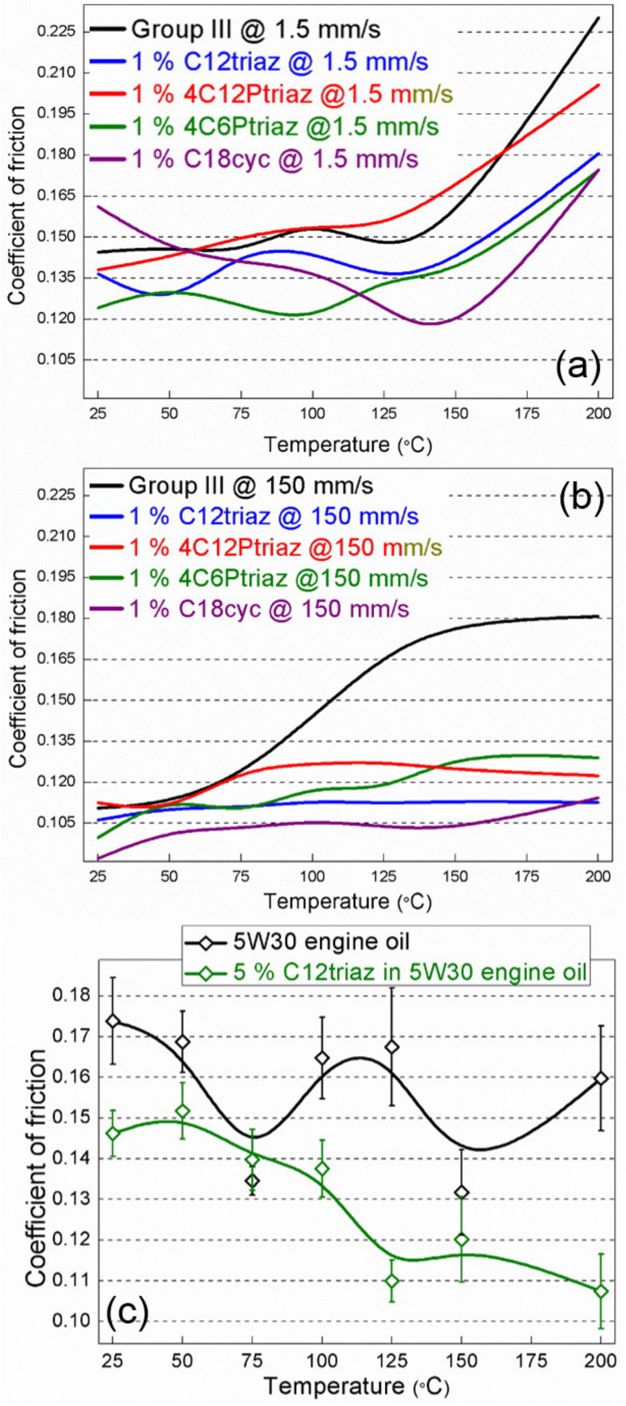

**FIGURE 4.** High temperature BL tests of different thermally stable additives in Group III oil at 1.5 mm/s (a) and 150 mm/s (b). High temperature BL tests of C12triaz in the 5W30 oil at 1.5 mm/s (c).

nanoparticle additives in base PAO 4 oil. A measurable friction reduction is achieved using the both nanoparticle additives, by more than 20%. Friction reduction of the capped $B_2O_3$ nanoprticles is affected by its concentration (Figure 5b). The voltage drop between the ball and the flat was measured to indicate the formation of a protective/non-conductive tribo-layer (Figure 5c). With the addition of $B_2O_3$ nanoparticles, the same oil exhibits a steady voltage drop of 10 mV. The oil with the capped nanoparticles appears to have developed significant tribo-layers. Figure 5d shows the results of scuffing tests comparing the PAO4 to the same with 1 wt% h-BN nanoparticles. Inclusion of h-BN nanoparticles enhances the scuffing resistance by a factor of three (from ~380 N to ~1,150 N).

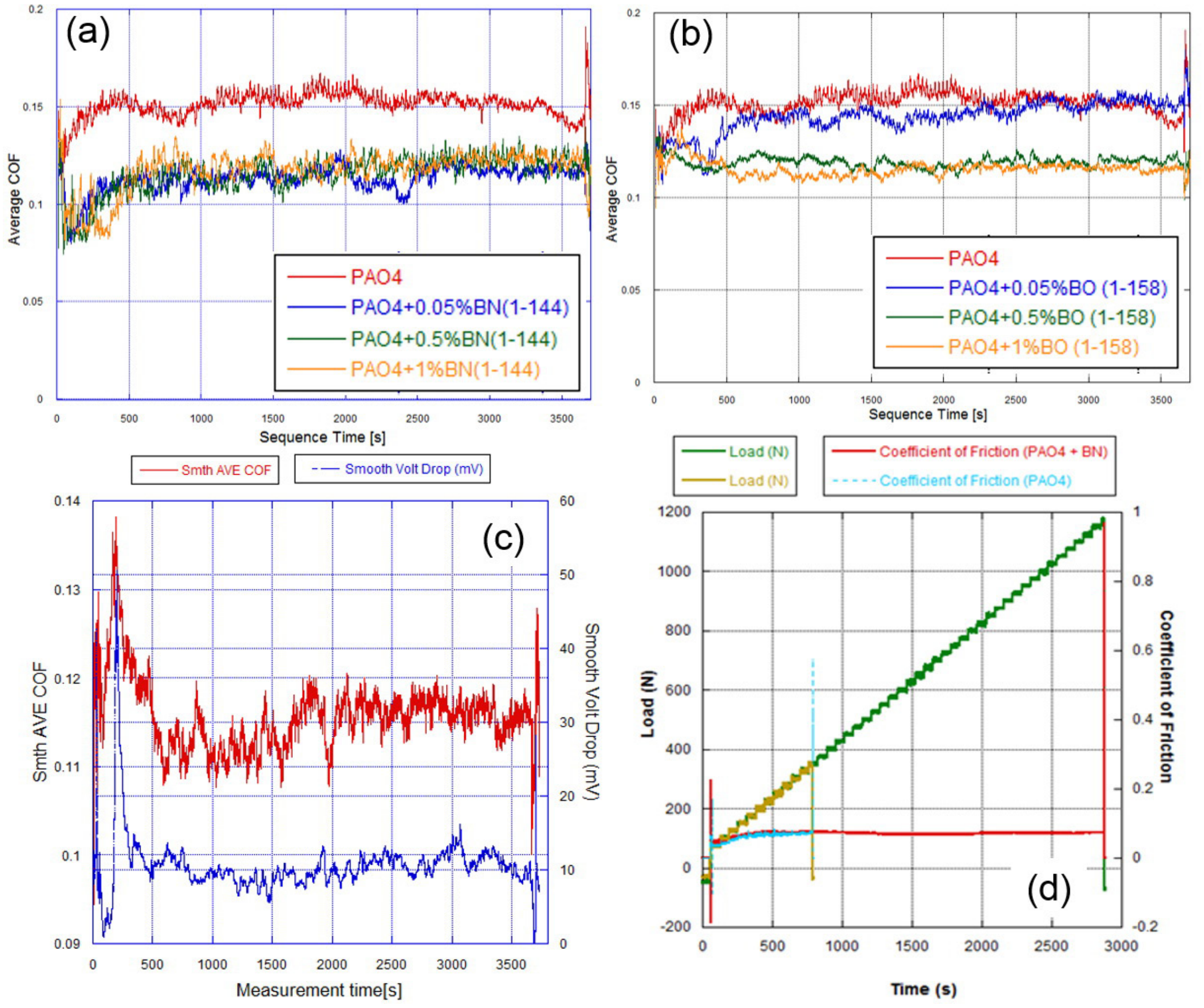

**FIGURE 5.** BL tests comparing PAO4 without and with different concentrations of capped h-BN (a) and $B_2O_3$ (b) nanoparticle additives. (c) Voltage drop measurements during the friction tests with addition of 1 wt% $B_2O_3$ in PAO4. (d) Scuffing load enhancement through the inclusion of h-BN nanoparticles.

**MD modeling of base fluids**. The approach of MD supported Berry and Fox modeling [7] has been developed to predict the viscosity of lubricants with different molecular structures of the same monomers. Based on the viscosity of one structure (C76) of polyethylene, viscosities of different lengths (up to C400) and mixtures of dimers and trimers are successfully predicted. The modeling results are found to agree well with experimental data.

## CONCLUSIONS

- The sulfur-and-phosphorus-free heterocyclic additives are promising in friction reduction in the BL regime.
- Hybridization and surface functionalization increase the oil solubility for different additives.
- The new BL additives are able to form lubricant films, and such films reduce up to ~40% friction at room temperature compared with the base oil friction.
- Aromatization and spacers are introduced to improve the additives' thermo-stability.
- The thermally stable BL additives have been found to reduce friction significantly (maximally by ~45%) in a wide temperature range.
- The new heterocycle-based molecules integrate the friction reduction capability with the wear resistance behavior in a single additive.

- The new BL additives do not affect the viscosity properties of the base fluids.
- The addition of 1 wt% h-BN nanoparticles enhances the scuffing resistance by a factor of three.

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# II.14 Improve Fuel Economy through Formulation Design and Modeling

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## Overall Objectives

The objective of this project is to develop novel lubricant formulations that are expected to improve the fuel efficiency of medium-duty, commercial and military vehicles by at least 2% (improvement based on comparative results from engine dynamometer testing, chassis dynamometer testing or test track, e.g., SAE International Technical Standard J1321) without adverse impacts on vehicle performance or durability. This will be accomplished through engine, transmission and axle lubricant formulation design, modeling and testing.

Target level of performance:

- Engine oil fuel economy improvement (~2%)
- Axle oil fuel economy improvement (~0.5%)
- Whole system—greater than 2% by SAE J1321
- Durability penalty—none, no detriment seen to component life at 2,000 hours engine tear-down

## Fiscal Year (FY) 2014 Objectives

- Complete formulations of two candidates each for engine oil and axle oil
- Use bench tests and proprietary modeling work to predict fuel economy performance and meet the target level
- Develop multiple formulae of transmission fluid for SAE#2 test

## FY 2014 Accomplishments

### Engine Oil

- Baseline: Commercially available CJ-4 15W-40.
- Candidate 1: PC-11 candidate, 5W-30, high temperature, high shear (HTHS) ~ 3.0. Formulation was finalized. The oil had been tested by an original equipment manufacturer.
- The modeling work shows a 2.04% fuel economy increase compared with the baseline. A milestone was logged on March 16, 2014.
- Candidate 2: 5W-20, HTHS ~2.8, with bio-base oil and friction modifier. Compared with the candidate 1 engine oil, this oil has higher viscosity index (VI), lower friction and lower traction. Formulation was finalized. The modeling work shows a 2.12% fuel economy increase compared with the baseline. A milestone was logged on September 29, 2014.

### Axle Oil

- Baseline: Commercially available J2360-approved 75W-90.
- Candidate 1: J2360-approved 75W-90. The formulation is done. The chemistry has been proved by field test. Modeling work shows a 0.61% fuel economy improvement under conditions of the New European Driving Cycles. A milestone was logged on March 28, 2014.
- Candidate 2: J2360-approved 75W-90. It will have field-proven chemistry plus Valvoline's proprietary technology. Compared with the candidate 1 axle oil, this oil has higher VI, higher thermal conductivity and lower churning loss. Modeling work shows a 0.73% fuel economy improvement under conditions of the New European Driving Cycles. A milestone was logged on September 26, 2014.

## Transmission Fluid

- Baseline: TES 295 Fluid on the market.
- Candidate: meets TES 295 performance, but has better efficiency performance. Multiple additive suppliers have provided detergent inhibitor packages. Formulations with different types of base oil combination have been carried out. Bench tests of high frequency reciprocal rig (HFRR) and mini traction machine (MTM) using clutch paper material as friction surface have been used for selecting the

final formulae to do SAE #2 tests. Two candidates have been selected for SAE #2 test.

## Future Directions

- For engine oil the next step is to run the National Renewable Energy Laboratory ISL 8.9-L Engine Fuel Efficiency verification test. Improvement of around 2% against the baseline is anticipated.
- For axle oil the next step is to run axle efficiency verification test and do reformulation if necessary. Greater than 0.5% improvement against the baseline is anticipated.
- Transmission fluid preparation of multiple candidates for SAE #2 tests is underway. Candidate will be picked after comparison of multiple properties with base line.
- Conduct SAE J 1321 test for the system of the aforementioned three types of lubricants at the Transportation Research Center Inc. in East Liberty, OH. Greater than 2% total fuel efficiency is expected.

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## INTRODUCTION

Automotive vehicles rely on lubricant films to provide wear protection to their moving components. Lubricant film thickness is in general determined by oil viscosity metrics; the higher the viscosity, the thicker the film. However, thicker oil films induce higher traction, which decreases the fuel efficiency. The general trend for fuel efficiency lubricants is to have lower viscosity. Nevertheless, this strategy introduces the possibility of reduced component durability and actual loss in fuel economy if lubricant film thickness is reduced and surface to surface contact of moving parts is increased beyond component capability. A state-of-the-art balance in automotive lubricant formulations is needed in order to have both wear protection and fuel efficiency. Automotive lubricants consist of base oils and additives like anti-wear agent, anti-oxidant, viscosity index improver, corrosion inhibitor and friction modifier. With advanced technology in lubricant additives, low-viscosity lubricants have been developed by adding special anti-wear agents and friction modifiers. Special base oils can also contribute to the performance of low viscosity lubricants with higher fuel efficiency.

Valvoline has the ability to formulate automotive lubricants from individual ingredients and conduct bench top, engine dyno and field tests. As an independent automotive lubricant marketer, Valvoline has opportunities working with every lubricant additive supplier and can thus combine the best additives to provide the best performance lubricants. Valvoline has been doing fuel economy improvement studies in heavy-duty oils since 2010 [1]. For example, using a Cummins ISB 6.7-L engine, a series of tests based on the viscosity matrix were performed. The fuel economy index results, when analyzed for DOE matrix, show very significant dependence for some of the viscometric parameters like VI and HTHS and for the oil operating temperature. Valvoline has also cooperated with Imperial College in developing modeling software to predict axle oil efficiency [2-3].

## APPROACH

Valvoline has profound and extensive experience in multiple types of lubricant formulation. In recent years Valvoline adopted the Design of Experiment method in lubricant formulation and modeling work to predict lubricant performance, which has been proven more efficient in bringing new technology and products to the market. The proposed tasks will combine oil formulation, experimental design and new additive/base oil combinations to control friction, wear and traction; employ mathematical modeling and prediction as well as original equipment manufacturer cooperation; and utilize bench, engine and fleet testing to reach the target.

## RESULTS

### Engine Oil

The key properties, proprietary modeling work and bench test results of engine oil candidates and their baseline are summarized in Tables 1 and 2.

**TABLE 1.** Property of Engine Oil Candidates and Their Baseline

| ASTM | Property | Candidate 1 | Candidate 2 | Baseline |
|---|---|---|---|---|
| ASTM D 445 | KV @ 100°C (cSt) | 9.6 | 8.56 | 15.42 |
| ASTM D 445 | KV @ 40°C (cSt) | 55.19 | 46.09 | 117.68 |
| ASTM D 2270 | Viscosity Index | 159 | 165 | 134 |
| Fuel Economy Improvement by Modeling (%) | | 2.04 | 2.12 | n/a |

KV - kinematic viscosity; n/a - not applicable

For bench-top wear tests, engine oil Candidate 1 shows a slightly higher number than its baseline. (See Table 2 for more details.) Please keep in mind that the tests are under fully boundary conditions. But the engine oil Candidate 2 has lower friction and wear than the

**TABLE 2.** HFRR and 4-Ball Wear Test Results of Engine Oil Candidates and Their Baseline

| HFRR: 1.25GPa, 20 HZ, 40°C for 10 minutes, 125°C for 2 hours | | | | ASTM D 4172: 4-ball |
|---|---|---|---|---|
| | Friction @40°C | Friction @125°C | Wear on Ball(μm) | Wear on Ball (μm) |
| Candidate 1 | 0.128 | 0.13 | 178 | 549 |
| Candidate 2 | 0.127 | 0.095 | 151 | 470 |
| Baseline | 0.13 | 0.13 | 161 | 527 |

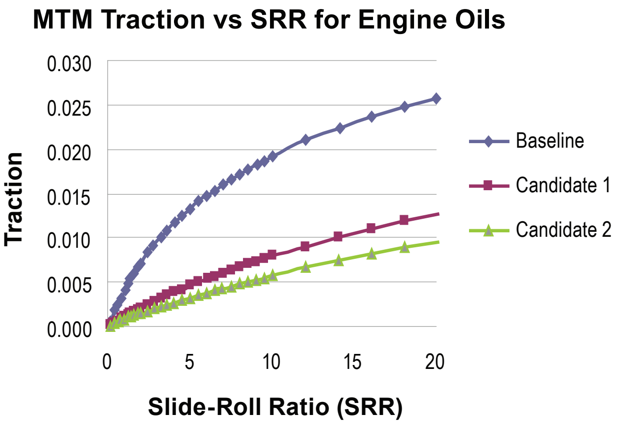

**FIGURE 1.** MTM vs. SRR for Engine Oils at 125°C under 1 GPa Hertz Contact Pressure

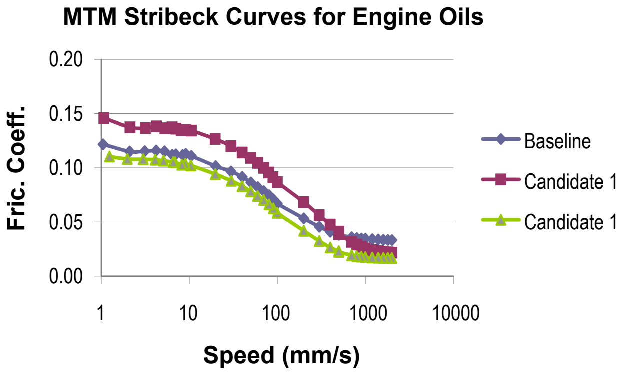

**FIGURE 2.** The MTM Stribeck Curves for Engine Oils at 125°C under 1 GPa Hertz Contact Pressure

baseline. The MTM tests show that engine oil Candidate 1 and 2 have much lower traction than their baseline. (See Figure 1 for more details.) However, again the Stribeck curves in Figure 2 show that in the boundary regime, the friction for engine oil Candidate 1 has a higher value than its baseline while engine oil Candidate 2 has lower friction than the baseline. Overall, engine oil Candidate 2 has the lowest friction, traction and wear due to its special chemistry. The proprietary modeling work results show that both oil candidates meet the fuel efficiency performance target of greater than 2% improvement.

## Axle Oil

The key properties and proprietary modeling work results of gear oil candidates and their baseline are summarized in Table 3.

**TABLE 3.** Property of Axle Oil Candidates and Their Baseline

| ASTM | Property | Candidate 1 | Candidate 2 | Baseline |
|---|---|---|---|---|
| ASTM D 445 | KV @ 100°C (cSt) | 15.63 | 15.47 | 15.28 |
| ASTM D 445 | KV @ 40°C (cSt) | 92.21 | 90.15 | 104.39 |
| ASTM D 2270 | Viscosity Index | 181 | 182 | 154 |
| Fuel Economy Improvement by Modeling (%) | | 0.61 | 0.73 | n/a |

Modeling work shows 0.61% and 0.73% fuel economy improvements for Candidate 1 and Candidate 2 respectively, compared to the baseline for the New European Driving Cycle. From MTM tests, Candidate 2 showed the best frictional performance for all test conditions compared to Candidate 1 and the baseline. Candidate 1 also has lower friction than the baseline under most testing conditions. Figure 3 shows the test results at 70°C under 1 GPa Hertz contact pressure.

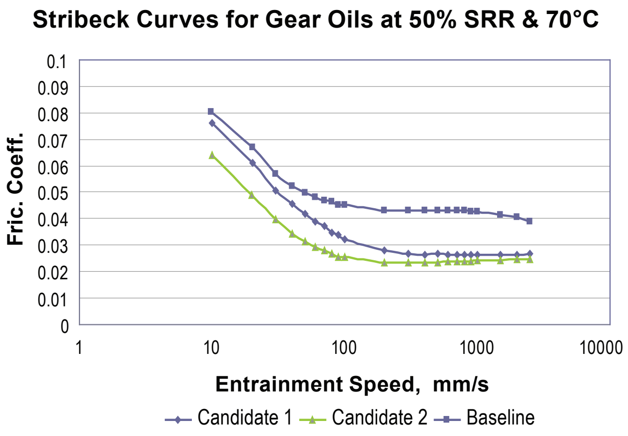

**FIGURE 3.** MTM Stribeck Curves for Gear Oils

### Transmission Fluid

The formulation and bench testing of transmission fluid is still underway.

## CONCLUSIONS

- Two engine oil candidates have been developed and modeling work showed they meet the target fuel economy improvements of greater than 2%. Tribological bench tests showed Candidate 2 has better wear and friction performance than the baseline.
- Two axle oil candidates have been developed and modeling work showed they meet the target fuel economy improvement of greater than 0.5%. MTM tests showed that both candidates have lower friction than the baseline under most testing conditions.

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**2.** A. Kolekar, A. Olver, A. Sworski, F. Lockwood, "The efficiency of a hypoid axle- a thermally coupled lubrication model," Tribology International, 2013, Vol:59, Pages:203-209.

**3.** A. Kolekar, A. Olver, A. Sworski, F. Lockwood, "Method of Reducing Churning Loss in Dipped Lubrication," U.S. Patent Application: 20140048354 A1.

## PATENT FILED

**1.** A patent application (14548850) related to this work was filed on Nov 20, 2014.

# II.15 Development of Polyalkylene Glycol-Based Lubricant for Light- and Medium-Duty Axle Applications

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Subcontractors
- Argonne National Laboratory, Argonne, IL
- Dow Chemical Company, Midland, MI

## Objectives

- Formulate new polyalkylene glycol (PAG)-based gear oils that will improve the fuel efficiency of light- and medium-duty applications by 2% over 75W140 grade axle oils without adverse impacts on vehicle performance or durability.
- Evaluate fundamental material properties with respect to gear oil formulations.
- Complete bench testing to understand intrinsic lubricant properties its contributions to wear and efficiency characteristics in an axle.
- Analyze lubricant additive-derived anti-wear films using surface sensitive analytical tools.
- Understand wear and efficiency performance characteristics in axles through specially designed test rigs.
- Estimate vehicle fuel economy and potential impact on emissions.

## Fiscal Year (FY) 2014 Objectives

- Selection of various PAG oils
- Selection of anti-wear, extreme pressure, and frictional additive components
- Demonstration of anti-wear and thermal performance of PAG oil

## FY 2014 Accomplishments

- Dow Chemical Company formulated several PAG oils to support various laboratory bench rig tests. Tests included were 4-ball wear test, Falex Extreme Pressure (EP) test, copper corrosion test and oxidation test on various PAG formulations.
- Argonne National Laboratory (ANL) completed friction and wear evaluations on PAG base oils and compared against the reference 75W140 gear oil.
- Ford Motor Company (FMC) initiated dynamometer based axle efficiency test.

## Future Directions

- Complete analyzing tribo-films formed on contacting surfaces to understand friction reduction mechanism(s)
- Complete laboratory bench rig friction and wear studies
- Conduct fatigue and micro-pitting studies at ANL
- Complete SAE International Technical Specification J2360 level tests (L-33-1 and L60-1)

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## INTRODUCTION

The intent of this project is to develop novel lubricant formulations that are expected to improve the fuel efficiency of light, medium, heavy-duty, and military vehicles by at least 2% over SAE 75W140 axle lubricants (improvement based on comparative results from engine dynamometer testing, chassis dynamometer testing or test track, e.g., SAE J1321) without adverse impacts on vehicle performance or durability.

With most gear oils, drag loss can be reduced by lowering oil viscosity. However, viscosity reduction creates concern for axle component durability due to reduced oil film thickness.

## APPROACH

The project team consists of technical personnel from FMC, Dow and ANL. The project is led by Arup

Gangopadhyay/Chintan Ved (FMC), Mr. John Cuthbert/Ashish Kotnis (Dow) and Dr. Ali Erdemir (ANL). All three partners will have key roles in achieving the project objectives. FMC is the prime contractor and will provide technical direction to ensure all bench/component and systems level 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, dynamometer and vehicle level testing to assess durability and axle efficiency. Test data will be used to estimate PAG fuel economy benefits and the results validated with chassis roll dynamometer tests.

## RESULTS

### PAG Formulations

Table 1 shows various PAG formulations that were developed by Dow. Several different PAG base fluids were evaluated and a base fluid with a viscosity index greater than 180 was used for additive package optimization. Viscosity profile of PAG C Mod version was selected for developmental work. Viscosity grade of PAG C Mod fluid is 75W85.

### 4-Ball Wear Test Evaluations

Testing was completed according to a modified ASTM D4172B procedure. Modifications included running the test for 120 minutes at 600 +/- 50 rpm RPM, as shown in Figure 1. PAG lubricants with each additive package show similar results as the 75W140 benchmark formulation, while the baseline PAG without additives shows significantly higher wear.

### Falex EP Evaluations

Falex testing was completed per the ASTM D 3233 test method A. PAG oil plus additive packages 1 and 3 show lower failure loads than the 75W140 formulation when tested in accordance with the ASTM D 3233 test method A. PAG oil plus additive package 2 shows higher failure loads than the 75W140 formulation (Figure 2).

### Turbine Oxidation Stability Test (TOST) Evaluations

Three PAG lubricant plus additive packages were evaluated using the oxidation/TOST test. Tests were completed using a modified ASTM D 5704 procedure. Modifications included:

- Temperature of 163°C and test of 50 hours
- Copper steel coil in the flask

**TABLE 1.** Various PAG Options Evaluated

| Base Fluid | Viscosity Index | Viscosity @ 100C (cSt) | Viscosity @ -40C (mPa.s) |
|---|---|---|---|
| Benchmark PAO | 170 | 25.04 | 135000 |
| PAG A | 190 | 10.90 | 99400 |
| PAG B | 168 | 11.30 | 94000 |
| PAG B Mod | 186 | 12.03 | 98861 |
| PAG C | 214 | 11.00 | 48100 |
| PAG C Mod | 216 | 12.02 | 52800 |
| PAG D | 197 | 7.60 | 22900 |
| PAG E | 176 | 11.80 | solid |
| PAG G | 218 | 11.92 | 44500 |
| PAG H | 194 | 11.97 | 55490 |

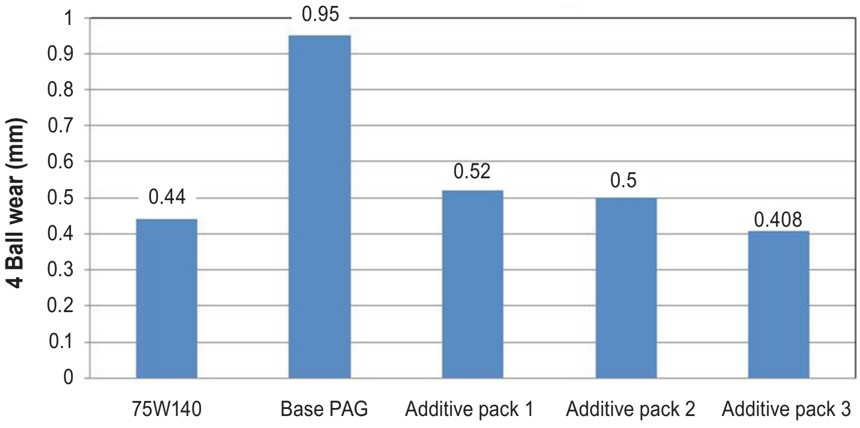

**FIGURE 1.** 4-ball Wear Test Results

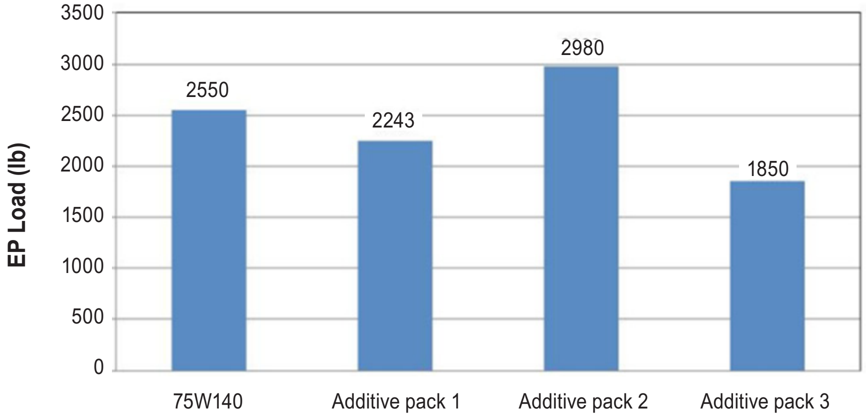

**FIGURE 2.** Falex EP Results

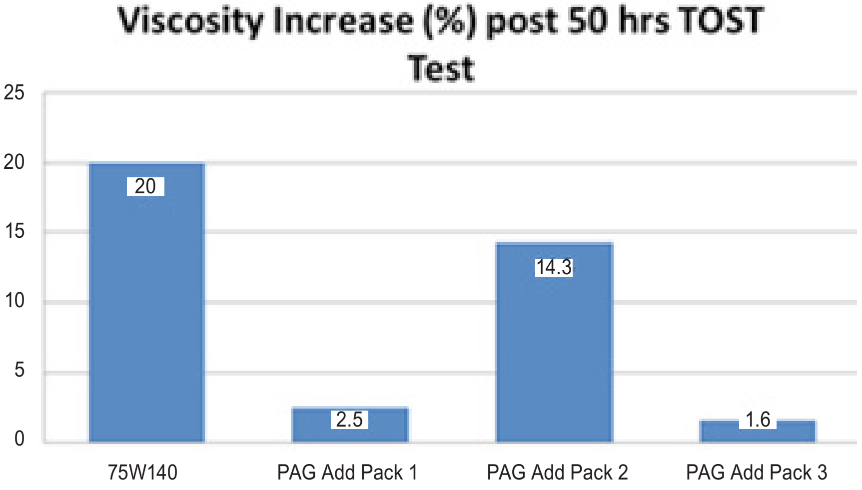

**FIGURE 3.** Post TOST Test Results

- Air bubbling
- Outlet air passes through condenser to condense the vaporized oil

The PAG lubricants with each additive package show better results (lower viscosity increase after the 50-hr TOST test) than the benchmark formulation 75W140. Results are summarized in Figure 3.

### Copper Corrosion Test

Testing was completed per the ASTM D130 (at 121°C for 3 hours) procedure. Additive Package 2 failed to meet the copper corrosion test and was optimized to retain wear and EP characteristics. Additive Package 2_1 modifications demonstrate performance comparable to 75W140. Additive Package 2_2 modifications ratings of 2c do not meet corrosion requirements of 75W140 and other reference gear oils 1b/2a.

### Frictional Performance

ANL generated data on various PAG-based formulations and baseline 75W140 gear oil. Three PAG lubricant plus additive packages were evaluated using SRV equipment. PAG-based gear oils provided reduced coefficient of friction when compared to 75W140 oil (Figures 4 and 5).

Wear tests were also conducted at room temperature, 40°C and 100°C, with 10 N load and contact pressure of 1.05 GPa.

- Additive Package 1: No further work will be done due to lower EP performance
- Additive Package 2: Better EP performance and similar wear compared to 75W140; modifications have addressed copper corrosion performance
- Additive Package 3: Lower EP performance and similar wear compared to 75W140 and meets

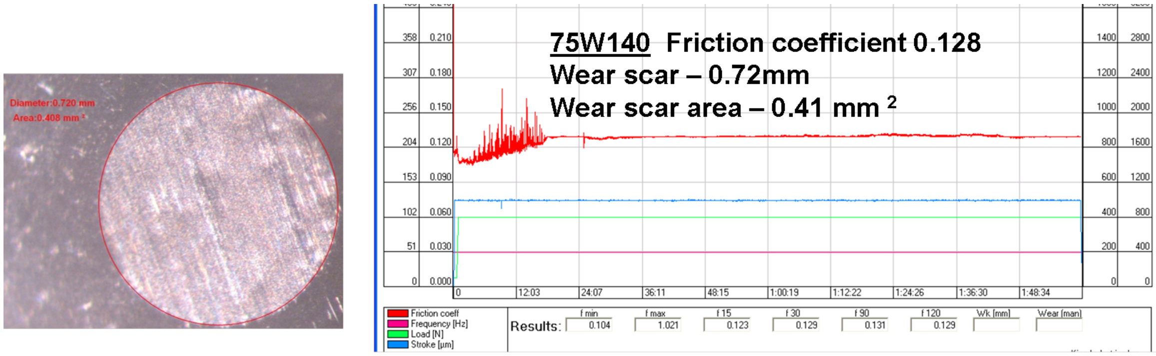

**FIGURE 4.** Coefficient of Friction and Wear Data for 75W140 oil

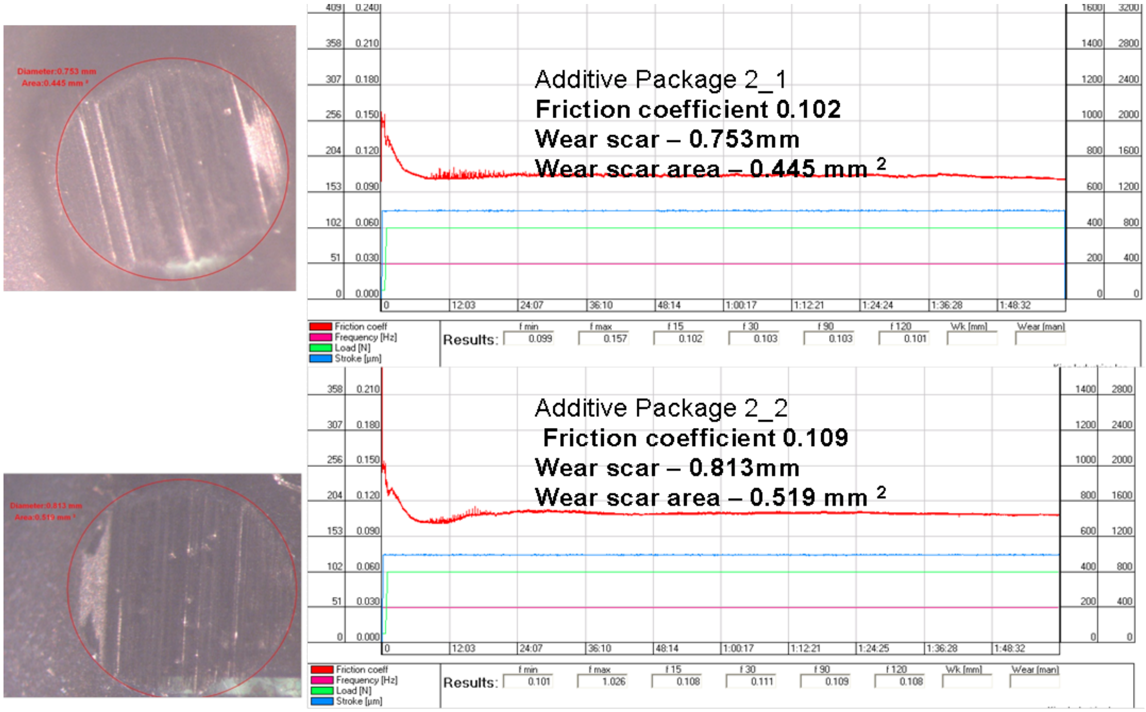

**FIGURE 5.** Coefficient of Friction and Wear Data for PAG Oils

copper corrosion and rust prevention requirement. Development of this package, however, will be lower priority compared to Additive Package 2.

## CONCLUSIONS

- Bench friction and wear tests have showed wear protection capability of PAG oils can be tailored by the choice of base oil chemistry and the anti-wear boost was effective in improving wear performance.
- Industry standard axle level tests and efficiency tests need to be conducted to verify performance improvement due to this technology.

# II.16 Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils

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## Overall Objectives

- Support DOE's mission to increase fuel economy by increasing fuel efficiency of gasoline internal combustion engines
- Develop novel polymers with a hyperbranched architecture to be used as viscosity modifiers (VMs)
- Develop a fundamental understanding of polymer architecture and ability to affect the viscosity of a base oil
- Correlate polarity and friction of carefully designed polymers
- The second phase of the project will focus the synthesis on analogs with built-in polarity which can affect friction
- Evaluate all promising materials at Oak Ridge National Laboratory (ORNL), prior to engine testing
- Based on ORNL's tribological results, refine design strategies and synthetic candidates
- Design and synthesize one compound which has a viscosity index (VI) of 150 or higher

## Fiscal Year (FY) 2014 Objectives

- Establish and acquire VMs to be used as benchmarks
- Synthesize polymers which are soluble in paraffinic base oils
- Establish a testing protocol for synthesized polymers
- Demonstrate proof of concept for hyperbranched polymers by modifying commercial materials, and synthesize in-house hyperbranched or hyperbranched-like polymers
- Evaluate conformational changes of various polymeric architectures as they pertain to viscosity changes, via computations/modeling
- Synthesize a dendronized polymer as a promising hybrid between a comb polymer, known to be a superior VM, and a hyperbranched polymer
- Select three VM candidates synthesized from commercial precursors, via end-capping, for viscosity studies based on molecular weight and end group polarity considerations
- Select three candidates for ORNL rheology/tribology studies, from compounds prepared in-house via polymerization

## FY 2014 Accomplishments

- Unadditized base oils (Group I and Group III) as well as VM benchmarks were obtained from partners and industrial connections
- Established screening protocol (Brookfield viscometer) for VI measurements at 40 and 100°C
- Synthesized several branched and hyperbranched polymers with adequate base oil solubility
- Established collaborations with scientists at Argonne for high-temperature high-shear (HTHS) testing.
- At least one compound synthesized in-house showed improved VI performance over benchmarks or similar performance at a lower concentration
- A variety of base oil-additive blends were sent to ORNL for viscosity testing to confirm performance metrics

## Future Directions

- Explore hybrid structures (comb, branched and star polymers) as well as dendronized polymers as potential next generation additives
- Re-evaluate molecular design targets based on tribological (ORNL) and HTHS (Argonne National Laboratory) data
- Hyperbranched polymer systems will be studied further and novel structural permutations will be investigated to increase their lipophilic (hydrocarbon, non-polar) character

- Discuss with our industrial partner other potential applications for hyperbranched polymers
- Develop structure-property relationships based on the friction data gathered from ORNL
- Continue to increase our industrial connections and strengthen our collaborations for future opportunities
- Demonstrate the value of modeling in predicting viscosity changes of various polymeric architectures

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## INTRODUCTION

The project seeks to increase fuel efficiency by designing and developing compounds, starting at the molecular level, which will improve engine lubrication by selectively controlling the lubricity at working surfaces and viscosity in the bulk fluid within the engine. These two parameters affect the internal friction in the engine. In principle, typical viscosity-improving polymer additives are large, roughly spherical molecules when cold. Upon heating, the polymer uncoils contributing to greater interaction with the base oil, becoming bulkier and more viscous. The dynamic effect of these additives is to reduce the tendency of the base oil to thin as temperature increases, making VMs an essential component for lubricant packages. PNNL will modify hyperbranched polymers, tailoring them by changing the repeat units, terminal groups, and molecular architecture (i.e., from globular to comb-like) to impart desirable changes in viscosity over useful temperature ranges, while ensuring that the resulting additives are compatible with existing lubricant packages for easy introduction to the legacy vehicle fleet. In addition, the hyperbranched polymer structures will inherently contain polar groups known to reduce friction by adhering to metal surfaces.

The project has two components: (i) Design, synthesis, and screening of molecular structures with hyperbranched architectures for proof-of-concept experiments as well as other structures which evolve in the process; (ii) Conduct rigorous friction and viscosity testing of our top candidates, followed by engine tests in a full package formulation. These activities will be led by our partners, Evonik and ORNL.

## APPROACH

The use of hyperbranched polymers, or hyperbranched comb-like hybrids as friction or VM additives for lubricating oils, is a very novel concept. In order to cover a wide structure space and efficiently scope properties, our research was prioritized as follows: (1) Investigate and modify commercial hyperbranched polymers. The modifications involve a simple coupling step to attach polar and non-polar end groups/chains, such non-polar alkyl chains. (2) Synthesize polyesters, poly(amide)amines, and aromatic polyesters, which are not commercially available, and test both the modified and non-modified version of each. (3) Synthesize comb-like hyperbranched polymers.

In the first phase of the project, the synthesis focus was on the modification of commercial hyperbranched polymers by affixing long non-polar chains (C10-C18) expected to provide functionality capable of entanglement, and thus the capability of changing the molecular volume with temperature. However, the results quickly indicated that the polarity of the core could not be overcome, and the approach was modified to generate a hyperbranched structure which contained aromatic esters (HBAE). This led to an interesting study of the effect of the core structure and molecular weight on the ability of the molecule to undergo conformational changes with temperature. Finally, our approach has changed significantly such that lipophilic targets with a moderate degree of branching were chosen for synthesis. More clarifying details are discussed in the following section.

## RESULTS

One of the first priorities that became apparent before any testing could commence, was finding the proper testing matrix, i.e. an unadditized base oil and benchmark additives currently used. This task turned out to be challenging at first, however three base oils and two VMs benchmarks were acquired from partners and industrial connections. Both of our benchmarks, Control 1 and Control 2, are well known and widely used, commercially available VMs. They have similar VIs but different viscosity profiles, in that Control 1 has a significantly higher viscosity at lower temperatures than Control 2, as illustrated in Figure 1, Block 1. Although Control 1 has the highest VI of all the compounds tested in-house and it is still a commodity VM, it is too viscous at low temperatures, and may pose problems during cold operation. A VM which has a moderate VI but displays a low viscosity at 40°C and sub-ambient temperatures (10°C) is potentially beneficial for certain applications, thus in our assessment of materials performance, we have to encompass both the VI and the viscosity profile. The kinematic viscosity (in cSt) measurements of nearly all analogs tested are illustrated in Figure 1, including the unadditized oil and the two benchmarks.

As mentioned in the previous section, our initial efforts involved the functionalization of commercial hyperbranched polymers, such as hydroxyl esters,

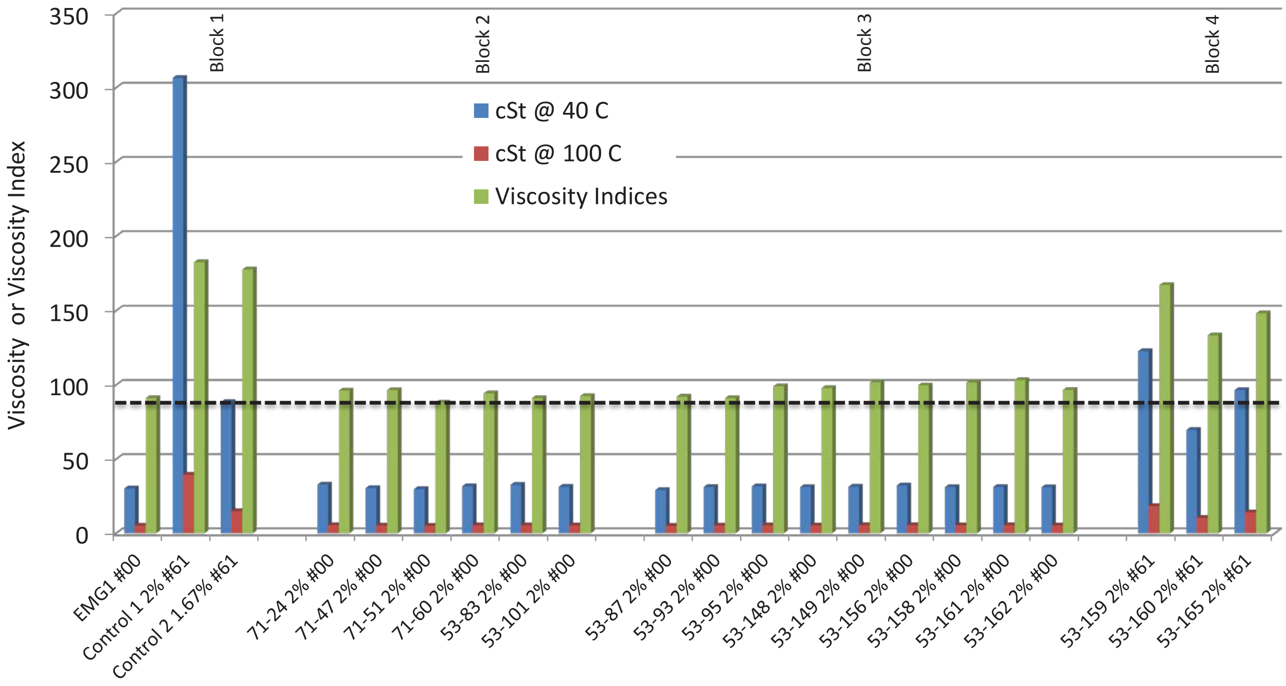

**FIGURE 1.** Kinematic viscosities and viscosity indices of synthesized polymers versus benchmarks: Block 1: benchmarks; Block 2: modified commercial materials; Block 3: series of hyperbranched aryl esters; Block 4: polyethylene-based lipophilic hyperbranched polymers.

polyethylene imine and polyhydroxy esters with long chain hydrocarbons (C16). The resulting compounds, shown in Block 2, Figure 1, had generally an unexciting performance as compared to the benchmarks. The results were attributed to the fact that most of the analogs have a very polar core, and ratio wise, the long chains were not providing enough lipophilicity to make the compounds fully soluble in the base oil. In addition, most of the compounds had a low molecular weight, the highest being around 12 kilodalton (kDa).

A new strategy had to be devised to overcome the very polar hyperbranched cores. A novel design was implemented to increase the non-polar character of the molecule in the form of hyperbranched aryl esters. The internal hydrocarbon chains were going to aid with the oil solubility, while the aromatic ring would provide the much needed thermal stability in a hot engine. We conducted a study based on this design where we varied the length of the internal hydrocarbon chain, the length of the terminal group/chain, as well as degree of polymerization. The study yielded an iteration of several analogs, whose viscosity index measurements are reflected in Block 3, Figure 1. The synthesis is illustrated in Figure 2, together with the proton nuclear magnetic resonance spectroscopy ($^1$HNMR) of the key structural features which were monitored during the polymerization.

The polymerization had to be very carefully monitored, because a high degree of polymerization (repeating units higher than 40 by $^1$HNMR) resulted in a resin, which was completely insoluble in base oil. Figure 1 Block 3 reflects various analogs obtained under different synthetic conditions. Unexpectedly, even relatively low molecular weight materials dissolved with difficulty in base oil at low concentrations (1 and 2% by weight), particularly those containing shorter alkyl chains (HBAE 1 + C12, shown in Figure 2). Gel-permeation chromatography of the analogs revealed that the highest molecular weight compound of the series was around 25 kDa, which is far smaller than either of the benchmarks, both being above 200 kDa. The combination of low solubility with increased molecular weight resulted in a serious limitation of the molecular design.

Once it became clear that the solubility of the materials is a limitation, the focus changed towards building very lipophilic polymers, using non-polar monomers such as ethylene. The general synthetic scheme and structure/topology of hyperbranched polyethylene are illustrated in Figure 3. There are several literature methods for generating hyperbranched polyethylene with controlled topology, as well as incorporating other heteroatoms in the back bone by co-polymerization [1,2]. The original authors even point out the potential of such strategies toward novel viscosity index improvers [3]. A similar strategy was employed here to achieve polymers which are soluble and possess a reasonably high molecular weight. The hyperbranched

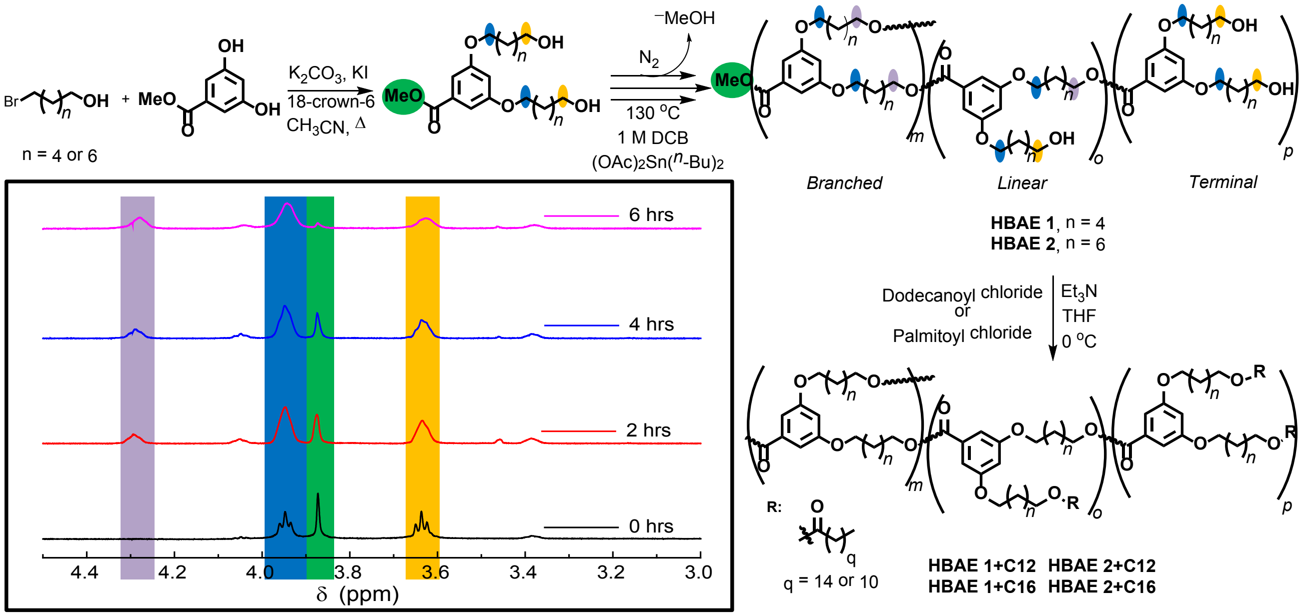

**FIGURE 2.** Synthetic scheme of hyperbranched aromatic ester polymer series and $^1$HNMR of in-progress polymerization.

polyethylenes that were generated explored not only the homopolymer, but a polymer which contains a small percentage of co-monomer, methyl 10-undecenoate, to provide polarity in the molecule as well as a synthetic handle for further modifications. The co-monomer was added in two different ways (at the beginning and at the end of the reaction) to probe the effects of polymer topology on friction behavior. The addition of 5% of co-monomer slowed the reaction and it had a slight negative effect on the VI. This short series suggests that these materials are soluble in base oil at a moderate co-monomer loading, the order of addition of the co-monomer did not affect the VI, however it remains to be seen whether friction performance was affected. Furthermore, it is evident from the data (Figure 1, Block 4) that hyperbranched polyethylene outperforms Control 1 and nearly reaches Control 2 as far as viscosity is concerned, even though the molecular weight is not as high as the benchmarks, at around 80 kDa. Overall, this seems like a very good strategy to obtain good VMs via simple synthetic routes.

Nearly all the compounds presented here were sent to ORNL for tribological measurements, of which the viscosity measurements are complete. The friction tests will reveal the influence of polarity on performance and will enable correlations between friction and polar groups. In parallel, several analogs were sent to Argonne National Laboratory for HTHS testing, which will probe the resistance of these materials to high temperature as well as shear and will provide a better understanding of molecular design requirements to achieve more desirable performance characteristics.

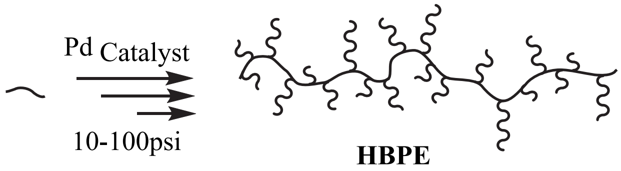

**FIGURE 3.** Hyperbranched polyethylene synthesis; resulting topology varies in the degree of branching depending on the pressure used during the reaction.

## CONCLUSIONS

- Great progress has been made in the development of hyperbranched VMs as well as understanding molecular features that impart solubility and thermoresponsive behavior
- A capability to perform lubricant viscosity measurements was established at PNNL, which was nonexistent nine months ago
- All scheduled tasks were successfully completed, although the first generation of materials did not perform as expected
- The relatively polar hyperbranched systems had both poor solubility in the unadditized oil and coupled with the low molecular weight of the polymer, led to very slight improvements in VI over the base oil
- Challenges were overcome by increasing lipophilicity and molecular weight of the polymers to achieve high VIs at moderate concentrations,

and reasonable viscosities at close to ambient temperatures

- The continued interaction and scientific exchange with our partners (Energetics: Ewa Bardasz and Bruce Bunting; ORNL: Jun Qu; Evonik: David Gray) have had a great impact on the progress of this project

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**1.** Work performed under this project was presented in October 2014 at the STLE Annual Meeting: "*Recent Research Results from the Department of Energy Vehicle Technologies Lubricant Program*." Bruce Bunting, Ewa Bardasz Energetics Incorporated, SMEs, Kevin Stork, U.S. DOE, Technology Manager.

**2.** *Advanced Polymer Design: Application Driven Research*; Presentation by Joshua Robinson at EOU, La Grande, OR.

**3.** *Modified Thermo-Responsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils*; Lelia Cosimbescu*; Joshua Robinson; Priyanka Bhattacharya; Tim Bays; ACS August, 2014 San Francisco, CA, oral presentation,

**4.** *Viscosity Modifiers for Improved Fuel Efficiency*; Joshua Robinson; Priyanka Bhattacharya; Tim Bays; Lelia Cosimbescu*; PNNL Post-Doctorate Research Symposium, Richland, WA, July 30th, 2014, poster presentation.

# II.17 High Efficiency Lubricant Oils and Additives Research

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## Overall Objectives

- Support DOE's mission in increasing fuel economy by increasing fuel efficiency of gasoline internal combustion engines.
- Design and develop multi-functional base oils by incorporating chemical/material functionality responsible for one or more of the properties typically provided by lubricant additives, while maintaining or improving lubricant performance.
- Develop and test novel oil additives that are expected to undergo tribopolymerization to improve fuel economy in gasoline internal combustion engines.
- Conduct fundamental research to support the awarded project on thermoresponsive hyperbranched polymers as viscosity modifiers. This work will provide a fundamental understanding of molecular size changes that occur with temperature.

## Fiscal Year (FY) 2014 Objectives

- Attain one new base oil structure by synthesizing/modifying at least one commercially available feedstock.
- Correlate one or more structural features to one or more properties for at least one new base oil.
- Establish testing protocol for tribopolymers.
- Demonstrate proof of concept for tribopolymerization by duplicating similar results reported in literature.
- Generate one tribological formulation that will reduce friction or wear by 80% versus unadditized oil (using the pin-on-disk method).
- Evaluate various polymeric architectures conformational changes with temperature, as they pertain to viscosity changes, via computations/modeling.
- Conduct dynamic light scattering (DLS) experiments of synthesized viscosity modifier analogs.

## FY 2014 Accomplishments

- A pin-on-disk wear measurement capability has been established at PNNL coupled with a profilometer and software to enable evaluation of wear. This is an important milestone, as the set-up will benefit multiple tasks within the lube projects.
- Initial base oil synthetic strategies led to several candidates.
- Implemented methodology for tribological additive task, and started preliminary tests of known additives.
- Completed initial calculations using model base oil compounds.
- Established collaboration with researchers at Oak Ridge National Laboratory's Small Angle Neutron Scattering facility and a co-authored proposal for beam time at the user facility.

## Future Directions

- Develop a protocol for evaluating new base oils.
- Evaluate at least three synthesized base oils for viscosity, wear and friction against unadditized commercial base oils.
- Develop structure-property relationships based on the series of materials prepared and continue to develop the series of compounds.
- Continue to investigate the potential of tribopolymers as a renewable in-situ additive and expand beyond caprolactams and caprolactones.
- Optimize testing conditions to achieve tribopolymers with known materials.
- Continue to explore conformational and size changes using DLS, diffusion-ordered spectroscopy (DOSY), and small angle neutron scattering (SANS).
- Demonstrate the value of modeling in predicting viscosity changes with temperature of viscosity modifiers.

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## INTRODUCTION

Efforts towards improving lubricant performance at PNNL span various aspects of lubrication, such as developing a synthetic lubricant with built-in functionality to decrease friction (Task 1), developing small molecular additives that undergo tribopolymerization at surfaces under normal engine operation thereby decreasing wear and friction (Task 2), and achieving a fundamental understanding of viscosity modifiers by probing for temperature-dependent molecular changes via modeling, DLS, SANS and DOSY (Task 3).

**Task 1:** Petroleum-derived base oils are to date the most efficient and reliable building blocks for lubricants. Their lack of chemical reactivity limits susceptibility to degradation in the harsh conditions encountered by engine lubricants, but also necessitates that additional desirable lubricant properties are added component by component, as opposed to varying the chemical nature of the base oil. These additives are numerous (10-15) and can be up to 30% by weight of the finished lubricant. To offset the disadvantages associated with lubricant additives, it is desirable to build a base oil which incorporates one or more additive properties into the base oil molecular structure.

**Task 2:** Additives are still a major component of the lubricant performance. A major challenge with existing oil additives is that they degrade over time, and are unable to maintain performance equivalent to fresh additive, i.e., until the next oil change. Secondly, subsequent portions of fresh additives are not able to restore performance to the original state. The reason for this is that used oil has a very different composition and impurity profile than “fresh” oil, and these impurities and degradation products typically interfere with fresh additive performance. Therefore the need for novel approaches and additives still exists.

**Task 3:** To date there are no published, fundamental studies that provide insight into the changes in molecular conformation that occur as viscosity modifiers reduce decreases in viscosity with increasing temperature, though there are many reasonable claims based on empirical data. Though it is a challenging task to glimpse into temperature-induced changes at the molecular level, DLS, SANS, DOSY and modeling will be applied to study such events.

## APPROACH

**Task 1:** Typically, petroleum-based oils are the desired base oil building blocks due to their thermal and oxidative stability. However, from a synthetic perspective, such compounds are too inert to easily affect a chemical transformation. The main strategy proposed is the modification of vegetable oils or other easily accessible synthetic oils to obtain synthetic polyesters. Synthetic polyesters are amenable to further modifications, as the core of our functional base oil. These materials were chemically modified to introduce desired functionality, screened at PNNL, and ultimately will be sent to Oak Ridge National Laboratory for further characterization.

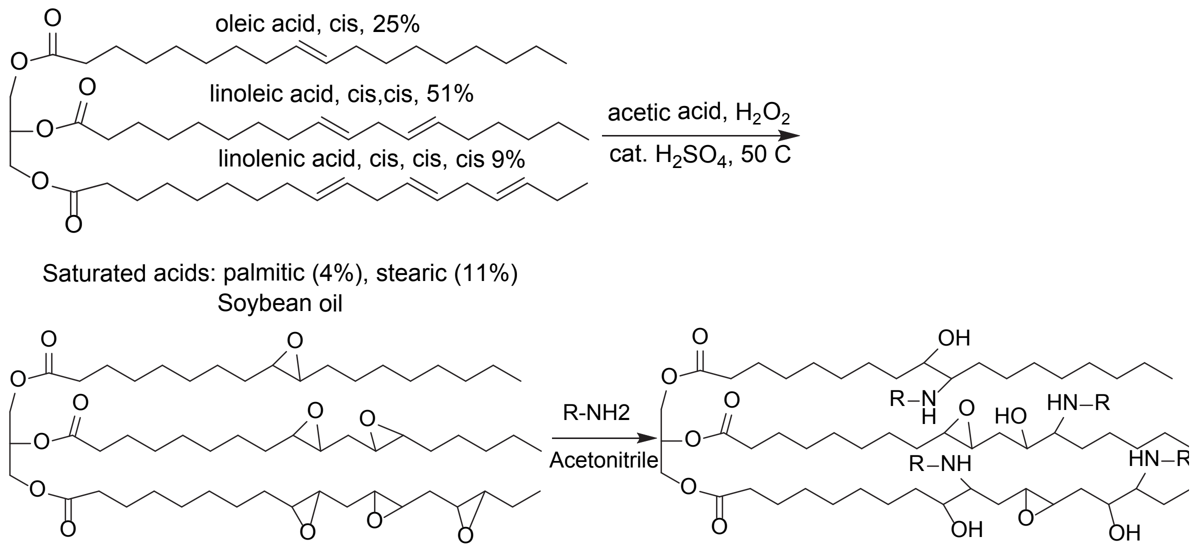
**Task 2:** Tribopolymerization is an advanced technology that uses monomers to create continually renewing films directly on the surfaces that require lubrication, such as the moving parts of an engine. This approach has been sparsely explored and has shown promising results in the past, in particular by one group at Virginia Polytechnic Institute led by Michael Furey [1,2]. We propose to extend Furey’s concept, using a ring opening polymerization of monomers such as lactones, lactams, or anhydrides to continually generate an active polymer at the working surface. During engine operation, the monomers will polymerize due to frictional heating at the metal surfaces.

**Task 3:** Initial fundamental modeling studies of viscosity modifiers will evolve to modeling studies of base oils. It has been shown previously that molecular-scale simulations can be used to predict bulk lubricant properties if the model accurately describes molecular structures and interaction energies. In parallel, proof of concept measurements will be conducted to probe for a molecular expansion of polymeric additives with heat, from room temperature to 100°C or as high as the measuring equipment will allow (DLS, SANS and DOSY). Data that clearly suggests an increase in size indicative of an uncoiling or expansion of the structure with heat, from a collapsed conformation, is considered a positive result.

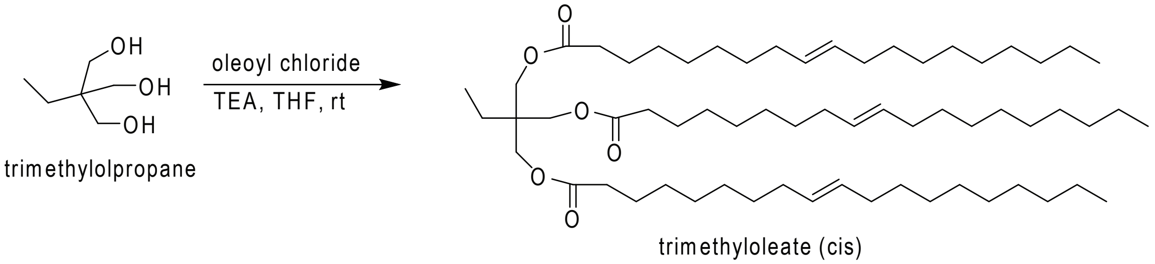
## RESULTS

**Task 1:** In order for any synthetic oil to be implemented, it has to make financial sense, so the oils have to have a cheap, commercially available source of starting materials to be able to stay competitive with any other petroleum-based oils. One of the strategies to this end, is the use of vegetable oil as a starting material, such as a soybean oil. Vegetable oils can be modified via epoxidation and subsequent ring opening of the oxirane ring to form alcohols, and amino alcohols, which can be further reacted to result in amides and esters. This transformation is illustrated in Scheme 1.

Similarly, an inexpensive poly alcohol (trimethylol propane) was used as a starting material. While this approach was previously reported [3], it serves as a flexible starting point for the synthesis of analogous triesters, as illustrated in Scheme 2.



**SCHEME 1.** Illustrative Chemical Transformation of Soybean Oil to Attain a Multi-Functional Base Oil



**SCHEME 2.** Synthesis of Polyester Base Oil

The compounds prepared via the two approaches were characterized by $^1$H nuclear magnetic resonance and their lubricant properties will be further evaluated (viscosity and pin-on-disk measurements). Both approaches including slight variations resulted in products which ranged in viscosity from oils to resins at room temperature, and proved beneficial in achieving polyesters with dual functionality, including polar groups that are expected to adhere to surfaces and lower friction.

**Task 2:** Initially, the additives were tested at room temperature only, similarly to the published reference, under low load/force conditions, 5 N, 10 N, 15 N, 20 N, 30 N to probe for an effect. The results are reported in Table 1 and Figure 1.

The proof of concept measurements consisted of testing a reported additive in a lubricant. Kadjas et al. reported caprolactam as an effective additive that underwent tribopolymerization at room temperature in

**TABLE 1.** Groove Areas for Four Additive Formulations (6B-6E) and the Baseline Group I oil (6F)

| | | | Ultrasonic cleaned | | | |
|---|---|---|---|---|---|---|
| **Groove #** | **61828-6B1** | **61828-6C1** | **61828-6C1u** | **61828-6D** | **61828-6E** | **61828-6F** |
| 1 | 549 | 744 | 783 | 592 | 619 | 252 |
| 2 | 364 | 517 | 503 | 370 | 445 | 137 |
| 3 | 206 | 279 | 282 | 317 | 334 | 94 |
| 4 | 106 | 204 | 209 | 196 | 202 | 51 |
| 5 | 44 | 98 | 110 | 84 | 123 | 20 |

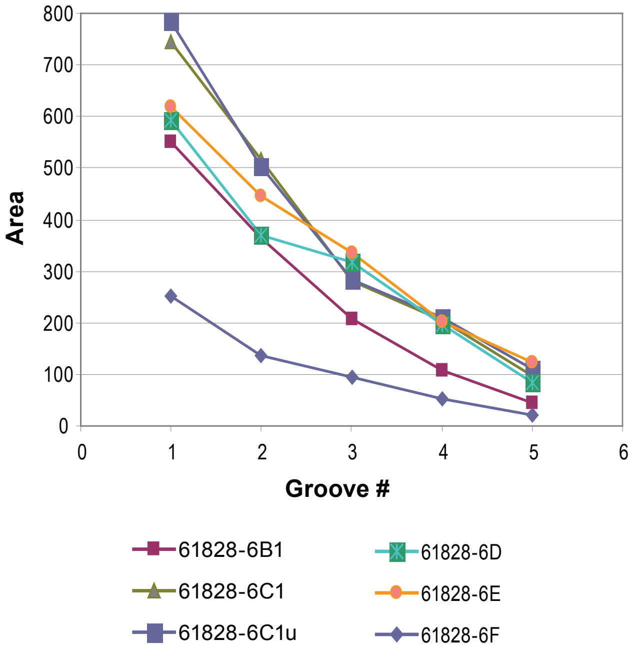


**FIGURE 1.** Wear Evaluation of Additive Formulations versus Group I Base Oil at 5 N (Groove 5), 10 N (Groove 4), 15 N (Groove 3), 20 N (Groove 2), 30 N (Groove 1)

hexadecane [1]. However, hexadecane is a poor lubricant and by itself provides no surface lubrication at all, which is not a realistic testing condition. Instead, our testing matrix was a Group I, Exxon-Mobil base oil. Unexpectedly, all additive formulations had a negative impact on the base oil, including the previously reported additive (6B and 6E). A path forward was devised to address the discrepancy and investigate the value of such technology: the matrix oil will be changed to an inferior mineral oil, the temperature and the force load will be increased and the effect of the additives re-evaluated. Furthermore, other tribological monomers will be explored.

**Task 3:** DLS is a physical technique that can be used to determine size distribution profile of small particles or polymers in solution. The monitoring of change in size of polymers with increasing temperatures has not been attempted before, and it is not without challenges. Factors such as polymer aggregation, fluctuations in diffusion and density with temperature, deviations from the spherical model particularly for polymers, make the data interpretation challenging at the very least. The test subjects for this task were polymers developed under a different project which are shown to be effective as viscosity modifiers, at various degrees and have a viscosity index in Group I oil in the following order: HBPE1>HBPE2>HBAE.

The data (Figure 2) shows that there is no expansion of HBAE with temperature and a small expansion of the HBPE-1 and HBPE-2 polymers with temperature. Although the effect is small, the same trend is indeed observed, and this data indicates that this technique can be used to potentially predict viscosity changes with temperature.

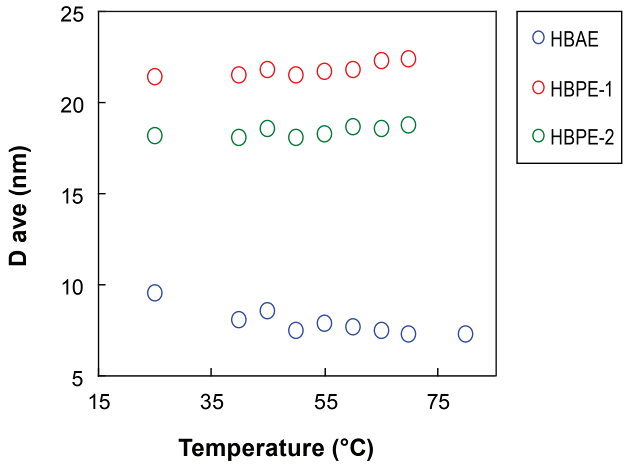


**FIGURE 2.** Average Diameters of 1% Polymers in Decane Determined by DLS as a Function of Temperature

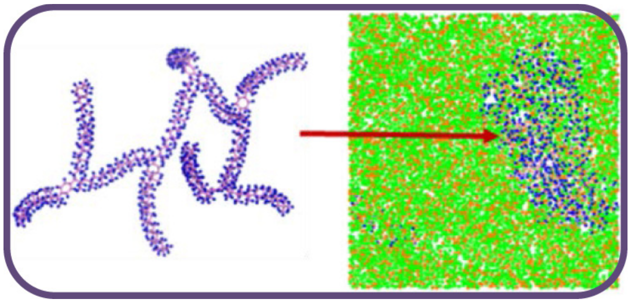


**FIGURE 3.** Simulation Structure of a Hyperbranched Polyisobutylene Polymer Surrounded by 9-Octylheptadecane

In the first stage of the project, fully atomistic simulations are being used to model representative viscosity index improvers, including linear, branched, star and hyper-branched structures. Initial model compounds are polyisobutylene polymers with 100 repeating units of different architectures and 9-octylheptadecane (9C) as the base oil mimic. A simulation structure for a hyperbranched polymer is illustrated in Figure 3.

Several parameters are used to evaluate changes in polymer size with temperature, such as radius of gyration (dimension of a polymer chain), Lmax (length of the major axis of an ellipsoid) and the aspect ratio (ratio of the length of the largest and smallest dimension). These parameters are reported as a percent change from a low temperature (20°C) to a high temperature (200°C), to maximize the differences. A large amount of data was generated for the four types of architectures including distribution profiles and average conformations. Determining which values are representative of realistic scenarios, is still work in progress.

## CONCLUSIONS

- A pin-on-disk wear measurement capability has been established at PNNL coupled with a profilometer and software to enable evaluation of wear. This is an important milestone, as the set-up will benefit multiple tasks within the lube projects.
- A large series of polyesters were synthesized in an effort to achieve a multi-functional base oil. Five of the compounds are oils at room temperature and their evaluation on wear/friction will commence soon.
- From a molecular design perspective, several empirical guidelines have taken shape: unsaturation and lack of symmetry are desirable features.
- Although the initial tribological investigations of additives were less than desirable, this is actually an opportunity to optimize our testing protocol of such additives, as well as investigate other tribo polymers.
- DLS measurements indicate a promising potential for detecting molecular size increase of polymers with temperature, in nonpolar media, especially those designed for lubricant applications.
- Preliminary modeling of various polymeric architectures in an oil-like matrix as a function of temperature, provides an insight into the molecular conformations and size, and hence viscosity changes with temperature.

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**2.** A critical assessment of tribopolymers as antiwear mechanism; MJ Furey; C Kajdas; GJ Molina, World Tribology Conference 2005; WTC2005-63308 (p621-622).

**3.** (a) Abd Hamid, H.; Yunus, R.; Rashid, U.; Choong, T.S.Y.; Al-Muhtaseb, A.H., Synthesis of palm oil-based trimethylolpropane ester as potential biolubricant: Chemical kinetics modeling. Chemical Engineering Journal 2012, 200, 532-540; (b) Abidakun, O.A.; Koya, O.A., Dika nut oil as base oil for lubricants - effect of processing conditions on physicochemical properties. Lubrication Science 2013, 25 (1), 29-38; (c) Chang, T.S.; Masood, H.; Yunus, R.; Rashid, U.; Choong, T.S.Y.; Biak, D.R.A., Activity of Calcium Methoxide Catalyst for Synthesis of High Oleic Palm Oil Based Trimethylolpropane Triesters as Lubricant Base Stock. Industrial & Engineering Chemistry Research 2012, 51 (15), 5438-5442; (d) da Silva, J.A.C.; Habert, A.C.; Freire, D.M.G., A potential biodegradable lubricant from castor biodiesel esters. Lubrication Science 2013, 25 (1), 53-61.

## FY 2014 PUBLICATIONS/PRESENTATIONS

**1.** Modeling work performed under this project was presented in October 2014 at the STLE Annual Meeting: “Recent Research Results from the Department of Energy Vehicle Technologies Lubricant Program”. Bruce Bunting, Ewa Bardasz Energetics Incorporated, SMEs, Kevin Stork, U.S. DOE, Technology Manager.

# III. Fuel Property Effects on Advanced Combustion Regimes

Fuel properties can be leveraged to expand the operating range of kinetically controlled combustion regimes in engines. These activities examine both high reactivity fuels (diesel-like) and low reactivity fuels (gasoline-like) in advanced compression ignition operation for low emissions and high efficiency. Both reactivity-controlled compression ignition (RCCI) with two fuels and single fuel compression ignition applications were examined.

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# III.1 Advanced Fuels Enabling Advanced Combustion in Multi-Cylinder Engines

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## Overall Objectives

- Investigate the opportunities and challenges that advanced 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) 2014 Objectives

- Demonstrate the potential of biofuels to expand the drive cycle coverage of reactivity controlled compression ignition (RCCI) combustion using vehicle system simulations with experimental engine data (Q2 Joule Milestone)
- Conduct apples-to-apples comparison of dual-fuel RCCI and single-fuel gasoline compression ignition (GCI) with the premixed RCCI piston

## FY 2014 Accomplishments

- Attained the 2014 technical target of demonstrating biodiesel blends allowed an improvement in RCCI operating range allowing for a simulated 75% coverage of the federal city and highway driving cycles
- Comparison of RCCI with conventional fuels and GCI with a 68 Research Octane Number (RON) gasoline for efficiency, load expansion and controllability on premixed pistons

## Future Directions

- Continue RCCI and single-fuel low-temperature combustion experiments with a variety of fuels on the stock diesel piston including transient effects
- 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 (i.e. ethanol and biodiesel)
- 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 GCI as compared to RCCI on the same engine, with the same hardware over a variety of gasoline-range fuels that seem well suited for GCI
- Identify alternative fuels that may have high enabling potential for advanced combustion

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## 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 duration and phasing. Research from ORNL has demonstrated RCCI sensitivity to fuel properties especially with low-load and high-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 and particulate matter 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. Other single-fuel advanced combustion modes such as GCI with gasoline range fuels also have shown potential to improve fuel efficiency and lower oxides of nitrogen and particulate matter emissions. How these approaches compare to RCCI on the same engine hardware is not clearly understood. 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.

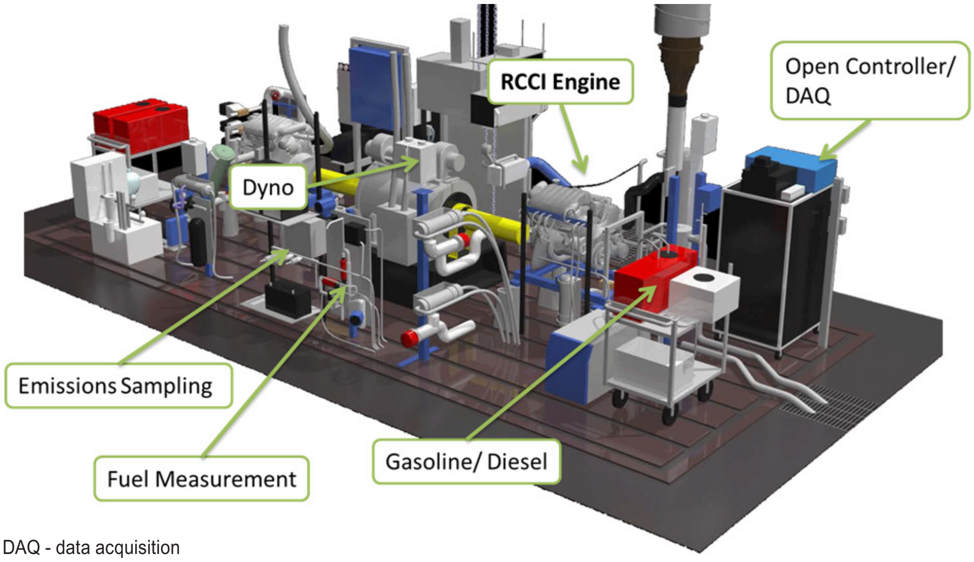
## APPROACH

For these activities, a light-duty multi-cylinder engine laboratory is in operation based on a General Motors 1.9-L common-rail turbocharged diesel in both the stock configuration and with pistons modified for RCCI operation. The research 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 multi-cylinder engine advanced combustion platform capable of RCCI or GCI is shown in Figure 1. A flexible microprocessor-based control system allowed for control over both fueling systems and complete authority over engine operating parameters allowing operation of both single-fuel and dual-fuel advanced combustion modes. 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

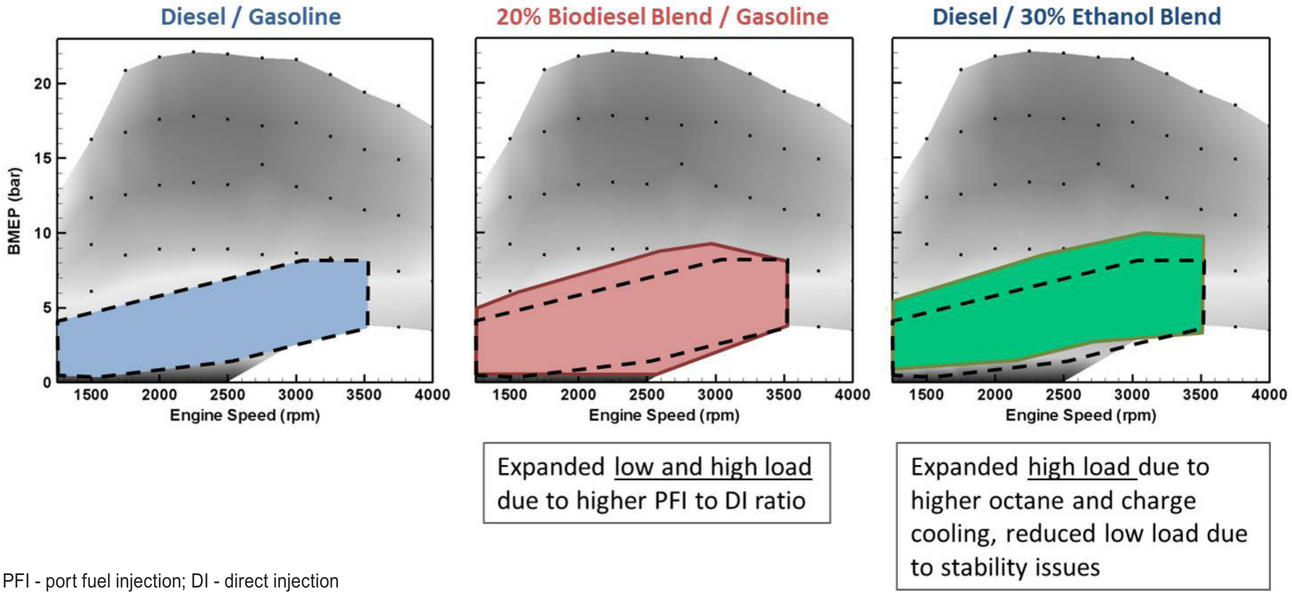
The primary focus during FY 2014 was meeting the JOULE level milestone of demonstrating 75% coverage of the non-idling city and highway drive cycles for RCCI allowed by unique properties of renewable fuels. This investigation aimed to estimate the drive-cycle coverage improvements through vehicle systems simulations using an experimental RCCI engine map created using certification gasoline and 20% biodiesel in diesel fuel (B20). To evaluate improvement in drive-cycle coverage, mapping data used to perform vehicle system simulations in Autonomie allowing for estimation of increases in drive-cycle coverage in terms of miles of drive cycle. A RCCI/diesel multi-mode strategy used for engine speed and load points outside the RCCI coverage from the current engine map. The vehicle systems simulation results showed greater than 75% drive cycle coverage with RCCI over the city and highway drive cycles with B20 and gasoline multi-mode operation which allowed an optimized transmission shifting schedule. This represents a 14% improvement over the city drive cycle coverage allowed with biodiesel as compared to RCCI with gasoline and diesel fuel. A revised RCCI map that used 30% ethanol in gasoline and diesel fuel did allow for high-load expansion at the expense of low-load operability which lowered the drive-cycle coverage as shown in Figure 2.

The secondary focus was experiments on non-currently available gasoline range fuels to enable GCI techniques (shown in Figure 3) for comparison to RCCI. Single-fuel GCI with a gasoline-range fuels were compared to dual-fuel RCCI on the ORNL RCCI multi-



DAQ - data acquisition

**FIGURE 1.** Multi-Cylinder Advanced Combustion Engine Cell for RCCI or GCI

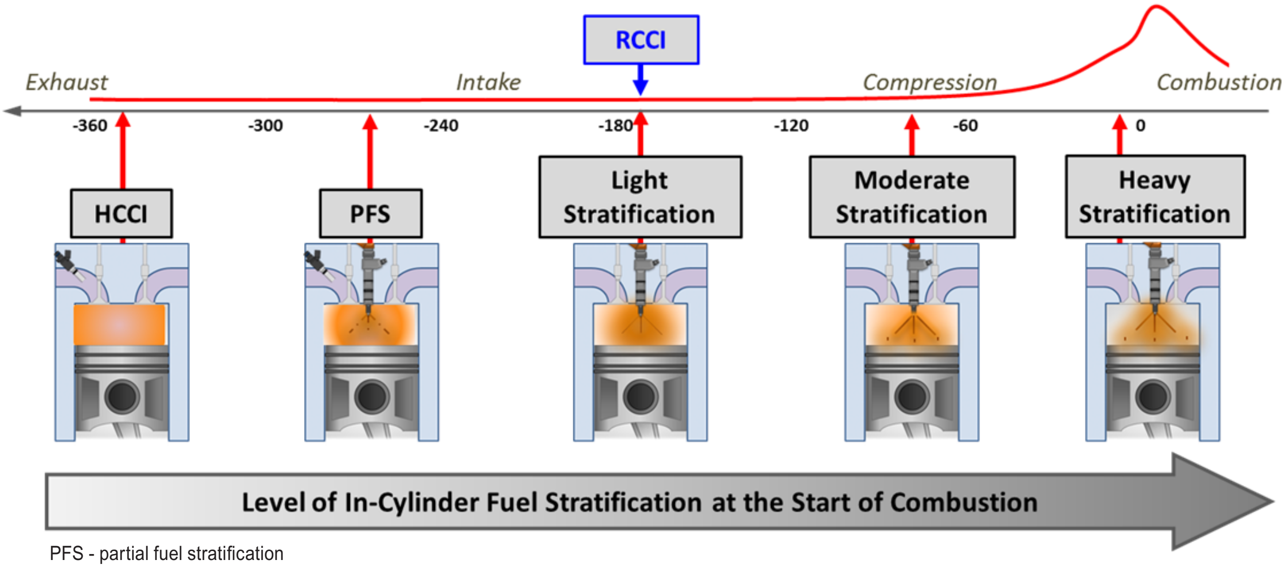


Expanded low and high load due to higher PFI to DI ratio

Expanded high load due to higher octane and charge cooling, reduced low load due to stability issues

PFI - port fuel injection; DI - direct injection

**FIGURE 2.** Fuel Effects on RCCI Engine Map Load Range Affecting Drive Cycle Coverage



PFS - partial fuel stratification

**FIGURE 3.** GCI Spectrum Based on Stratification (level of premixedness)

cylinder engine setup for an apples-to-apple comparison of RCCI and GCI on the same base GM 1.9-L diesel engine with pistons designed for premixed combustion concepts. The base fuel for GCI was a 68 RON fuel which is of current interest to community. A majority premixed low temperature GCI strategy was identified and a detailed parametric study was completed focusing on operating conditions on pilot injection timing as shown in Figure 4. Specifically the paper explored the effect of sweeping the direct-injected pilot timing from -91° to -324° after top-dead center (ATDC), which is just after the exhaust valve closes for the engine used in this study. During the sweep, the pilot injection consistently contained 65% of the total fuel (based on command duration ratio), and the main injection timing was adjusted slightly to maintain combustion phasing near top dead center. The study was conducted at a fixed speed/load condition of 2,000 rpm and 4.0 bar brake mean effective pressure. The pilot injection timing sweep was conducted at different intake manifold pressures, swirl levels, and fuel injection pressures. The effect of boost on brake thermal efficiency highlighting the effect of pumping losses is shown in Figure 4. A joint paper with Chevron was authored covering the majority-premixed low-temperature GCI

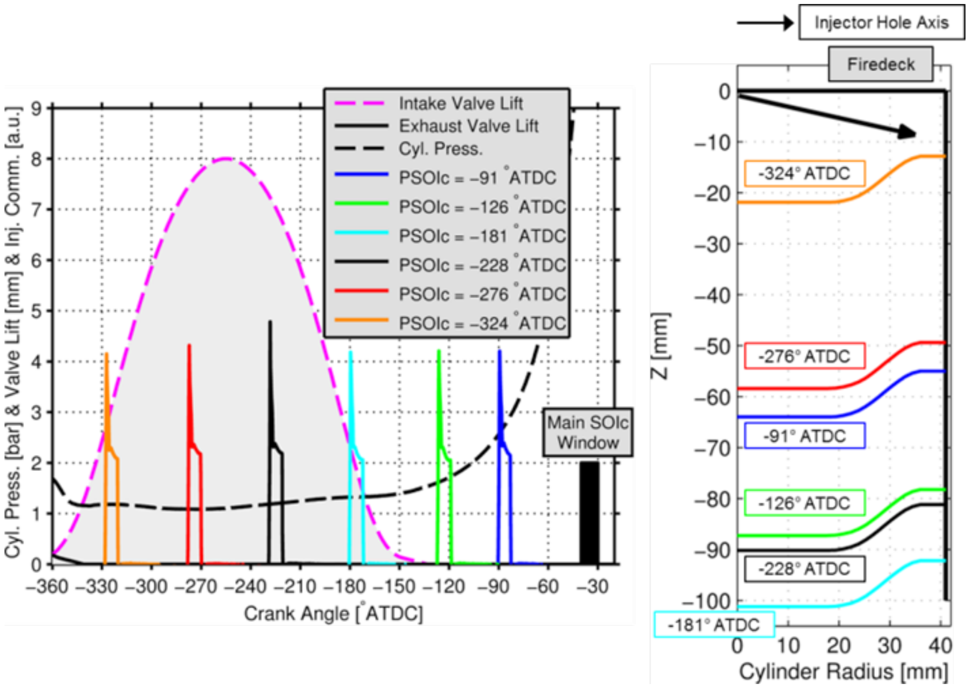
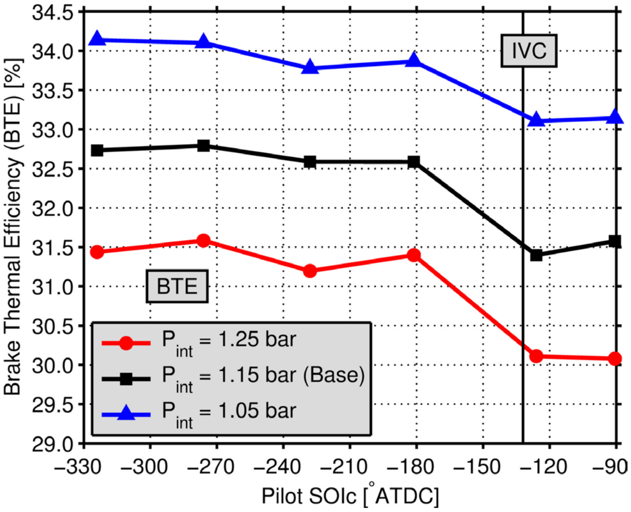


**FIGURE 4.** Illustration of the Relationship between Pilot Start of Injection (SOI) Timings and the Intake Valve Lift; Right: Injector Hole Spray Axis and Piston Locations for the Pilot Injection Timings



IVC - intake valve closing

**FIGURE 5.** Relationship between Boost Level and Brake Thermal Efficiency for GCI as a Function of Pilot Timing

experiments with a 68 RON gasoline-range fuel. The next step in the project is to perform GCI experiments with the stock piston. The findings on the stock piston GCI experiments will help determine which piston is used for the complete RCCI-GCI comparison with the suite of gasoline range fuels provided by Chevron. This work was highlighted in a number of ORNL presentations listed in the publications section.

## 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. Both RCCI and GCI with the 70 RON gasoline-range fuel were shown to achieve higher than diesel brake thermal efficiency at the 2,000 rpm, 4.0 bar brake mean effective pressure point with significantly increased CO and hydrocarbon emissions compared to diesel combustion. Initial comparisons between RCCI and combustion similar to partially premixed 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 GCI on the same engine with the same production-viable hardware.

## FY 2014 PUBLICATIONS/PRESENTATIONS

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**2.** Wagner R., Curran, S., and Green, J., "Global Fuel and Combustion Opportunities for Future Internal Combustion Engines" SAE 2014 Energy Savings & Emission Reduction Forum, Nov 5, 2014 Shanghai, China.

**3.** Dempsey, A.B., Curran, S.J., Wagner, R.M. and Cannella, W., "Effect of Premixed Fuel Preparation for Partially Premixed Combustion with a Low Octane Gasoline on a Light-Duty Multi-Cylinder Compression Ignition Engine," Paper No. ICEF2014-5561,ASME 2014 Internal Combustion Engine Division Fall Technical Conference. + Presentation

**4.** Curran, S., et al., "Advanced Combustion Engines Technology Analysis and Evaluation," DOE VSST Deep Dive Program Review, Oct, 2014 Golden, CO.

**5.** Curran, S.J., et al, "Emission Challenges and Opportunities for Multi-Cylinder RCCI on a Light-Duty Diesel Engine," Presentation, 5th International CTI Conference: Emissions Challenges Troy, MI: Sept 2014). [Invited]

**6.** Dempsey, A.B., et al., "Effect of First Injection Timing on LTC Gasoline Compression Ignition Using a Low Octane Fuel," Presentation, Advanced Engine Combustion Program Review (Southfield, MI: Aug 2014).

**7.** Curran, S.J. et al," Fuel Economy Estimates of RCCI/Diesel Multi-Mode Operation Using Vehicle System Simulations," Presentation, Advanced Engine Combustion Program Review (Southfield, MI: Aug 2014).

**8.** Wagner, R., et al., "Next generation combustion engines and future fuel opportunities," Technical Workshop on Sustainable Fuels: Production & Combustion. University of Alabama, July 2014. [Invited]

**9.** Wagner, R., Curran, S., and Szybist, J., "Transitioning advanced combustion concepts to multi-cylinder engines," 36th Task Leaders Meeting, International Energy Agency, Energy Conservation and Emissions Reduction in Combustion, Stavanger, Norway, 2014.

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

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## 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 accurate, rapid, and cost-effective computational engine optimization for evolving fuels
- Unbiased guidance to stakeholders regarding which emerging fuel/combustion-strategy combinations are most promising

## Fiscal Year (FY) 2014 Objectives

- Formulate and blend a set of diesel surrogate fuels exhibiting different levels of accuracy in matching the compositional characteristics of a single real-world target fuel (i.e., different "compositional fidelities"), for testing in engine and combustion-vessel experiments as well as computational fluid dynamics (CFD) simulations.
- Evaluate the combustion performance of methyl decanoate (MD), an "optimal" biodiesel component, in mixing-controlled combustion experiments in an optical engine.
- Develop and employ a novel laser-induced incandescence (LII) technique to better understand and quantify fuel effects on the production, oxidation, and distribution of soot within the combustion chamber.

## FY 2014 Accomplishments

- Co-led a U.S./Canadian team of researchers under the auspices of the Coordinating Research Council in formulating and blending a set of diesel surrogate fuels with different compositional fidelities relative to a single target fuel.
- Conducted optical-engine experiments on MD in a mixing-controlled combustion mode, showing that this biodiesel component can effectively eliminate engine-out soot emissions.
- Developed and applied a new LII imaging technique to show the distribution of soot in almost the entire region above the piston bowl throughout the expansion stroke, and used the images to estimate the total mass of in-cylinder soot as a function of crank angle.

## Future Directions

- Conduct engine tests on a target #2 diesel fuel and the set of corresponding diesel surrogate fuels described in this report to determine the level of surrogate-fuel compositional fidelity required to adequately match the target-fuel combustion performance.
- Compare the combustion performance of MD to that of an ether/diesel-fuel blend with similar properties at injection pressures up to 2,400 bar, to determine how oxygenate molecular structure affects the ability of a fuel to mitigate in-cylinder soot formation.
- Assess the efficacy of injecting fuel through in-cylinder ducts as a means to enhance mixing rates and mitigate in-cylinder soot formation, to enable the deployment of less-expensive fuels and exhaust-gas aftertreatment systems.

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## INTRODUCTION

A primary objective of the DOE Fuel & Lubricant Technologies Program is to overcome technical barriers to the utilization of new renewable and unconventional fuels in advanced reciprocating engines. This project directly supports that objective by providing an enhanced understanding of the fundamental mechanisms by which fuel composition affects engine efficiency and emissions, as well as high-quality data for the assessment and improvement of CFD simulations. The three main tasks completed in FY 2014 contributed to this enhanced understanding and experimental database.

The first task involved the formulation and blending of a set of diesel surrogate fuels for engine and combustion-vessel testing. Surrogate diesel fuels, being simpler representations of real-world diesel fuels, are of interest because they can provide a better understanding of fundamental fuel composition and property effects on combustion and emissions-formation processes. In addition, the application of surrogate fuels in CFD simulations with accurate vaporization, mixing, and combustion models could revolutionize future engine designs by enabling computational optimization for evolving real fuels [1]. The second task involved engine testing of MD combustion. MD is in some sense an optimal biodiesel component because it has excellent oxidative stability, good cold-flow performance, and a more desirable boiling point than the methyl esters in biodiesels produced from soybeans or rapeseed [2]. The third task involved the development and application of a novel experimental technique to measure in-cylinder soot. Soot is second only to carbon dioxide as a climate-forcing species [3], is toxic to humans, requires expensive aftertreatment devices for mitigation, is difficult to model accurately in CFD simulations, and its levels in engine exhaust can be strongly affected by fuel composition (as is evident from comparisons between MD and a hydrocarbon diesel fuel shown in Figure 2).

## APPROACH

In the first task, the principal investigator co-led Coordinating Research Council Project AVFL-18a that formulated, blended, and is in the process of testing four #2 ultra-low-sulfur diesel (ULSD) surrogate fuels. This constituted a large team effort, requiring close collaboration among approximately a dozen research groups in the U.S. and Canada. In the second task, the combustion performance of MD was studied in the optical engine at two fuel-injection pressures and three intake-oxygen mole fractions ($X_{O2}$), and the results compared to those for an emissions-certification #2 ULSD fuel, denoted CF. In the third task, a new LII diagnostic was developed and evaluated at three $X_{O2}$ levels using CF as the baseline hydrocarbon fuel.

## RESULTS

The surrogate-development task began with characterization of the CF target-fuel composition using new two-dimensional gas chromatography techniques developed by Rafal Gieleciak and co-workers at CanmetENERGY [4]. Based on this detailed compositional information, 13 representative "palette" compounds were selected for formulation of the surrogate fuels. Sources for these ≥98%-purity, <15-ppm-sulfur compounds were identified, including commercial procurement, custom synthesis, and purification. As needed, the ignition qualities of certain palette compounds were measured by Matt Ratcliff's group at the National Renewable Energy Laboratory, and fundamental thermo-physical properties were measured and modeled by Tom Bruno's group at the National Institute of Standards and Technology. The four surrogate fuels were then formulated using a regression model developed by Marcia Huber at the National Institute of Standards and Technology. The model uses a methodology created in an earlier phase of this project that strives to simultaneously match the mole fractions of different carbon-bond types (as determined by nuclear magnetic resonance spectroscopy); ignition quality; volatility; and density of the target fuel [1]. The extents of carbon-bond type matching for the simplest and most complex surrogates are shown in Figure 1. Small batches of the surrogates were created to assess blending-model accuracy and to identify any potential problems with the surrogates before larger batches were blended. It was found that oxidation-inhibiting and lubricity-improving additives would be required. Surrogate fuel batches of sufficient volume to enable engine and combustion-vessel testing were then blended and additized by Bill Cannella's group at Chevron and distributed to the Army Research Laboratory, National Research Council Canada, and Sandia National Laboratories for testing in FY 2015.

The second task evaluated the combustion performance of MD [5] and its potential to eliminate the production of in-cylinder soot by achieving "leaner lifted-flame combustion," i.e., equivalence ratios at the flame lift-off length, $\phi(H)$, of two or less [6]. As shown in Figure 2, MD has effectively zero smoke emissions for the three $X_{O2}$ levels and two injection pressures studied, a dramatic reduction relative to the CF hydrocarbon reference fuel. While these results are encouraging, in-cylinder imaging revealed that MD did not enable the achievement of leaner lifted-flame combustion, as evidenced by $\phi(H)$ values greater than two and low but finite levels of spatially integrated natural luminosity (i.e., incandescence from hot soot) for MD, as shown in Figure 3.

In the third task, an LII technique featuring a vertically oriented and vertically propagating laser

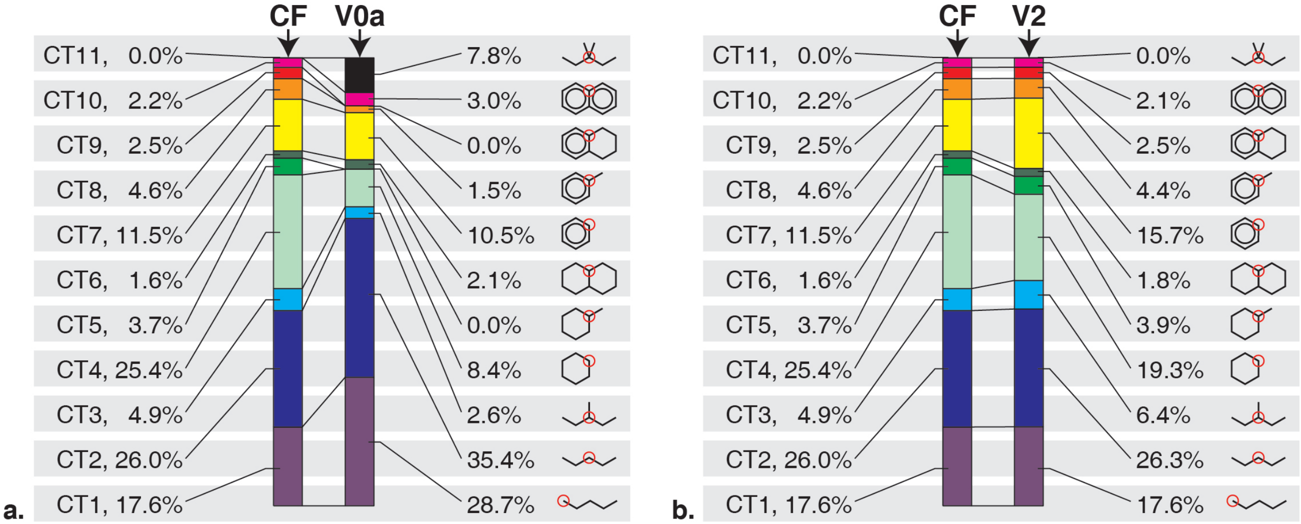

**FIGURE 1.** Mole fractions of the 11 carbon-bond types (CTs) in the CF target fuel and selected surrogate fuels. Each gray horizontal bar in the background corresponds to a different numbered CT shown by the red circle in the structural diagram on the right. **a**. Generally poor matching is observed between the target fuel and the simplest surrogate, V0a, which contains only four palette compounds. **b**. Significantly improved matching is evident for the most complex surrogate, V2, which contains nine compounds.

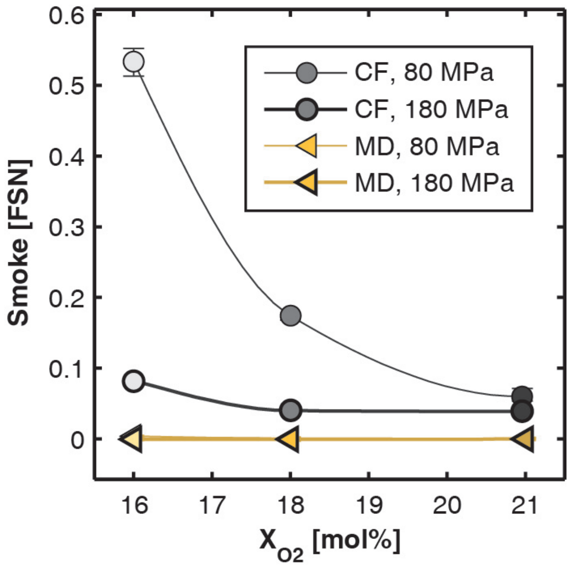

**FIGURE 2.** Engine-out smoke emissions (filter smoke number, FSN) as a function of intake oxygen mole fraction ($X_{O2}$) for methyl decanoate (MD) and diesel certification fuel (CF) at two injection pressures and three dilution levels. Smoke emissions for MD at both injection pressures are effectively zero and thus appear as a single flat line.

sheet was developed and applied at three different $X_{O2}$ conditions [7]. The technique allows the visualization of in-cylinder soot distributions in almost the entire volume above the piston bowl throughout the expansion stroke, an example of which is shown in Figure 4. The diagnostic also can be used to estimate the total mass of in-cylinder soot as a function of crank angle. Neither of these capabilities was previously available. Total in-cylinder soot mass estimates for the three studied dilution levels are shown in Figure 5. Interestingly, the estimated total in-cylinder soot mass increases as long as heat release is occurring. In other words, net soot oxidation does not exceed net soot production until after the end of primary heat release, and there is no quasi-steady period for soot under the investigated conditions.

## CONCLUSIONS

- Four diesel surrogate fuels were formulated and blended, featuring varying degrees of compositional fidelity relative to the CF target fuel. The surrogate fuels will be used to determine the compositional properties required to adequately match the combustion performance of CF.
- Optical-engine experiments show that the "optimal" biodiesel compound MD can effectively eliminate engine-out soot emissions, but this is due to complete soot oxidation rather than the prevention of in-cylinder soot formation by the achievement of leaner lifted-flame combustion.
- A new LII diagnostic was developed to view the soot distribution in almost the entire region above the piston bowl, and to estimate the entire mass of in-cylinder soot as a function of crank angle. These previously unavailable capabilities are critical for assessing the accuracy of CFD simulations.

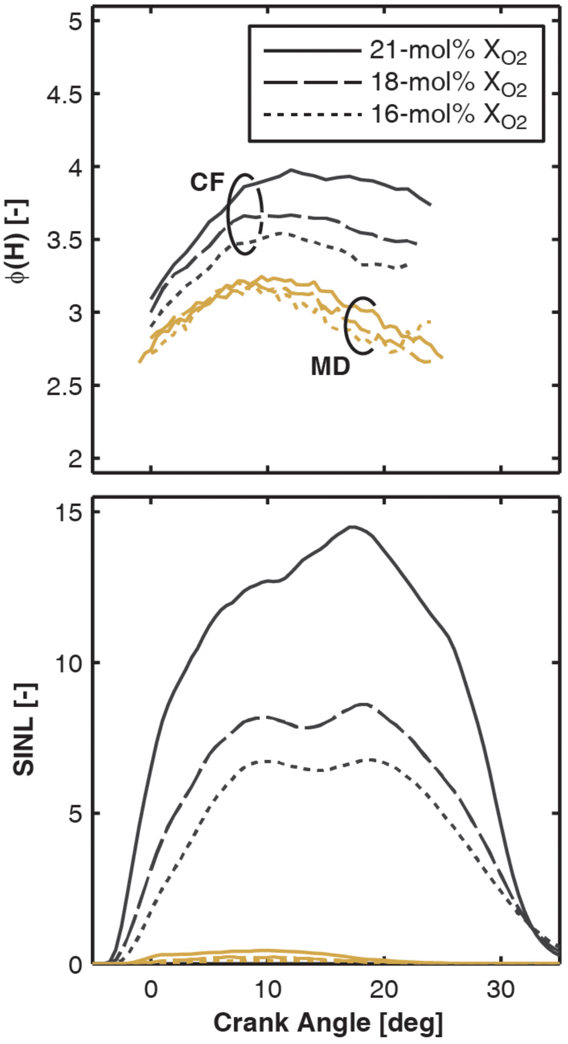

**FIGURE 3.** Equivalence ratio at the lift-off length, φ(H), and spatially integrated natural luminosity, SINL (a measure of hot soot), as functions of crank angle for MD and CF at an injection pressure of 180 MPa and $X_{O2}$-levels of 21, 18, and 16 mol%.

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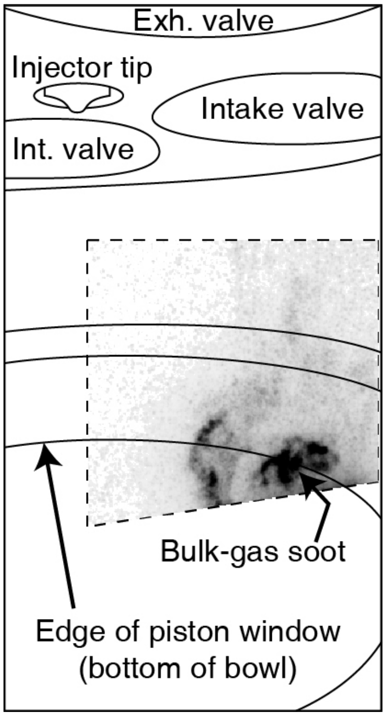

**FIGURE 4.** Bulk gas soot distribution in the region above the piston bowl as viewed through a window in the cylinder wall. Soot in a vertical plane is imaged using LII. Almost the entire region above the piston bowl is viewable by translating the vertical laser sheet.

## FY 2014 PUBLICATIONS

**1.** Mueller, C.J., Cannella, W.J., and Kalghatgi, G., "Fuels for Engines and the Impact of Fuel Composition on Engine Performance," Encyclopedia of Automotive Engineering, Eds.: Crolla, D., Foster, D.E., Kobayashi, T., and Vaughan,

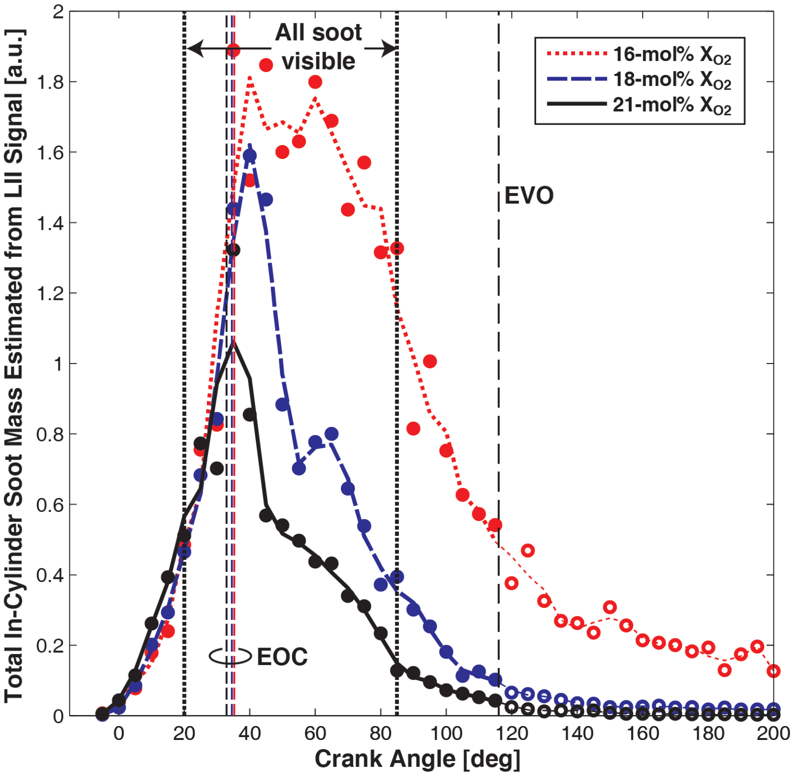

**FIGURE 5.** Total mass of in-cylinder soot as estimated from the vertical-sheet LII (VLII) diagnostic. EOC = end of combustion, EVO = exhaust valve opens.

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**7.** Nilsen, C.W. and Mueller, C.J., "Ducted Fuel Injection for Compression-Ignition Engines," *Science Undergraduate Laboratory Internship (SULI) Program Final Report*, DOE Office of Science, September 2014.

## FY 2014 PRESENTATIONS

**1.** Mueller, C.J., "Status Update on AVFL-18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling," Coordinating Research Council Advanced Vehicles, Fuels, and Lubricants Committee Meeting, San Antonio, TX (January 23, 2014).

**2.** Lilik, G.K., "The Visualization of Soot Late in the Diesel Combustion Process through Laser Induced Incandescence with a Vertical Laser Sheet," Advanced Engine Combustion Program Review Meeting, Livermore, CA (February 13, 2014).

**3.** Mueller, C.J., "Introduction to Compression-Ignition Engine Session," CRC Advanced Fuels and Engine Efficiency Workshop, Baltimore, MD (February 25, 2014).

**4.** Mueller, C.J., "Optical-Engine Experiments to Assess the Feasibility of LLFC with Oxygenated Fuels," DOE FOA 239 Project Meeting with Ford Motor Co., by teleconference (March 14, 2014).

**5.** Dumitrescu, C.E., "An Experimental Study of Diesel Fuel Property Effects on Mixing-Controlled Combustion in a Heavy-Duty Optical CI Engine," 2014 SAE International Congress and Exposition, Detroit, MI (April 9, 2014).

**6.** Mueller, C.J., “Fuel Effects on Mixing-Controlled Combustion Strategies for High-Efficiency Clean-Combustion Engines,” DOE Office of Vehicle Technologies Annual Merit Review Meeting, Washington, DC (June 19, 2014).

**7.** Mueller, C.J., “Fuel Effects on Emissions and Efficiency under Mixing-Controlled Combustion Conditions,” Advanced Engine Combustion Program-Review Meeting, Detroit, MI (August 19, 2014).

**8.** Mueller, C.J., “A Review of Fuel-Effects Research Reported at Advanced Engine Combustion (AEC) Program-Review Meetings in FY14,” USCAR Crosscut Team Meeting, Detroit, MI (September 11, 2014).

**9.** Mueller, C.J., “Non-Petroleum-Based Fuels – or – Fuel and Combustion-Strategy Effects on CI Engine Performance,” USCAR Crosscut Team Meeting, Detroit, MI (September 11, 2014).

**10.** Mueller, C.J., “Status Update on AVFL-18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling,” Coordinating Research Council Advanced Vehicles, Fuels, and Lubricants Committee Meeting, San Francisco, CA (September 16, 2014).

## AWARD

**1.** C.J. Mueller received a Society of Automotive Engineers (SAE) Lloyd L. Withrow Distinguished Speaker award at the 2014 SAE International Congress and Exposition in Detroit, Michigan.

## PATENTS PENDING

**1.** US Patent Application #13014154, “Ducted Combustion Chamber for Direct-Injection Engines and Method,” filed January 26, 2011.

**2.** Provisional US Patent Application #62058613, “Ducted Fuel Injection,” filed October 1, 2014.

# III.3 Alternative Fuels Direct-Injection Spark-Ignited Engine Research

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## Overall Objectives

Provide the science-base needed by industry to understand:

- How emerging alternative fuels impact highly-efficient direct-injection spark-ignited (DISI) light-duty engines being developed by industry.
- How engine design and operation can be optimized for most efficient use of future fuels.

## Fiscal Year (FY) 2014 Objectives

- Continue work towards a conceptual model of stratified spark-ignition (SI) combustion that incorporates the effects of fuel on combustion rate, ignition stability and exhaust emissions formation.
- Identify and explain combinations of fuel characteristics and operating strategies that enable stable and efficient well-mixed lean SI operation.
- Conduct initial tests with advanced ignition systems.

## FY 2014 Accomplishments

- Demonstrated combined effects of gasoline-ethanol blend ratio and spark-timing strategy on exhaust soot.
- Quantified and examined in detail factors that govern heat-release rate and its variability when the stratification level is tailored to the fuel composition. This included optical measurements of spray variability, flow field and flame development.
- Quantified lean stability limits and fuel efficiency gains for 85% ethanol and 15% gasoline (E85) and gasoline fuels.
- Examined combined effects of intake heat and fuel type on the ability to achieve controlled end-gas autoignition for higher combustion efficiency for lean-SI operation.
- Conducted a combined optical/performance study of advanced multi-pulse transient plasma ignition for E85, explaining fundamental ignition requirements for stable ultra-lean combustion.
- These accomplishments address one of the barriers identified by DOE Vehicle Technologies Office: Inadequate data for fuel property effects on combustion and engine efficiency optimization.

## Future Directions

- Examine the use of intake boost for load-range extension of stratified-charge operation.
- 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.
- Continue examination of well-mixed lean/dilute operation, using both regular spark and advanced multi-pulse ignition systems in combination with 0% to 30% ethanol-gasoline blends (E0-E30).
- Examine the effect of fuel type on combustion and fuel economy gain for SI operation with partial fuel stratification.

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## INTRODUCTION

Due to concerns about future petroleum supply and accelerating climate change, increased engine efficiency and alternative fuels are of interest. This project contributes to the science-base needed by industry to develop highly efficient DISI engines that also beneficially exploit the different properties of alternative fuels. Lean operation is studied since it can provide higher efficiencies than traditional non-dilute stoichiometric operation. Since lean operation can lead to issues with ignition stability, slow flame propagation and low combustion efficiency, focus is on techniques that can overcome these challenges. Specifically, fuel stratification can be used to ensure ignition and completeness of combustion, but may lead to soot and oxides of nitrogen emissions challenges. Advanced ignition system and intake air preheating both promote ignition stability. Controlled end-gas autoignition can be used maintain high combustion efficiency for ultra-lean well-mixed conditions. However, the response of both combustion and exhaust emission to these techniques depends on the fuel properties. Therefore, to achieve optimal fuel economy gains, the combustion control strategies of the engine must adopt to the fuel being utilized.

## APPROACH

The Alternative Fuels DISI Engine Lab at Sandia houses an engine that is set up for both performance testing and in-cylinder optical diagnostics. First, performance testing with an all-metal engine configuration is conducted over wide ranges of operating conditions and alternative fuel blends. Second, in-cylinder processes are examined with high-speed optical diagnostics, including advanced laser-based techniques. 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

In the following, examples of accomplishments during FY 2014 are presented.

Stratified Charge Operation - Previous work on stratified-charge combustion using E85 and gasoline showed that the spark timing relative to the fuel injection has to be adjusted with the fuel type to maintain misfire-free operation [1]. Exhaust emissions can also dictate what spark-timing strategy needs to be employed. This is exemplified for an engine load corresponding to indicated mean effective pressure, net ($IMEP_n$) = 320 kPa in Figure 1.

Here, smoke emissions are compared for operation across a range of gasoline-ethanol blends using two different spark-timing strategies. “Head ignition” was accomplished by timing the spark ignition so that it coincides with the beginning of the fuel-injection event, thereby igniting the leading edge of the two fuel sprays near the spark-plug gap. This minimizes the time available for premixing of fuel and air prior to combustion. In contrast, for “tail ignition” the spark timing coincides with the last liquid passing by the spark-plug gap, thereby igniting the end of the fuel sprays near the spark-plug gap. This allows more time for fuel-air mixing, thereby reducing both the degree of stratification and the fuel/air-equivalence ratios in flame regions. An engine speed of 1,000 rpm was used and start of injection was fixed at -23° crank angle for all data points. Figure 1 shows that the engine-out smoke level is acceptably low (<0.1 filter smoke number, FSN) for E85 and neat ethanol regardless of the spark-timing strategy. However, if the head-ignition strategy is used for gasoline or E35 very high smoke levels result. Hence, the smoke emissions mandate the use of tail ignition for gasoline and E35 fuel. (Further reduction of smoke to below 0.1 FSN can be achieved for gasoline by advancing the injection timing, but these data are not shown in Figure 1.)

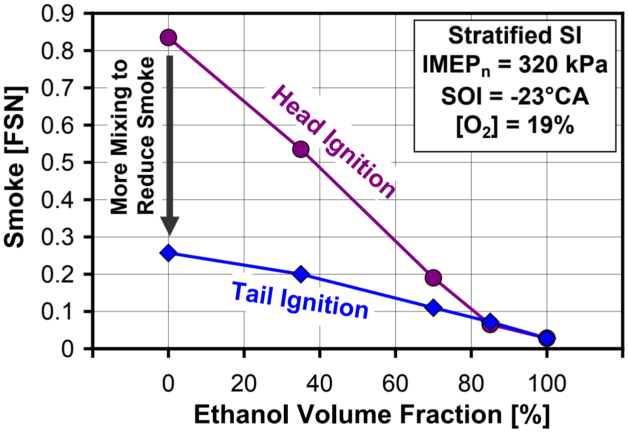

**FIGURE 1.** Engine-out smoke level as a function of volume fraction of ethanol in gasoline for operation with single injection at two different levels of stratification, as controlled by the spark timing relative to the fuel-spray development.

Since the sooting propensity of the fuel dictates what spark-timing strategy can be used, the fuel type indirectly affects the heat-release rate and how it scales with changes to the engine speed. This basic, but very important aspect is illustrated in Figure 2. The time-based apparent heat release rate (AHRR, in kW) of well-mixed stoichiometric combustion scales nearly 1:1 with the engine speed, as is well-known from the engine combustion literature on turbulent premixed deflagration [2]. In contrast, the AHRR for highly stratified operation with head ignition only increases slightly with engine speed. As discussed in Ref. [3], for highly stratified spray-guided combustion, the heat-release rate of the main combustion phase is primarily controlled by mixing rates and turbulence level associated with fuel-jet penetration. Figure 2 shows that the trend for operation with tail ignition falls in between those of well-mixed and head-ignition. This indicates that the AHRR is controlled by fuel-air mixing and turbulence associated with both the fuel spray and the intake-generated flow.

The intake-generated flow is not only important for the heat-release rate. Performance testing reveals that operation with intake-generated swirl reduces cycle-to-cycle variations of stratified combustion, especially for higher engine speeds. Extensive particle image velocimetry measurements have been conducted to

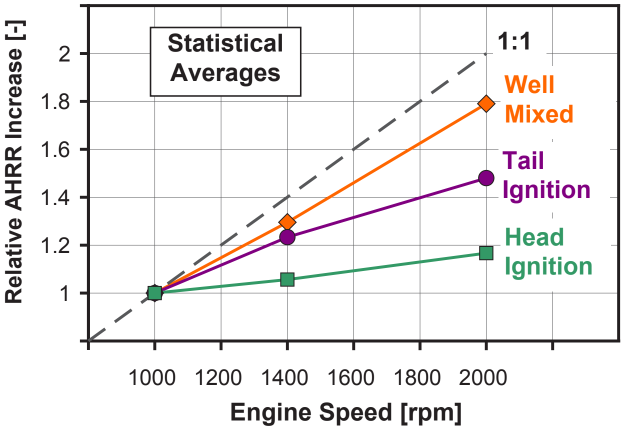

**FIGURE 2.** Scaling of peak heat-release rate (in kW) with engine speed for well-mixed stoichiometric 70% ethanol in gasoline (E70) operation and for two different levels of stratification using gasoline (tail ignition) and E70 (head ignition).

clarify the stabilizing mechanism of swirl, as reported in Ref. [4]. These included operation with and without swirl, and operation with and without injection. In addition, these flow measurements were combined with engine performance testing using gasoline fuel. Figure 3 demonstrates some of the key findings. At this engine speed of 2,000 rpm, operation with intake-generated tumble flow results in a coefficient of variation of IMEP = 3.5%, which is higher than desirable. By applying a combination of swirl and tumble, the IMEP variability can be strongly reduced. Figure 3 shows that this stabilization of combustion is correlated with an increase of the 'flow similarity.' 'Flow similarity' quantifies how similar an individual cycle is to the ensemble-averaged flow field [4]. Figure 3 demonstrates that after the end of injection, a representative single cycle exhibits a flow field with high resemblance to the ensemble-averaged flow. Flame imaging (not presented here) reveals that the early flame development is more stable when the flow near the spark plug is repeatable from cycle to cycle. This is consistent with the reduced variability of IMEP.

Well-Mixed Operation – Figure 4 demonstrates some of the observations from well-mixed lean operation, comparing the performance of gasoline and E85. The engine speed was maintained at 1,000 rpm, and the injected amount of fuel was held constant for each data set while the intake pressure was increased to lean out the charge, reducing ϕ. Figure 4b shows that a substantial increase of the efficiency can be obtained. Without intake air preheating, the relative fuel economy gain is roughly 12% for both gasoline and E85 at ϕ = 0.67-0.70. When intake air preheating is applied, Figure 4c shows that the lean stability limit shifts to lower ϕ for both fuels. Associated with this is a greater relative fuel economy

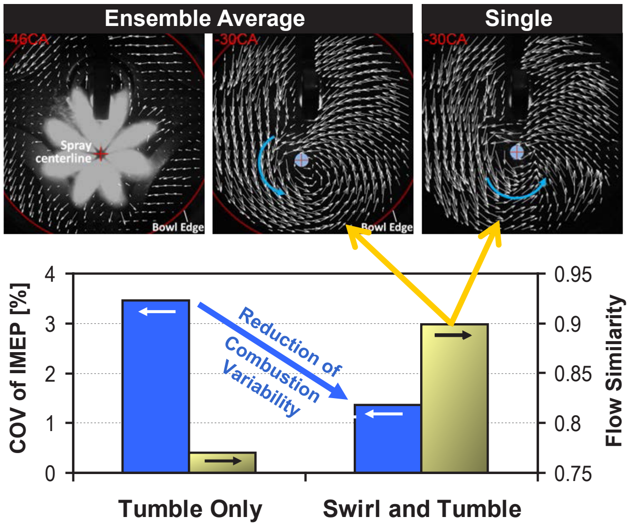

**FIGURE 3.** Spray-swirl interaction causes flows that are more repeatable from cycle-to-cycle. The increased flow similarity is correlated with a reduction of combustion variability for spray-guided stratified-charge operation using gasoline. 2,000 rpm, IMEP$_n$ = 370 kPa, intake O$_2$ = 19%.

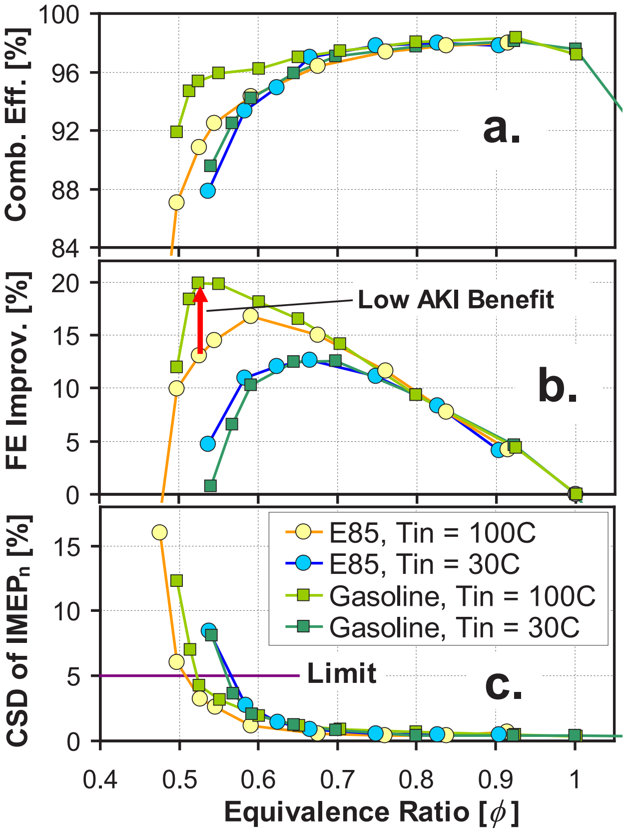

**FIGURE 4.** Combined effects of fuel type and intake heating on lean SI operation. a) Combustion efficiency. b) Fuel economy improvement relative stoichiometric operation. c) Relative IMEP$_n$ instability.

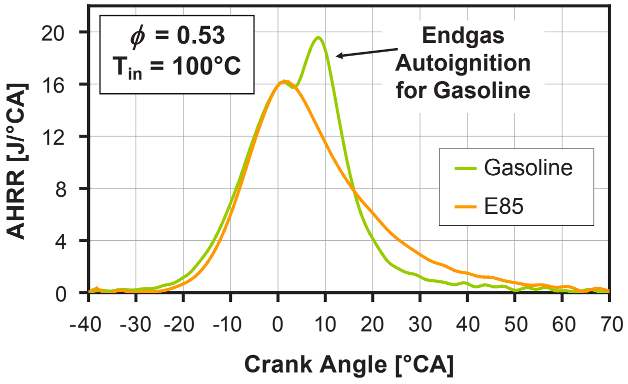

**FIGURE 5.** Effect of fuel type on late-cycle combustion for lean well-mixed SI operation using pre-heating of the intake air.

improvement for both fuels. However, gasoline benefits more from the intake air preheating, showing a 20% fuel economy improvement relative to stoichiometric ($\phi$ = 1) operation for $\phi$ = 0.53. The difference between the fuels arises due to the appearance of repeatable end-gas autoignition for the lower octane gasoline fuel, as Figure 5 illustrates. This end-gas autoignition consumes fuel ahead of the slow turbulent flame, thereby increasing both combustion efficiency (Figure 4a) and thermal efficiency. This example demonstrates that end-gas autoignition can be used beneficially to enable ultra-lean SI operation, but that a change of fuel type or increased octane number needs to be factored in by the control algorithms of the engine. For more details of these experiments and for a demonstration of the use of advanced ignition for lean operation, please refer to Ref. [5].

## CONCLUSIONS

- The alternative fuels DISI engine lab at Sandia contributes to the science base needed by industry to take full advantage of future fuels in advanced internal combustion engines.
- Continued and substantial progress has been made towards a conceptual model of stratified SI combustion that accounts for fuel type, degree of stratification, and the intake-generated flow field.
- Gasoline/ethanol blend proportions influence optimal spark-timing strategies for stratified operation since more mixing time is required for gasoline-dominated fuel blends to avoid excessive soot formation.
- Factors that govern the heat-release rate for stratified-charge operation change with fuel type due to different spark-timing strategies.
- Increasing engine speed can challenge the combustion stability of stratified-charge operation.

  Highly stratified operation with high-ethanol blends is affected differently than less stratified operation with gasoline. Interaction between intake-generated swirl and fuel sprays creates a strong and stable vortex that contributes to stable combustion.
- For DISI operation with well-mixed charge and no intake heat, lean stability limits and fuel economy gains are identical for E85 and gasoline. However, for operation with intake-air preheating, the lower octane gasoline fuel exhibits a fuel economy advantage due to repeatable endgas autoignition that helps maintaining high combustion efficiency.
- Multi-pulse transient plasma ignition demonstrates strong benefits to stabilize lean operation by offering a faster transition to fully turbulent combustion compared to regular spark ignition.

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**4.** W. Zeng, M. Sjöberg, and D.L. Reuss, “PIV Examination of Spray-Enhanced Swirl Flow for Combustion Stabilization in a Spray-Guided Stratified-Charge DISI Engine”, in press for Int. J. of Engine Research, 2014. doi:10.1177/1468087414564605

**5.** M. Sjöberg, W. Zeng, D. Singleton, J.M. Sanders, and M.A. Gundersen, “Combined Effects of Multi-Pulse Transient Plasma Ignition and Intake Heating on Lean Limits of Well-mixed E85 DISI Engine Operation”, SAE Int. J. Engines 7(4):1781-1801, 2014.

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**2.** M. Sjöberg, W. Zeng, and D.L. Reuss, “Soot and $NO_x$ Considerations for a Stratified-Charge DISI Engine using Gasoline/Ethanol Blends,” presented at 2013 Hyundai-Kia International Powertrain Conference, Hwaseong, South Korea, Oct 2013.

**3.** M. Sjöberg, W. Zeng, D. Singleton, J.M. Sanders, and M.A. Gundersen, “Combined Effects of Multi-Pulse Transient Plasma Ignition and Intake Heating on Lean Limits of Well-mixed E85 SI Engine Operation," presented at AEC Program Review Meeting, Sandia, Livermore, CA, Feb 2014.

**4.** W. Zeng, M. Sjöberg, and D.L. Reuss, "Combined Effects of Flow/Spray Interactions and EGR on Combustion Variability for a Stratified DISI Engine," presented at AEC Program Review Meeting, Sandia, Livermore, CA, Feb 2014.

**5.** M. Sjöberg, "DISI with Gasoline/Ethanol Blends," presented at CRC Advanced Fuel and Engine Efficiency Workshop, Baltimore, MD, Feb 2014.

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**12.** W. Zeng, M. Sjöberg, and D.L. Reuss, "PIV Examination of Spray-Enhanced Swirl Flow for Combustion Stabilization in a Spray-Guided Stratified-Charge DISI Engine," in press for Int. J. of Engine Research, 2014. doi:10.1177/1468087414564605

## SPECIAL RECOGNITIONS & AWARDS

**1.** Magnus Sjöberg received an SAE Excellence in Oral Presentation Award for a presentation of stratified DISI operation using E85 fuel at the SAE/KSAE 2013 Powertrains, Fuels & Lubricants meeting in Seoul, South Korea.

## ACKNOWLEDGEMENTS

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# III.4 Non-Petroleum Fuel Effects in Advanced Combustion Regimes

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## 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) 2014 Objective

- Complete a study to estimate vehicle fuel economy showing fuel-based differences in energy consumption using experimental multi-mode engine maps that were collected during FY 2013 and include spark-ignited (SI) combustion, dilute SI combustion, and homogeneous charge compression ignition (HCCI) combustion.
- Retrofit an existing multi-cylinder experiment at ORNL to operate on cylinder with the Sturman variable valve actuation system to enable investigations of fuel-specific differences on reforming processes and brake efficiency in a multi-cylinder engine.

## FY 2014 Accomplishments

- Concluded through vehicle fuel economy estimates that for a vehicle with a downsized/downsped engine designed to run on 30% ethanol, the fuel energy density penalty associated with ethanol can be recovered by increased engine and vehicle system efficiency.
- Found that HCCI is more compatible with larger engine displacement, and may be counter to current industry trends of downsizing and downspeeding.
- Completed the installation of a unique flexible multi-cylinder engine to pursue the ORNL in-cylinder reforming strategy.

## Future Directions

- Investigate fuel effects of the exhaust gas recirculation (EGR) dilution limits for SI combustion both with and without simulated reformate.
- Characterize fuel-specific differences of the ORNL in-cylinder reforming strategy on the flexible multi-cylinder engine.

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## INTRODUCTION

Consumption of non-petroleum-based fuel is steadily increasing, displacing conventional petroleum-derived gasoline and diesel fuel in accordance with the Energy Independence and Security Act of 2007. Concurrently, advanced combustion strategies are being developed for 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 efforts in FY 2014 had two primary focuses. The first was to complete the reporting and analysis of experiments that were largely conducted in FY 2013. The second was to reconfigure the experimental facilities to begin a new experimental effort based on the conclusion from the previous work.

## APPROACH

The approach in FY 2014 consisted of using experimental efficiency maps across the applicable speed/load operating ranges using three common fuels with conventional and advanced operating strategies. All of the experiments were conducted on the same SI engine 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 valvetrain, and several different pistons that allow the compression ratio to be changed. The majority of the experiments 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).

Steady-state vehicle fuel economy was simulated for vehicle speeds of 20, 30, 40, 50, 60, and 70 mph for conventional SI combustion, 15% EGR dilute SI combustion, and HCCI for each of the fuels. The engine speed and displacement were varied to maintain drivability. The assumption used was that the steady-state cruise speed could not be more than 40% of the stoichiometric engine peak torque at that engine speed.  he simulated vehicle was a generic mid-size sedan weighing 3,750 lbs, and the required power at the wheels was estimated by from eight 2014 vehicles with this weight from the Environmental Protection Agency databa se (http://www.epa.gov/otaq/tcldata.htm). The comparisons were made with a compression ratio of 11.85:1. While the simulation is a useful way to estimate the impact of fuel effects, many practical considerations are neglected, such as turbocharger lag, transient operation, and shift schedule/transmission matching.

## RESULTS

Experimental results show that the engine power density under SI and dilute SI combustion modes is a strong function of the fuel type (Figure 1), with the power density of E30 being nearly double that of regular-grade gasoline at this compression ratio. As a result, for similar drivability the E30 and the IB24 engines can have a significantly smaller displacement and/or be operated at a slower engine speed. A simulation of an apples-to-apples fuel economy comparison is shown in Figure 2, where the engine operating on regular-grade gasoline has a displacement of 2.5-L, the 24% iso-butanol engine has a displacement of 2.0-L, and the E30 engine has a displacement of 1.5-L. Despite E30 having a volumetric energy density that is 10.4% lower than regular-grade gasoline, the estimated fuel economy for E30 is better than that of gasoline in this dedicated engine.

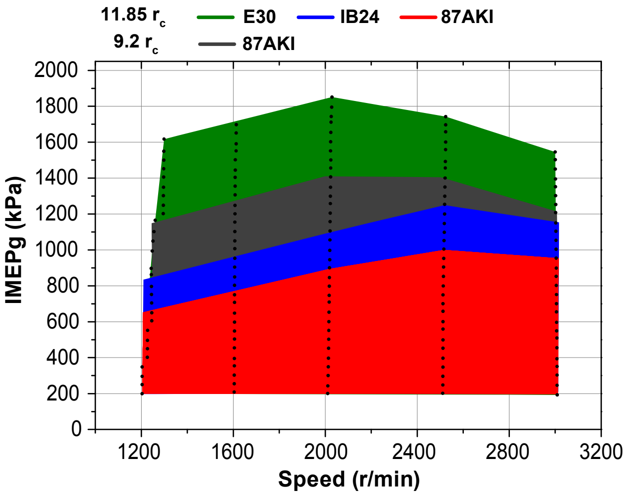

**FIGURE 1.** Operable speed/load range for each fuel for conventional SI combustion at a compression ratio of 11.85:1, and for 87 AKI at a compression ratio of 9.2:1.

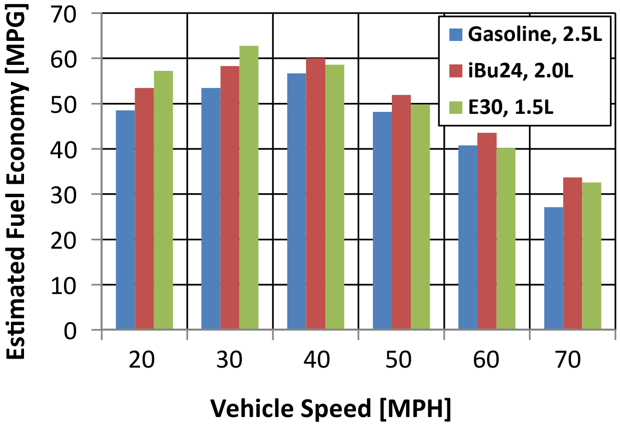

**FIGURE 2.** Estimated steady cruise fuel economy for a 3,750 lb vehicle with an optimally downsized and downsped engine for each fuel at an engine compression ratio of 11.85:1.

There are further efficiency benefits enabled by operating under EGR dilute conditions. The majority of the efficiency benefits can be categorized as system-level benefits as a result of downsizing and downspeeding rather than improvements in thermodynamic efficiency. This is because downsizing and downspeeding allow the engine load to be increased to a higher-efficiency region of the engine operating map, and reducing engine speed and size reduces engine friction. A breakdown of where the efficiency benefits come from for dilute E30 relative to regular-grade gasoline at 60 mph is shown in Figure 3.

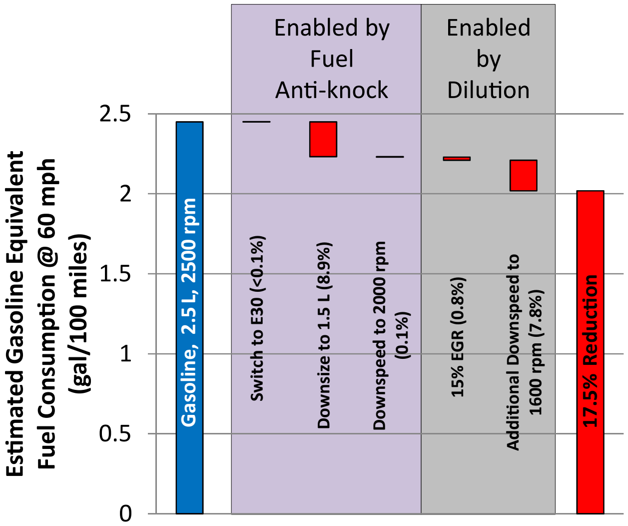

**FIGURE 3.** Breakdown of the efficiency gains enabled by switching from regular grade gasoline to E30, downsizing, downspeeding, and EGR dilution. Note that this efficiency improvement equates to an estimated fuel economy of 40.8 mpg with regular grade gasoline to 44.4 mpg with E30 despite the energy density decrease.

Mixed-mode SI with HCCI was also included in the fuel economy estimation. The peak HCCI load, which was limited by the peak cylinder pressure of 100 bar, was the same for all of the fuels: 8 bar on a gross indicated mean effective pressure basis. In some case where the exhaust temperature was low, though, the calculated brake mean effective pressure was reduced significantly because of air handling requirements. The requirement of the steady cruise conditions being less than 40% of the peak torque effectively meant that the peak torque was met by conventional SI combustion rather than HCCI.

At steady cruise conditions where HCCI is applicable, it does provide a significant efficiency and fuel consumption benefit. Figure 4 shows a fuel economy improvement of more than 10% at 50 mph for regular-grade gasoline in a 2.5-L engine. However, HCCI is not applicable everywhere on the engine map, and was shown to be more compatible with the larger engine displacement required for regular gasoline than for the downsized and downsped configurations enabled by the higher octane fuels, E30 and IB24. This is because the peak mean effective pressure for HCCI is the same for all fuels, but the peak mean effective pressure for the higher octane fuels under SI condition is significantly higher for the iso-butanol blend and E30, allowing them to be downsized and downsped. Thus, HCCI covers a smaller fraction of the E30 and the iso-butanol operating map compared to gasoline. So, the trend of higher specific output engines enabling downsizing and downspeeding appears to be a competing technology to HCCI rather than a complementary technology.

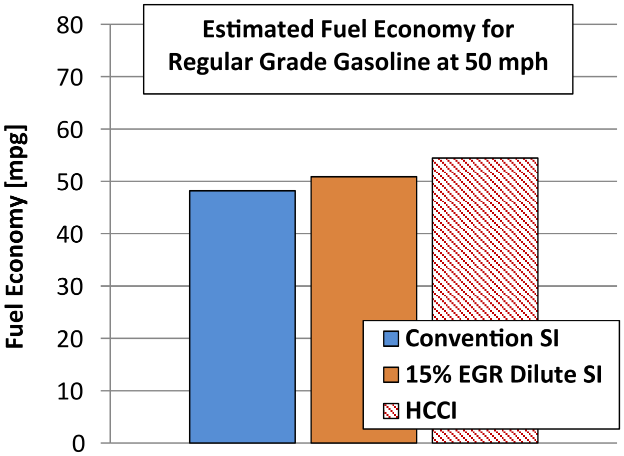

**FIGURE 4.** Estimated fuel economy at a 50 mph cruise for regular grade gasoline under conventional SI conditions, 15% EGR dilute SI, and for HCCI.

Based on these results, continuing efforts will focus on investigating fuel effects that enable dilute SI combustion, which is complementary with downsizing and downspeeding. Dilute SI combustion offers many of the efficiency benefits of HCCI. Specifically, if a flame front can be supported under dilute conditions, then known developed technologies can be employed to realize comparable efficiency benefits without the controls challenges presented by HCCI. To pursue this, modifications have been made to the single-cylinder engine platform to investigate the limits of dilute combustion both with and without simulated reformate. Additionally, as part of a collaborative effort between this project and the Stretch Efficiency project (Advanced Combustion Engine project II.19), a flexible multi-cylinder engine has been developed and commissioned at ORNL to investigate in-cylinder reforming. The engine is equipped with hydraulic valve actuation on one cylinder of the engine to allow operation of the in-cylinder reforming strategy. A picture of the modified engine head is shown in Figure 5, and a picture of the installed engine is shown in Figure 6. The engine will be used in FY 2015 for this project to investigate fuel effects on in-cylinder reforming processes.

## CONCLUSIONS

Experimental investigations on fuel effects of three different combustion modes were extended to vehicle fuel economy. The simulation assumed that the engine and transmission were designed around each fuel, so that the fuel can enable downsizing and downspeeding. The following conclusions were made from the simulation:

**FIGURE 5.** Modified cylinder head for the flexible ORNL engine platform to investigate in-cylinder reforming.

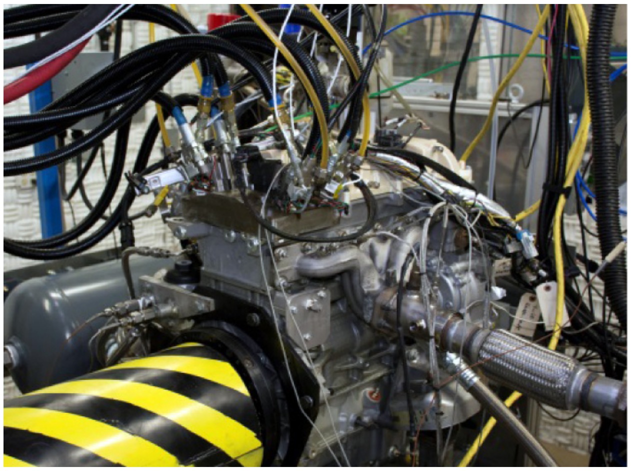

**FIGURE 6.** ORNL installation of the function multi-cylinder engine designed to investigate in-cylinder reforming.

- High-octane fuels, such as IB24 and E30, enable a significant amount of downsizing and downspeeding for significant fuel economy improvements.
- The efficiency improvements for E30 compared to regular-grade gasoline are larger than the 10.4% volumetric energy density difference between these fuels, allowing the E30 fuel economy to be as good as, or better than the regular-grade gasoline.
- HCCI combustion provides fuel economy improvements where it is applicable, but it is not applicable at all normal driving conditions.
- HCCI is more compatible with larger engine displacement, and may be counter to current industry trends of downsizing and downspeeding.

## FY 2014 PUBLICATIONS/PRESENTATIONS

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**5.** Szybist, J., Steeper, R., Splitter, D., Kalaskar, V., Pihl, J., and Daw, C., “Negative Valve Overlap Reforming Chemistry in Low- Oxygen Environments,” *SAE Int. J. Engines* 7(1):2014, doi:10.4271/2014-01-1188.

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# III.5 Fuel Properties to Enable Lifted-Flame Combustion

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Subcontractors
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- University of Wisconsin, Madison, WI

## Overall Objectives

- Identify fuel properties 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 to enable ELOC and also meet other fuel system requirements (e.g. lubricity, oxidative stability, cold flow)
- Enhance combustion models to capture the effect of fuel properties on combustion

## Fiscal Year (FY) 2014 Objectives

- Complete fuel properties testing
- Complete optical engine testing
- Optimize combustion system for fuel-enabled ELOC
- Compile list of desirable fuel properties based on modeling results
- Identify test fuels, upgrade hardware and complete single-cylinder engine (SCE) testing

## FY 2014 Accomplishments

- Completed master list of oxygenated fuels and measurements of key oxygenate properties.
- Conducted further cetane rating testing to investigate differences between cetane test methods. It is hypothesized the disparity in cetane results between methods is attributed to differences in auto-ignition temperature dependence between tri-propylene glycol methyl ether (TPGME) and hydrocarbons combined with differences in temperature/pressure boundary conditions. Further study is planned.
- Developed a new TPGME kinetic mechanism and validated it against G15, G33 and G50 spray results. Simulations show good agreement with experimental results for ignition delay, flame lift-off, soot magnitude and soot location.
- Assessed the effect of oxygenate structure on sooting by comparing mixtures of TPGME, methyl decanoate (MD) and dimethyl ether (DME). Results showed soot precursors decreased primarily as a function of fuel oxygen ratio, but that the lift-off length and the number of fuel C–C bonds were also important.
- Completed optical engine experiments evaluating a 50-50 blend of TPGME and ultra-low sulfur diesel (ULSD) fuel (T50) using a two-hole nozzle. Leaner lifted flame combustion (LLFC) was achieved and sustained at realistic operating conditions, producing zero soot, lower indicated specific NOx (ISNOx) and comparable fuel-conversion efficiency to a base condition using standard fuel.
- Validated models against experiments for various oxygenates to project the minimum fuel oxygen ratio needed to meet soot standards without a diesel particulate filter.
- Optimized nozzle with the new fuel system to reduce nozzle hole size, thus increasing air entrainment while achieving full load targets. Characterized the new combustion system with baseline fuel.
- Selected a 6% fuel oxygen ratio blend of TPGME and certification fuel for initial SCE LLFC experiments. Tested blends of proposed fuels to verify peroxide levels and their influence on cetane number were acceptable.

## Future Directions

- Complete study of TPGME and hydrocarbon fuels with different cetane rating methods to better understand cetane rating results and the disparity between test methods.
- Complete modeling projects at University of Wisconsin in December 2014, finalizing the investigation of the effect of fuel structure on soot formation.

- Use models to finalize an improved combustion system design to enable SCE LLFC.
- Complete optical engine experiments using a six-hole nozzle and T50 fuel.
- Demonstrate non-sooting diesel combustion on a SCE with modern power density requirements.

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## INTRODUCTION

The intent of this project is to identify how fuel properties can be used to achieve controllable ELOC with low NOx and particulate matter 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 (Ford), Dr. Lyle Pickett and Dr. Charles Mueller (SNL) and Professor Rolf Reitz (UW).

## APPROACH

All three partners have key roles in achieving the project objectives. Together, Ford and UW will develop and integrate three-dimensional combustion models to capture fuel property combustion effects. Ford will use modeling results to modify the single cylinder combustion system and demonstrate fuel-enabled ELOC, and will also lead fuels activities to identify appropriate test fuels. 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 Ford efforts.

## RESULTS

### Fuels Development and Property Testing and SCE

A master list of oxygenate compounds and properties was completed and used for fuel selection. Investigation of cetane number of TPGME previously uncovered differences in cetane number and derived cetane number measurements. The disparity in cetane number results is thought to be attributed to differences in autoignition temperature dependence between TPGME and hydrocarbons given differences in temperature/pressure boundary conditions for each test method. Further study is planned.

The combustion system was optimized with the new fuel system to enable a 17% reduction in nozzle flow. The engine was characterized at key operating conditions with a standard diesel fuel. A 50-50 blend of TPGME and Ford certification fuel was chosen for an initial SCE LLFC demonstration.

### Modeling

A reduced kinetic mechanism for TPGME was further developed and combined with n-hexadecane to validate against SNL spray results for G15, G33 and G50 (15, 33, and 50 volume% TPGME blended with n-hexadecane). Spray ignition delay and lift-off length matched well to experimental results, as well as soot levels and location.

The importance of oxygenate structure was then studied comparing G50 with MD and M50, a simulated fuel with G50 physical properties, but a chemical mixture of n-hexadecane and DME. Despite having similar fuel oxygen ratios, the G50 fuel showed the lowest soot levels. It is hypothesized that while soot production is highly dependent on the fuel oxygen ratio, lift-off length and the number of fuel bound carbon-carbon bonds are also important.

A model using chemical kinetics was developed and validated against SCE data at nine operating conditions for three fuels of different fuel oxygen ratios. To predict the effect of fuel oxygen ratio, a soot formation constant was adjusted as a function of fuel oxygen ratio, resulting in good agreement with experimental results at all operating conditions. The minimum fuel oxygen ratio to meet Low Emission Vehicle III particulate matter was estimated using this model.

### Spray Work and Optical Engine

Optical engine experiments were conducted using a two-hole nozzle tip at various boundary conditions to compare three fuels: ULSD, MD and T50.

At 180 MPa injection pressure, the T50 fuel provided a longer flame lift-off and similar soot luminosity than MD despite the higher aromatic content. While engine-out soot emissions were below detection limits, in-cylinder was still observed. Further testing at 240 MPa with 95°C and 50°C intake manifold temperature further reduced soot, finally achieving LLFC with the lower IMT. In addition to producing zero engine-out smoke, LLFC with T50 also produced lower ISNOx emissions and comparable fuel-conversion efficiencies as ULSD at 180 MPa and 95°C intake manifold temperature.

## CONCLUSIONS

- The disparity in TPGME cetane rating between methods may be a result of differences in temperature/pressure boundary conditions for each test method combined with TPGME's unique autoignition temperature dependencies relative to hydrocarbons.
- A model for TPGME blends has been validated for ignition delay, flame lift-off, soot location and soot magnitude at typical modern diesel engine boundary conditions.
- Modeling suggested soot production is not only dependent on the fuel oxygen ratio, but also lift-off length and the number of carbon-carbon bonds in the fuel.
- A 17% reduction in nozzle flow rate was possible while still meeting full-load requirements, which will help enable SCE LLFC operation.
- LLFC operation was achieved under realistic boundary conditions using a two-hole nozzle tip with T50 fuel.

## FY 2014 PUBLICATIONS/PRESENTATIONS

**1.** SNL and FMC published and presented the following paper at the *SAE 2014 International Powertrains, Fuels & Lubricants Meeting*: "Effects of Oxygenated Fuels on Combustion and Soot Formation/Oxidation Processes" (2014-01-2657).

**2.** SNL and FMC has submitted the following paper for publication at the 2015 ASME conference: "Investigation of a Tripropylene-Glycol Monomethyl Ether and Diesel Blend for Soot-Free Combustion in an Optical Direct-Injection Diesel"

# III.6 Fuel and Lubricant Effects on PM Formation in Direct Injection Spark-Ignited Engines

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## Overall Objectives

- Quantify fuel and lubricant effects on particulate matter (PM) formation in gasoline direct injection (GDI) combustion, with an emphasis on component effects
- Quantify importance of transient operation to overall GDI PM emissions, including start-stop operation

## Fiscal Year (FY) 2014 Objectives

- Determine fuel effects on GDI PM reactivity using the soot oxidation profile
- Evaluate stop-start effects on the PM from a GDI vehicle using gasoline-alcohol blends

## FY 2014 Accomplishments

- Demonstrated major fuel effects on GDI PM oxidation for both ethanol and isobutanol
- Characterized start-stop PM emissions for a 2014 GDI vehicle operating on gasoline, gasoline-ethanol, and gasoline-isobutanol blends

## Future Directions

- Quantify fuel effects on the GDI vehicle start-stop PM emissions
- Evaluate fuel effects on the oxidation kinetics of the PM collected on gasoline particulate filter (GPF) cores

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## 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 offer the benefits of higher fuel economy when replacing larger displacement engines. GDI engines tend to produce more PM than their port fuel-injected counterparts, as well as diesel vehicles equipped with diesel particulate filters [1-6]. Additionally, as the implementation of the higher corporate average fuel economy standards approaches, many vehicles are likely to implement start-stop technology to improve fuel economy. Start-stop technology saves fuel used in idling, by shutting off the engine when the vehicle comes to a stop and re-starts when when the driver releases the brake. Because PM from gasoline vehicles, in particular GDI vehicles, is associated with rich transients such as start-up, it is important to understand the start-stop effects on PM. Controlling PM from GDI engines helps meet DOE goals of enabling high-efficiency engine technologies and reducing pollutants.

The Energy Independence and Security of 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.

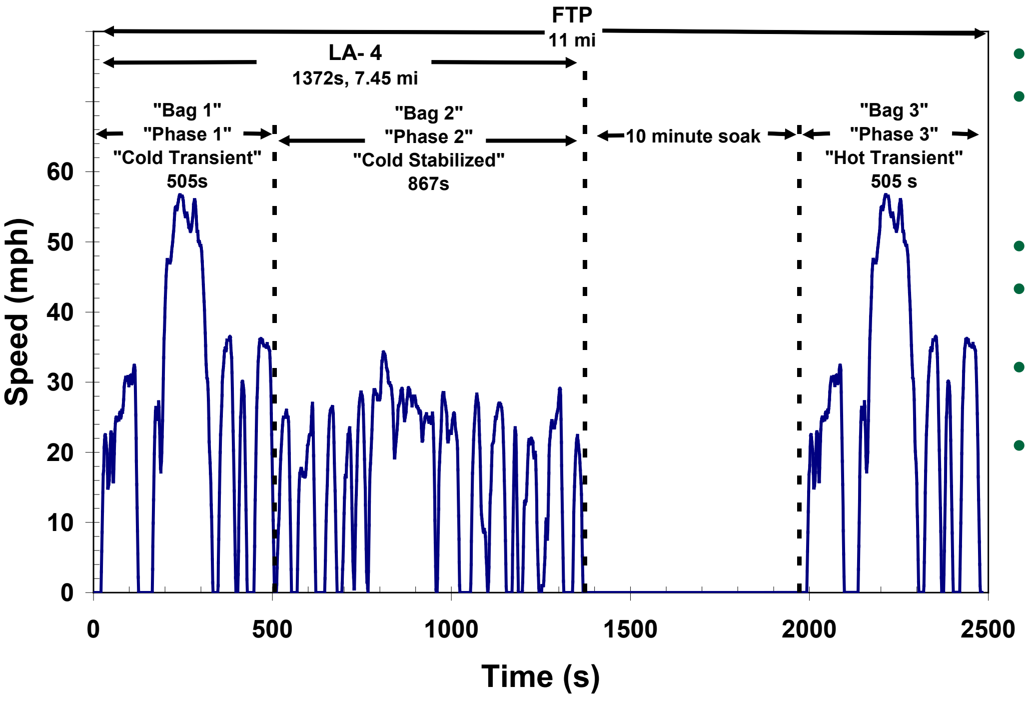
## APPROACH

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 air-to-fuel ratio, as well as the real-time soot concentration, was measured during acceleration transients to determine a representative steady-state 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 [7,9]. Gasoline, as well as gasoline blended with ethanol or butanol, were used as fuels. Fuels included unleaded gasoline (E0, 87 Anti-Knock Index), 30% ethanol and 70% E0 by volume (E30), 48.2% isobutanol and 51.8% E0 by volume (iBu48), and 24% isobutanol and 76% E0 by volume (iBu24). The isobutanol blend compositions were chosen to provide an oxygen mass fraction equal to that of E30 and E15. For the soot oxidation studies described in this report, PM was collected in miniature GPF substrates.

Soot oxidation experiments were carried out for GDI PM collected in GPF cores coated with three-way catalyst as well as uncoated GPF cores. The soot was produced with E0, E30, iBu48, and iBu24 used in a 2.0-L GDI engine. As described previously, the engine was operating at a steady-state point representative of the fuel-rich conditions observed during acceleration transients. The soot oxidation experiments were carried out in an automated bench flow reactor to characterize the reactivity of soot generated from the four fuel blends. One GPF sample was loaded at a time into a quartz tube fitted with stainless steel end-caps and loaded into a horizontal tube furnace. In the reactor, the samples were exposed to a temperature profile of 100-750°C under a nitrogen gas stream carrying 5% $H_2O$ and 1% $O_2$. The resulting CO and $CO_2$ products of soot oxidation were measured with Fourier transform infrared spectroscopy.

For the start-stop PM emissions characterization, a 2014 Chevrolet Malibu was used. The standard model is equipped with a 2.5-L GDI engine with the start-stop feature. Once the engine is warm, the vehicle's control system will stop the engine when the vehicle comes to a complete stop. When the driver's foot lifts off of the brake, the engine restarts so that power is available immediately to launch the vehicle. For this study, triplicate experiments were done for each fuel, and for the vehicle operating in stop-start mode, and with the start-stop mode disabled. An experiment consisted of a cold start LA-4 drive cycle followed by nine hot-start LA-4 cycles. In order to accumulate enough PM for gravimetric and chemical analysis, the sample filters were exposed over multiple cycles. Thus, for the cold cycle, duplicate filters were collected over all three cold cycles of the same fuel/start-stop condition, with each filter having three cold cycles. For the nine hot cycles each day, a single filter accumulated the PM mass for those cycles. The LA-4 cycle consists of the first two phases of the Federal Test Procedure (FTP) used to certify vehicles, and includes 13 complete stops in the cycle. The LA-4 cycle is illustrated in Figure 1.

The PM collected on the cycle-average filters were characterized for chemical species using thermal desorption/pyrolysis gas chromatography mass spectrometry. The technique is described extensively



- **Three phases**
- **Phase 1 and 3 are identical except for engine temperature**
- **11 miles total**
- **19.5 mph average speed**
- **57 mph Maximum speed**
- **3.3 mph/s maximum acceleration**

**FIGURE 1.** FTP is used for emissions compliance testing and for city fuel economy in U.S. FTP is also known as the City Test, or the Urban Dynamometer Driving Schedule (UDDS).

in a published study [9]. Briefly, PM is removed from the sample filter, placed in a stainless steel thimble, and heated under helium, an inert gas. The resulting products are then analyzed by gas chromatography mass spectrometry.

## RESULTS

The renewable fuel blends examined in this study included E30, iBu24, and iBu48. 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 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]. The iBu24 blend was chosen to represent the highest blend of isobutanol expected in the marketplace.

The results of the soot oxidation experiments are shown in Figures 2 and 3. Figure 2 shows the normalized oxidation rate of the soot as a function of temperature. There are fairly big differences in the oxidation behavior for these soots, indicating that the fuel had an effect on soot structure. The iBu24 lines up well with the iBu48 indicating similar soot structure, with the addition of a higher volatility portion. Figure 3 shows a bar chart with the $T_{90}$ values for the four soot samples. For the second part of the study, the soot oxidation kinetics will be studied to determine what factors might be causing the differences in the observed oxidation.

The start-stop studies showed some differences in cycle-averaged emissions and fuel economy between fuels and for stop-start vs. no start-stop operation. As expected, the fuel economy improved about 3-5% for start-stop operation vs. no start-stop operation. Figure 4 shows the results for the composite PM mass emissions over the FTP. The vehicle easily meets the current PM limit of 10 mg/mile, and comes close to the future limit (Tier 3) of 3 mg/mile. The cold portion of the test dominated PM emissions, typically having 5 to 10 times higher PM than the warm portion of the test, so the composite number is dominated by the cold portion. Note that the emissions typically go down for non start-stop operation, with the exception of the E30. The start-stop operation is only enabled when the vehicle is warm, so the first 120 s of the cold start is identical for both start-stop and non start-stop operation. Further analysis of the

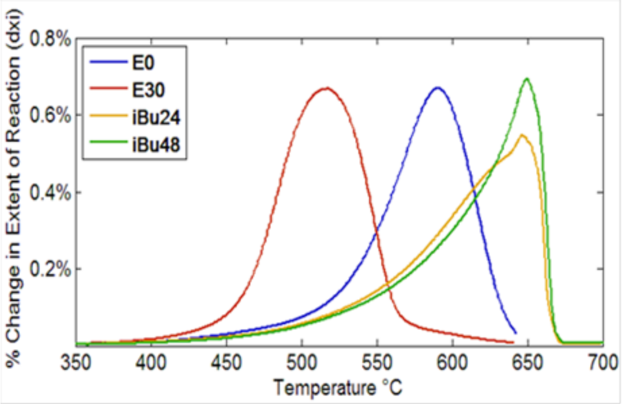


**FIGURE 2.** Oxidation profiles for GDI soot with gasoline-alcohol blend fuels. E0 is gasoline, E30 is 30% ethanol in gasoline, iBu24 and iBu48 are 24% and 48% isobutanol in gasoline, respectively.

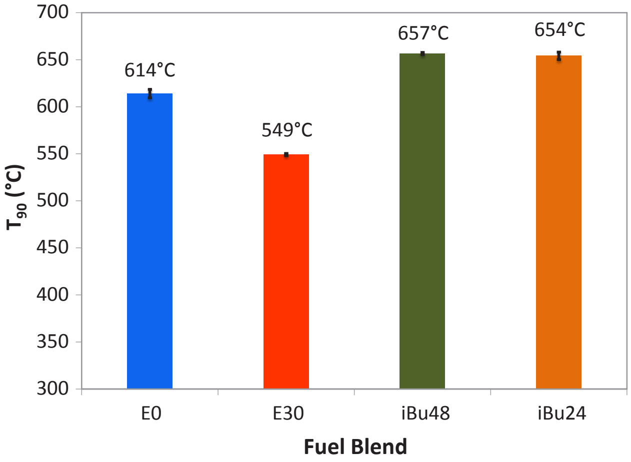


**FIGURE 3.** Temperature values for the 90% oxidation ($T_{90}$) of GDI soot produced with gasoline and gasoline alcohol blends. E0 is gasoline, E30 is 30% ethanol in gasoline, iBu24 and iBu48 are 24% and 48% isobutanol in gasoline, respectively. Note the >100°C difference in oxidation temperature between the $T_{90}$ for E30 and the iBu blends.

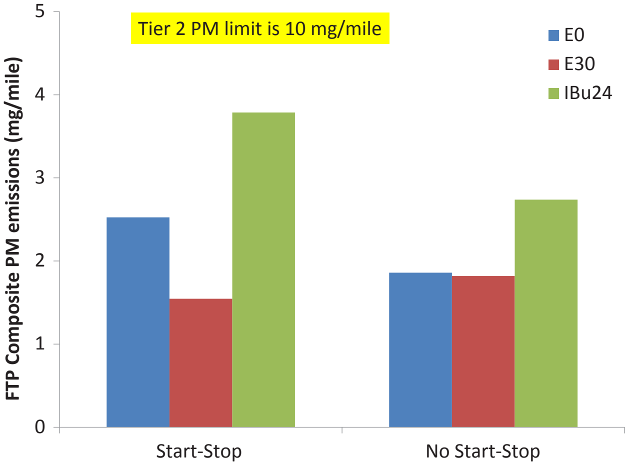


**FIGURE 4.** Composite FTP PM emissions for the 2014 Chevrolet Malibu GDI 2.5-L equipped with idle shutoff. The vehicle was operated with both idle shutoff active (“start-stop”) and the idle shutoff disabled ( “no start-stop”.)

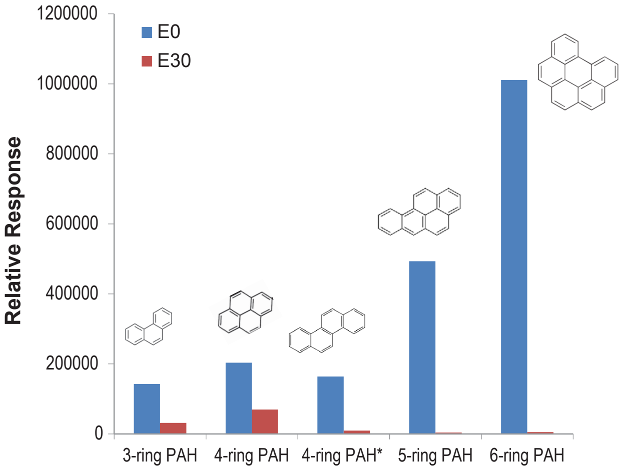


**FIGURE 5.** Comparison of polycyclic aromatic hydrocarbon compounds found on the PM from operation with E0 and E30. Hot LA-4 cycle. The structures are representative of the types of compounds present.

PM size and real-time soot carbon measurements will enable a more detailed identification of the effects.

The results of chemical characterization for two of the filter samples are shown in Figure 5. The samples were collected over multiple hot LA-4 cycles, one with E0, the other with E30. In general, relative to the small GPF core samples collected from the engine operating in the fuel rich-condition, the samples had very low amounts of adsorbed hydrocarbons. The polycyclic aromatic hydrocarbons (PAHs) identified in Figure 5, are typically products of combustion that are soot precursors as well as being identified as carcinogens. Consistent with the previous study [9], the use of E30 appears to have reduced the levels of these compounds. During combustion, the ethanol is thought to interfere with the formation of small soot precursor compounds.

## CONCLUSIONS

The influence of renewable fuel on GDI PM emissions is characterized both in terms of soot oxidation behavior and intermittent vehicle operation. An understanding of soot oxidation behavior is critical to mitigating GDI PM, both in-cylinder and with aftertreatment. Because rich operation, whether at cold start or during load changes, will likely remain the cause of the highest GDI PM emissions, examining the influence of start-stop operation on PM emissions is important as more vehicles adopt start-stop as a fuel economy strategy. Future work continues to analyze the effects of both fuel and operating mode on GDI PM emissions.

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## FY 2014 PUBLICATIONS/PRESENTATIONS

**1.** Storey, J.M.E., Lewis, S.A., Szybist, J.P., Thomas, J.F., Barone, T.L., Eibl, M.A., and Kaul, B. "Novel Characterization of GDI Engine Exhaust for Gasoline and Mid-Level Gasoline-Alcohol Blends," *SAE Int. J. Fuels Lubr.,* vol. 7, pp. 1-8, 2014.

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# III.7 Advanced Combustion and Fuels Research at NREL

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## Overall Objectives

- Address technical barriers of inadequate data and predictive tools for fuel and lubricant 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 Research and Development program for high-efficiency engines with cost-effective emission controls.

## Fiscal Year (FY) 2014 Objectives

- Develop experimental and simulation tools to characterize fuel ignition behavior in support of advanced combustion engine development, especially for low-temperature combustion.
- 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 2014 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 a range of diesel and gasoline range fuels, including over broad temperature sweeps.
  - Evaluated and validated reduced kinetic mechanisms for fuel surrogate compounds and simple blends.
  - Bridged fundamental ignition experiments to engine testing.
  - Explored the effects of lubricating oil on fuel charge autoignition, to support research to mitigate low-speed pre-ignition (LSPI) in gasoline direct injection (GDI) engines.
- Conducted a parametric study with NREL's direct-injection, spark-ignition single-cylinder engine (SCE) research facility to isolate various fuel chemistry effects with the potential to increase engine efficiency, including isolation of heat of vaporization fuel effects.

## 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 advanced biofuels.
  - Establish links between IQT-based ignition characterization and engine-based combustion performance and emissions.
  - Collaborate with other DOE and Canadian national laboratories, academia, and corporate industrial partners via the Coordinating Research Council and Advanced Engine Combustion Memorandum of Understanding to:
    - Expand fuel 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.
  - Explore oil droplet contamination of fuel/air charge on ignition kinetics, to mitigate LSPI in GDI engines.

- Continue parametric GDI single-cylinder engine research to isolate various fuel chemistry effects with the potential to increase engine efficiency, and correlate novel fuel ignition measurements adapted from the IQT.

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## INTRODUCTION

Development of more energy-efficient and environmentally sustainable transportation vehicles demand simultaneous increases in powertrain efficiency and reduction in emissions. Necessary advances in internal combustion engines for these vehicles 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. Significant research is necessary to understand the relationships between fuel chemistry and engine performance and emissions to advance internal combustion engine efficiency, reduce emissions, and eliminate barriers for increased use of alternative and renewable fuels. The DOE Vehicle Technologies Office's Fuel and Lubricant Technologies program supports R&D to address these needs, including 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.
- Supporting development and validation of accurate, efficient fuel kinetic mechanisms.
- Using engine-based studies to correlate bridging data for experimental and simulation efforts.

AC&F's team members closely collaborate with relevant industry stakeholders, academic researchers, and DOE and Canadian national laboratories colleagues. AC&F participates in the DOE Advanced Engine Combustion Memorandum of Understanding, ensuring our work is in close alignment with and supports DOE Vehicle Technologies Program's Advanced Combustion Engines 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 2014 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). In addition, AC&F collaborated with Dr. Stephanie Villano at CSM in her research on high-pressure rate rules for detailed modeling of low-temperature alkane oxidation under diesel-like conditions.

## RESULTS

### Ignition Kinetics Research

During FY 2014, 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, focusing on development of the IQT as an experimental research platform to quantify fuel autoignition behavior, allowing links to fuel physicochemical properties [1]. NREL's development of the IQT into a research platform provides an alternative source of experimental kinetics data, complementing data voids present with shock tubes, rapid compression machines, and jet-stirred reactors. 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 expanded IQT operation beyond its intended operating point to measure ignition delay time and calculate Derived Cetane Number [4]. Collaboration with Prof. Tony Dean and Prof. Greg Bogin at CSM resulted in characterization of the IQT and understanding of the unique critical experimental ignition data produced [2,3,5,6]. A valuable collaboration with Prof. J. Y. Chen at University of California, Berkeley, CSM and NREL developed a KIVA-3V computational fluid dynamics (CFD) model of the IQT injection and combustion process, coupling it with CHEMKIN to evaluate kinetic mechanisms. 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 experimental and simulation studies with the IQT to probe negative temperature coefficient region ignition for $C_7$ isomers [6] and larger compounds, including 2,2,4,4,6,8,8-heptamethylnonane [7]. NREL's focus on larger compounds expanded to larger *n*-alkanes, including decane ($C_{10}H_{22}$), dodecane ($C_{12}H_{26}$, a jet fuel surrogate), and hexadecane ($C_{16}H_{34}$, a diesel surrogate). Conducted in collaboration with CSM, Lawrence Livermore National Laboratory, University of California, Berkeley, and Argonne National Laboratory, this research provides critical feedback for development of both full and reduced mechanisms. An FY 2014 publication included validation of a new 237-species skeletal reduced mechanism for *n*-hexadecane (developed by J. Y. Chen at University of California, Berkeley) [8], highlighted in Figure 1. *n*-Hexadecane defines the cetane number value of 100, and is included in a new diesel surrogate blend developed project under Coordinating Research Council project AVFL-18 [9].

NREL applied the temperature sweep study techniques developed above to gasoline reference fuels. The project involved a preliminary study of gasoline surrogate primary reference fuel (PRF) and toluene standardization fuel (TSF) blend ignition performance over broad parametric space. Blends with ethanol were also studied. Ignition delay data were compared to the Research and Motor Octane Numbers (RON and MON) to determine if a new bench-scale test platform and methodology could one day supplement octane number tests and provide a more comprehensive measurement of fuel ignition knock resistance performance relevant to modern engine technologies, such as GDI. IQT-based measurements highlighted significant differences in ignition performance at Derived Cetane Number conditions for different fuel blend chemistries having identical octane numbers. IQT-based measurements also provide valuable information on low-temperature heat release and ignition performance over variable temperature (shown in Figure 2), which will be critical to support development of advanced combustion technology such as reactivity controlled compression ignition and gasoline compression ignition. A review of the preliminary results with members of the USCAR Fuels Working Group resulted in significant interest.

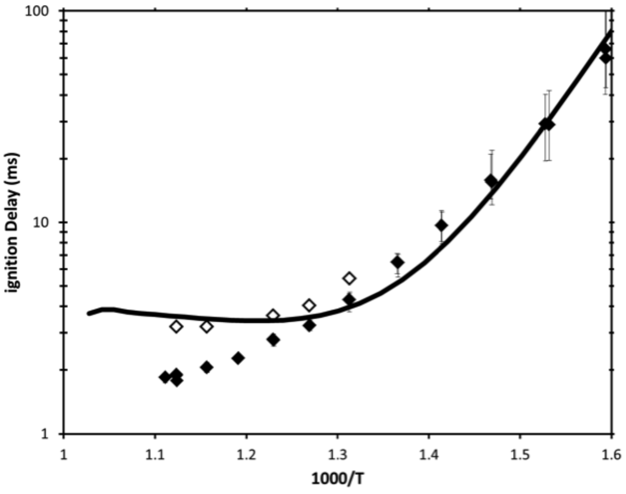


**FIGURE 1.** Comparison of IQT model-predicted ignition delay (ID) and measured ID for n-hexadecane: (■) 0-dimensional adiabatic batch model, (<>) KIVA CFD model, and (◆) IQT experiment. For ID less than ~40 ms, spray physics comprise a significant portion of total ID, so full CFD modeling in KIVA was used to test the mechanism instead of the 0-D model.

## Lubricants Research

NREL also applied IQT-based research to LSPI, a limiting factor for high compression ratio, downsized, highly-boosted GDI engines. While the root cause of LSPI is poorly understood, one hypothesis is that lubricating oil micro-droplets ejected from the piston rings are autoigniting, igniting the cylinder charge prior to spark. A preliminary study established that the IQT could detect ignition performance differences between fuel/air mixtures with and without trace amounts of lubricating oil, as well as differentiate between lubricating oil chemistries. The preliminary study utilized gasoline surrogates doped with trace amounts of known cetane improvers, as surrogates for lubricating oil, operated over GDI like conditions where LSPI is known to occur. As shown in Figure 3, the surrogate work demonstrated that the IQT could measure ignition differences between compounds and doping levels. This research is currently being extended to actual lubricating oil compounds. With these data, the validity of the LSPI lube oil hypothesis can be evaluated quantitatively in a well-controlled, repeatable test which complements engine studies.

## Gasoline Direct Injection Engine Research

NREL also employed the GDI SCE research facility in a parametric study to isolate various fuel chemistry effects with the potential to increase engine efficiency. This project included a significant upgrade to the SCE to add upstream fuel injection to permit isolation of heat of vaporization fuel effects. The research was intended to complement research conducted by others related to GDI engine performance gains permitted by octane increases, notably Oak Ridge National Laboratory [10], Massachusetts Institute of Technology [11], AVL [12], and Ford Motor Company [12-14]. This study included knock limited and peak pressure limited spark advance/load sweeps of a research grade gasoline (Coordinating

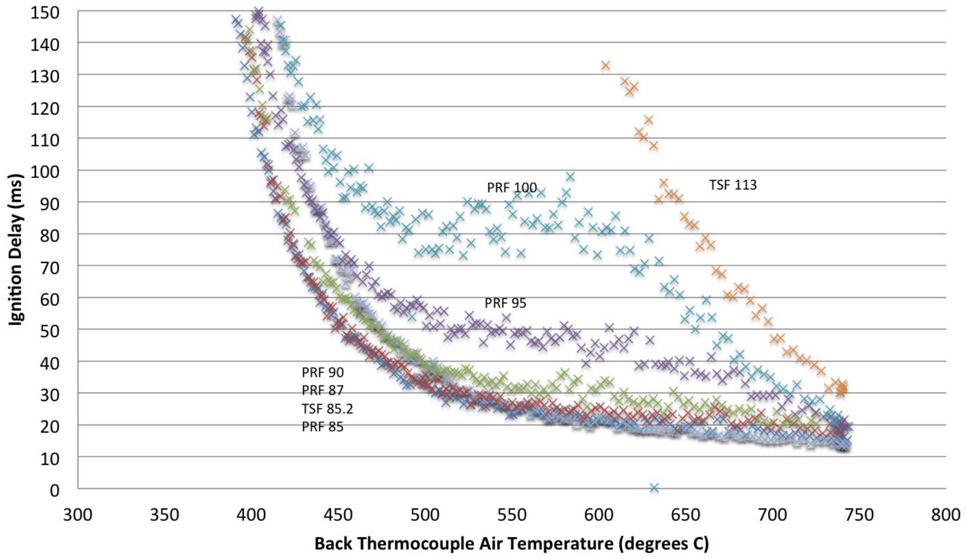
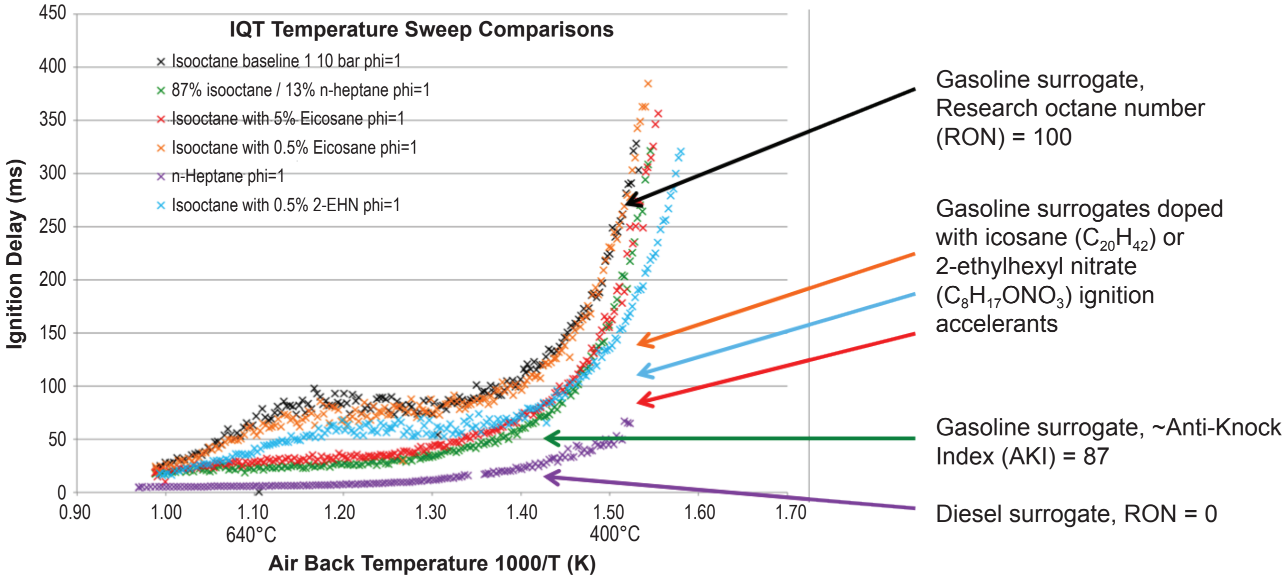


**FIGURE 2.** Ignition delay for a range of various PRFs and TSFs with defined octane numbers were studied over GDI-relevant conditions. These data show the potential to provide a significantly more descriptive measurement of knock resistance with a relatively simple bench-scale test.



Gasoline surrogate, Research octane number (RON) = 100

Gasoline surrogates doped with icosane ($C_{20}H_{42}$) or 2-ethylhexyl nitrate ($C_8H_{17}ONO_3$) ignition accelerants

Gasoline surrogate, ~Anti-Knock Index (AKI) = 87

Diesel surrogate, RON = 0

**FIGURE 3.** Ignition delay performance under GDI conditions of various gasoline surrogates for reference along with iso-octane (RON = 100) doped with cetane improvers. The preliminary study supports use of the IQT to investigate lubricating oil chemistry effects to mitigate LSPI.

Research Council FACE research gasoline “B”) and ethanol blend, E25, (a 25% ethanol blend of FACE “B”) with direct and upstream fuel injection, as illustrated in Figure 4. This project was intended to establish operation for NREL’s SCE as a tool to evaluate advanced gasoline fuel blends in terms of efficiency potential. While other researchers often focus on engine combustion development (exhaust gas recirculation tolerance, spark advance limits, boost levels, etc.), their research is generally conducted with fuels from a RON or MON perspective. NREL’s longer-term contribution is to evaluate fuel performance in engines from a broader fuel chemistry perspective. This includes linking SCE-based performance and efficiency studies with other fuel properties beyond single-condition measurements like RON and MON, such as advanced heat of vaporization characterization and IQT-based temperature sweeps of ignition delay. These experiments provided the baseline

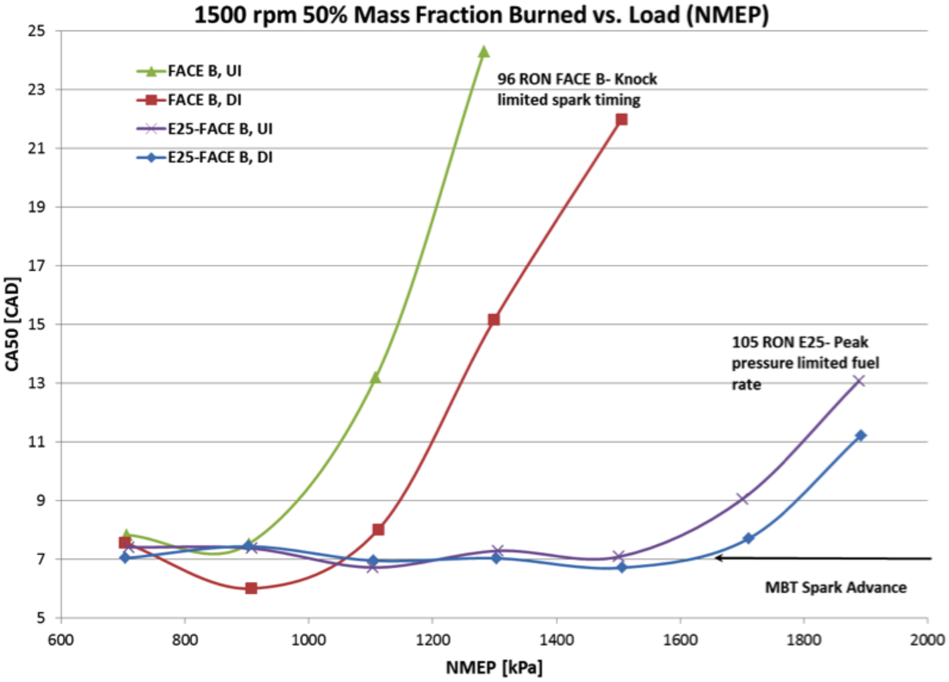


**FIGURE 4.** 1,500 RPM load sweeps in direct injection (DI) and upstream injection (UI) modes. Upstream fuel injection permitted the separation of heat of vaporization effects.

conditions and data necessary to continue studies in FY 2015 with various cellulosic biomass-derived oxygenate blends.

## 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. The recently developed temperature sweep capability also enabled lubricant effects studies for LSPI as well as novel investigations of gasoline knock resistance. Complementary research SCE experiments produced data that may permit links with other fuel properties beyond single-condition measurements like RON and MON, such as advanced heat of vaporization characterization and IQT-based temperature sweeps of ignition delay. The resulting fuel performance measurements and models will enable manufacturers to develop advanced engines that operate on higher blends of renewable fuels.

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# IV. Petroleum Displacement Fuels/Fuel Blending Components

The incorporation of biofuels and other blending streams into petroleum gasoline and diesel can substantially lower greenhouse gas emissions as well as enhance energy security. Ethanol is now ubiquitous in gasoline, and biodiesel is often blended at low levels or as a 20% blend commercially. Both of these fuels benefited from previous investments made by the Fuels Technology subprogram into understanding the effects these components might have on combustion, emissions, lubrication, and materials. Similarly, future blending components are now being studied to understand benefits and potential issues of their incorporation into transportation fuels. In addition to performance and compatibility measures, well-to-wheel analysis of greenhouse gas emissions is performed to understand the tradeoffs between the emissions from manufacturing the blending component and its tailpipe emissions.

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# IV.1 New Fuels and Lubricants Properties, Emissions, and Engine Compatibility Assessment

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## Overall Objectives

- Identify fuel properties and specific combustion products to provide data for a better understanding of the properties, combustion characteristics, and systems compatibility of advanced fuels and lubricants
- Identify the biofuel contribution to the organic fraction of engine exhaust particulate matter (PM) emissions

## Fiscal Year (FY) 2014 Objectives

- Demonstrate a method for determining the chemistry of PM as a function of size of the PM
- Identify the potential sources of hydrocarbon-bound oxides of nitrogen (NOx) in advanced combustion modes

## FY 2014 Accomplishments

- Developed a chemical analysis method for a defined soot particle size range utilizing a micro-orifice uniform deposit impactor (MOUDI) and thermal/pyrolysis gas chromatograph-mass spectrometry.
- Measured nitroalkanes in the exhaust of a reactivity-controlled compression ignition (RCCI) engine. Nitroalkanes can be a NOx sink at some operating points.

## Future Work

Evaluate the size dependent chemical composition of particulate matter derived from the combustion of advanced biofuels and biofuel blends.

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## INTRODUCTION

The purpose of this project for many years has been to accelerate the implementation of advanced fuels and high-efficiency engines by characterizing exhaust species unique to their operation, as well as those species resulting from novel, low-friction lubricant formulations. Using analytical science to address the complexities of engine operation, fuel/lubricant chemistry, and control technologies is a core capability of ORNL's Fuels, Engines, and Emissions Research Center. Analytical methodologies and techniques are constantly evolving to identify barriers to efficiency caused by exhaust species that are created by advanced combustion modes or novel fuel and lubricant chemistries. This activity serves as a resource for several Fuel and Lubricant Technologies projects at ORNL as well as for industry partners. In FY 2014, we addressed two areas of concern: PM from gasoline direct-injection (GDI) engines and unique nitrogen-containing hydrocarbons (HCs) associated with advanced combustion.

GDI engines can offer improved fuel economy and higher performance over their port fuel-injected counterparts, and are now appearing in increasingly more U.S. and European vehicles [1]. Small displacement, turbocharged GDI engines are replacing large displacement engines, particularly in light-duty trucks and sport-utility vehicles, in order for manufacturers to meet more stringent fuel economy standards. GDI engines typically emit more PM than port fuel-injected engines, with the highest emissions during periods of rich operation such as start-up and acceleration. These emissions are thought to occur due to heterogeneities in the mixing of fuel and air in the cylinder; locally rich zones near cooler surfaces can lead to pool fires and other rich combustion events. Morphological evidence in previous studies has shown that GDI soot particles contain a variety of primary particle sizes, from <10 nm to 50 nm [2]. Diesel soot, in contrast typically has a very narrow size range for primary particles; for the modern light-duty diesel engines in our laboratory, the primary particle size is 22-24 nm. Beyond the morphology, size-dependent PM chemistry may offer insight into the origins of the PM in GDI combustion and thus lead to strategies that mitigate GDI PM formation.

With the recent development of advanced, low-temperature engine combustion modes, such as RCCI, that use dual fuels such as gasoline and diesel, a need for new analytical methods to perform analysis for atypical exhaust species has developed. Atypical organic species originating from the combustion products dual fuel modes include small polar heterogeneous organic compounds such as nitromethane, nitroethane and nitrophenol. These compounds are believed to be formed when $NO_2$ reacts with the large amount of unburned HCs typical of low-temperature combustion regimes, and can form a "sink" for *measured* NOx that is then liberated after the exhaust passes over an oxidation catalyst.

## APPROACH

### Size-Selective PM Chemistry

A light-duty GDI engine was operated under fuel-rich conditions ($\lambda$=0.90) at typical loads for acceleration on a 91 anti-knock index certification grade gasoline. Air-fuel ratio and soot carbon were monitored during acceleration transients to determine an operating condition (2,600 rpm, 8 bar brake mean effective pressure) that was representative, yet could be sustained in steady-state operation in order to sample the PM. The exhaust was diluted and the PM was sampled with a MOUDI onto fluorocarbon filter substrates for several hours. The MOUDI uses unique, rotating stages to deposit aerodynamically sized particles onto impaction plates. In addition to the MOUDI sample, an integrated filter sample (all sizes) was obtained at the same time for comparison. A new method for soot HC speciation [3] is introduced in this study using a direct, thermal desorption/pyrolysis (TDP) inlet for the gas chromatograph–mass spectrometer (GC-MS). Soot was harvested from the substrate using a gentle vacuum and placed directly into Inconel thimbles for TDP-GC-MS analysis. Typically, about 200-500 µg of soot is needed. The soot was desorbed under helium using a temperature ramp from 40–325°C. The desorbed compounds were separated on a DB-5 column and analyzed with positive ion MS. The second pyrolysis step was a flash heating to 550°C, followed by GC-MS analysis. The pyrolysis results in the formation of small organics that reveal the surface structure of the soot.

After collection, a novel soot transfer method was developed which incorporates the transfer of the soot from the filter to the sample vessel by use of vacuum. The thermal analysis of the soot sample was conducted by purging the sample with helium then thermally desorbing it at 300°C onto the head of the GC column for separation and detection by the MS.

### Nitroalkanes in RCCI Exhaust

A novel solid phase extraction collection method was developed for the analysis of these compounds. This method has shown an 8x improvement of sensitivity in our laboratory when compared to direct dilute exhaust measurement via canister or bag sampling, typically done for HC speciation of exhaust. The engine exhaust is first diluted to lower its temperature dewpoint and then dilute exhaust is sample over solid phase extraction cartridges containing magnesium silicate and silica gel which make the cartridges highly-selective to polar organic compounds. More importantly, the abundant non-polar HC species in RCCI exhaust, such as fuel components, do not get retained by these cartridges, thus making the analysis much less cumbersome. The nitroalkanes are then eluted from the cartridge with solvent and analyzed via GC-MS.

## RESULTS

### Size-Selective PM Chemistry

Results showed the presence of polycyclic aromatic hydrocarbon (PAH) compounds in the PM, including downstream of the catalytic converter. PAHs, fuel and oil HCs were present in the thermal desorption analysis. Figure 1 compares the presence of fuel-borne PAHs with the major PAH formed in combustion desorption analysis. Figure 1 compares the presence of fuel-borne PAHs with the major PAH formed in combustion (pyrene). The data are shown relative to the predominant alkane (C18) to normalize for different loadings on the stages. Stages 5 and 6 (0.7-1 µm) and 7 and 8 (0.3-0.5 µm) were combined due to the small sample size. Stage 9

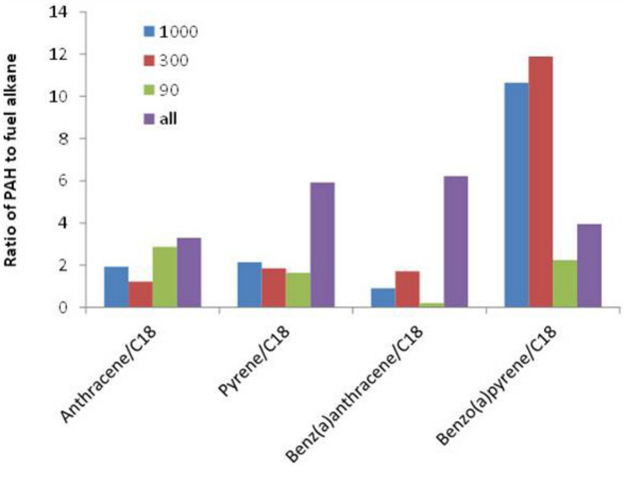

**FIGURE 1.** Ratio of adsorbed PAHs to predominant fuel alkane (C18) on soot for various size fractions as well as an integrated filter sample. Anth = anthracene, Pyr = pyrene, BaA = Benz(a)anthracene, BaP = Benzo(a)pyrene.

(0.09 µm) was analyzed individually because it had the most PM present, which is typical for GDI engines.

The data for the heaviest PAHs, benz(a)anthracene and benzo(a)pyrene, showed that there levels were higher relative to the smallest particle size fraction. If the large particles represent PM from incomplete combustion, they would be expected to have higher levels of PAH than PM from regions with more complete combustion. The lack of trend for anthracene and pyrene may result from these PAH being formed in combustion as opposed to being the result of unburned heavy fuel fractions.

### Nitroalkanes in RCCI Exhaust

Figure 2(a) shows the results of this sampling and analysis method, and Figure 2(b) illustrates the canister method results for the same kind of exhaust. The difference in nitromethane abundance values between the solid phase extraction cartridge and canister reflects

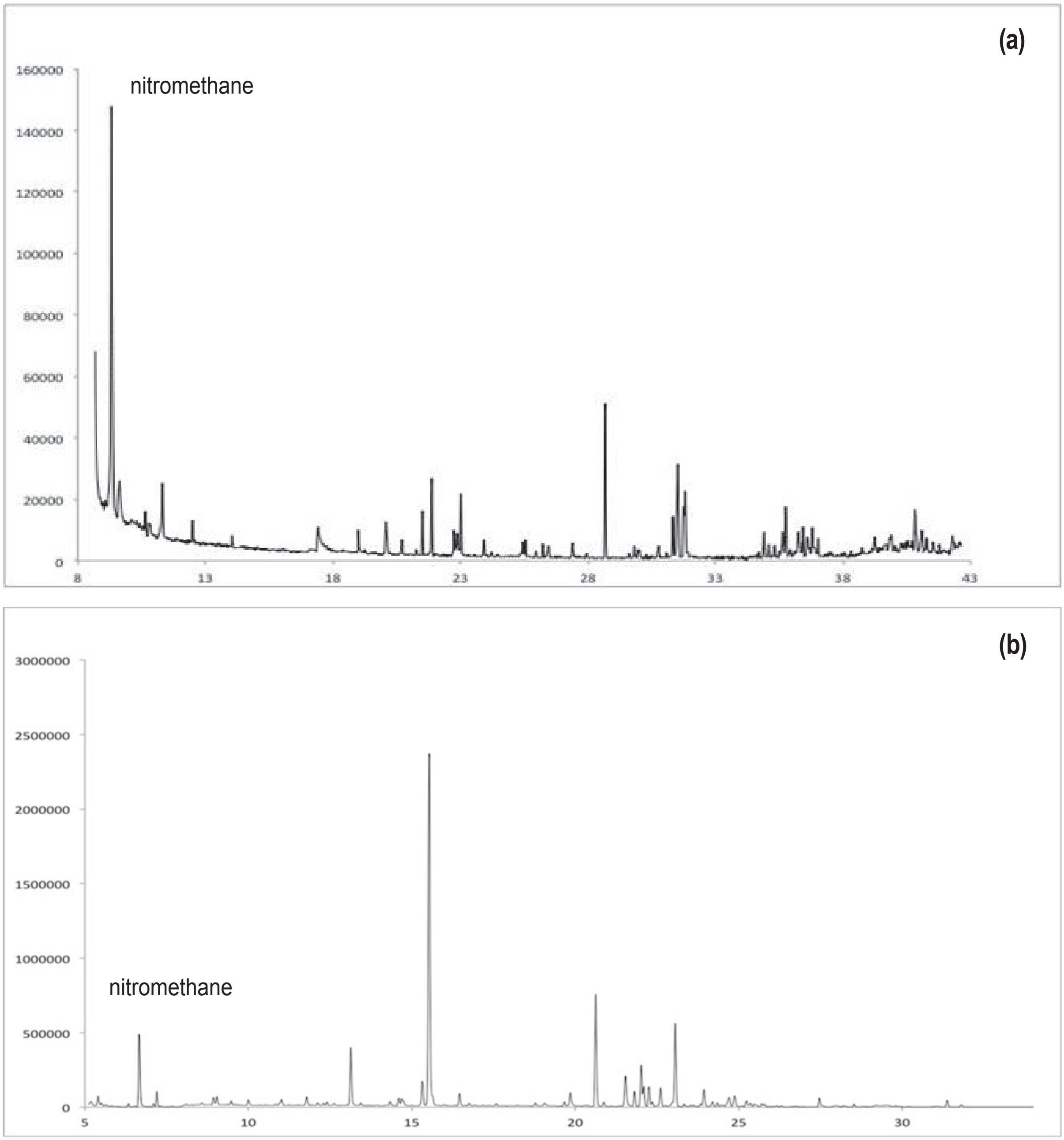

**FIGURE 2.** GC-MS traces of nitroalkanes extracted from RCCI exhaust. (a) results from the solid phase extraction method. (b) results from the canister method.

the positive biasing of the phase towards polar organic compounds, such as nitroalkanes, thus allowing a larger sample volume without the swamping of the gas chromatograph/ mass spectrometer with nonpolar organic species, such as toluene and the xylenes, abundant in RCCI engines operating with gasoline as their non-reactive fuel. In addition, the solid phase extraction samples show a presence of nitroethane and nitrophenol in the engine exhaust. Nitroethane and nitrophenol were not detected in the canister samples due to its lack of sensitivity. While research is continuing on nitroalkanes in RCCI exhaust, preliminary results indicate that as much of 40% of the exhaust NOx can be “lost” in nitroalkanes and then released by the oxidation catalyst. This method will provide valuable data for understanding the interactions between $NO_2$ and unburned HCs in low-temperature combustion modes and exhaust aftertreatment.

## CONCLUSIONS

The advanced chemical characterization effort has focused on chemical speciation of engine exhaust gases and particles from both advanced biofuels and novel combustion methods. The TDP-GC-MS analyses are ongoing for several PM size ranges providing insight into unique particle chemistry. The soot thermal/ pyrolysis method and characterization efforts have led to the identification of compounds that make up a large fraction of the PM’s organic carbon component which is critical for understanding the influence of biofuel on this PM fraction . The identification of nitroalkanes in RCCI exhaust will lead to potential strategies to further mitigate NOx emissions from these engine systems. RCCI and other advanced combustion modes which utilize biofuels are expected to have more precursor species for nitroalkanes, thus making their measurement critical as the use of biofuels expands in advanced combustion.

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# IV.2 Unconventional Hydrocarbon Fuels

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## Overall Objectives

- Facilitate the successful introduction of future fuel feedstocks compatible with future advanced combustion engines to help reduce the U.S. dependence on foreign oil.
- Develop analytical approaches correlating fuel component molecular structure to fuel properties and fuel performance.

## Fiscal Year (FY) 2014 Objectives

- Utilize one- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy, and gas chromatographic techniques, to correlate fuel substructures with fuel properties, including diffusion-ordered spectroscopy (DOSY) and heteronuclear correlation experiments.
- Attend an Analytical Work Group Meeting to foster a collaborative relationship and information exchange with groups such as Natural Resources Canada (CanmetENERGY) and the Coordinating Research Council (CRC).

## FY 2014 Accomplishments

- Continued development of new NMR approaches for identifying structure-property relationships of diesel fuels, focusing on the two-dimensional NMR technique, single-bond proton-carbon correlation (heteronuclear single quantum coherence, or HSQC).
- PNNL and CanmetENERGY continued collaboration to develop structure-property relationships for diesel fuel lubricity using NMR and gas chromatography-field ionization mass spectrometry data.
- Continued collaborative efforts with the CRC through participation in the Fuels for Advanced Combustion Engines (FACE) Working Group, and contributions to CRC Projects: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling (AVFL-18/18a), Characterization of Advanced Alternative and Renewable Fuels (AVFL-19a), and Data Mining of FACE Diesel Fuels (AVFL-23).
- Presented an analysis of shale oil-derived diesel fuel at the 248th American Chemical Society National Meeting, August, 2014 in San Francisco, CA [1,2].
- Attended the Advanced Fuel and Engine Efficiency Workshop, February 2014, Baltimore, MD, and a FACE Working Group meeting at Oak Ridge National Laboratory, May 2014, both sponsored by the CRC.

## Future Directions

- Continue to develop structure-property correlations built upon data obtained from current fuel sets.
- Identify key molecular structures 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 Coordinating Research Council's Working Group and the Alternative and Surrogate Fuels projects.

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## 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 transport, unconventional hydrocarbon fuels may 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 may be unreliable predictors for unconventional fuels.

Chemistry and structural differences that occur with unconventional fuels may result in new fuel requirements for use with current engines and fuel system components, or future advanced combustion and after-treatment performance demands may drive fuel requirements in order to achieve optimum performance. PNNL will work collaboratively with other laboratories in developing and employing a full suite of analyses and engine tests for unconventional fuels, notably upgraded shale oil, upgraded bitumen from oil sands, and renewable sources. 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 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 drastically impact the introduction of these fuels. An additional 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 reblends of three FACE diesel fuels.[†] Biofuels analyzed included products of raw and hydrotreated pyrolysis oils and oils resulting from hydrothermal liquefaction.

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 two-dimensional NMR techniques, such as HSQC; two-dimensional gas chromatography; and DOSY. Two-dimensional NMR techniques reduce overlapping signals produced from the structures of hundreds to thousands of chemical components within a fuel and in some cases, these techniques isolate structural 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 individual chemical components contained within a fuel sample, which can then be further correlated with fuel properties and performance. DOSY is expected to provide diffusion information that is related to the molar volume distribution of the components and may correlate with lubricity, soot formation, kinematic viscosity, and cloud point [3]. 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 quantify contributions of fuels from alternate feedstocks entering into the market. While these analysis techniques are complex, once key parameters are identified, the analyses can be streamlined to select for the identified key 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

Building upon our FY 2013 efforts utilizing two-dimensional NMR techniques to elucidate more detailed structural information from fuel samples, PNNL has continued to apply heteronuclear correlation techniques to several sets of fuels, including fuels from commercial, unconventional, and renewable sources. Many of these fuels were obtained through our collaborations with the CRC. The approach PNNL and others have applied to one-dimensional NMR spectra is to define discrete regions as belonging to specific chemical environments. Because of the large number of 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. 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 alkyl- 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

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[†] 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.

on discrete spectral regions in one dimensional NMR. Figure 1 overlays the aromatic regions of three HSQC spectra of shale oil provided by Red Leaf Resources, at several stages during the upgrading process [1,2]. In this figure, the effect of upgrading can clearly be observed as fused-ring aromatics and species containing heteroatoms are reduced. Concomitantly, naphthenic species are produced. This shift in chemical speciation may be expected to have significant effects on the properties of the resulting fuel. Future work will determine the magnitude of these effects and whether the effects will be discernable. While two-dimensional NMR techniques, such as HSQC, are more complex and sometimes more time consuming to obtain, for cases where overlap of important species is expected, these techniques can improve our understanding of the species present.

Previous work at PNNL examined a series of fuels using the distortionless enhancement of polarization transfer (DEPT) NMR technique. Because of the complexity of the aliphatic region of the fuels being examined, overlapping resonances in DEPT spectra were not sufficiently resolved. The chemical shift region associated with 2-methyl-alkanes in the DEPT spectra was found to be crowded with resonances from substructures having overlapping chemical shifts, introducing unacceptable ambiguity in making peak assignments. HSQC measurements, with and without spectral editing provide a much cleaner and clearer assessment of not just 2-methyl-alkanes, but also the presence of other tertiary carbon substructures. Figure 2 shows the aliphatic region of an HSQC spectrum for a gas-to-liquid (GTL) fuel with tertiary carbons identified from the left and several resonances assigned to methylenes adjacent to tertiary carbons identified on the right. Similar information was obtained for more complex fuels than GTL, but the GTL spectrum is presented as a simplified example. This assessment of 2-methyl-alkanes 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, and other tertiary carbons, have implications for both octane and cetane number by adding one or more branch points over the *n*-alkane. By using HSQC measurements, resonances assigned to 2-methyl-alkanes can be determined and quantitatively assessed using one-dimensional NMR techniques.

In collaboration with researchers at CanmetENERGY, PNNL undertook a comprehensive statistical analysis of the proton-decoupled, carbon-13 ($^{13}C\{^1H\}$) and $^1H$ NMR data for four fuels and distillate cuts from each fuel. This analysis addresses two questions. First, do certain NMR features attributable

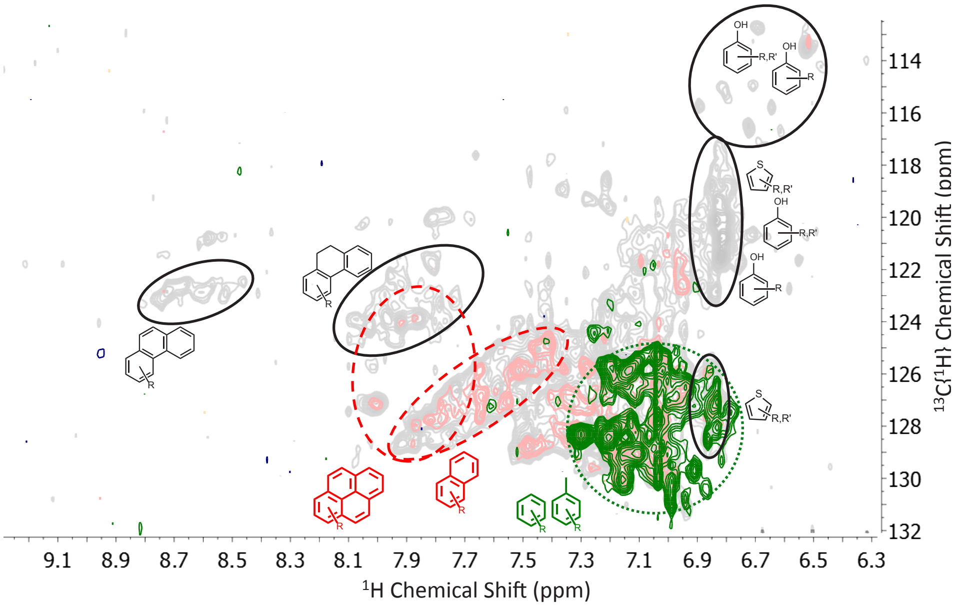

**FIGURE 1.** Overlaid HSQC NMR spectra of shale oil at three stages of upgrading. This two-dimensional NMR spectrum is a contour plot showing the correlation of protons attached directly to carbons of the fuel components in the aromatic region. The horizontal axis represents the $^1H$ NMR and the vertical axis represents the $^{13}C\{^1H\}$ NMR. The overlaid spectra show the successive elimination of fused-ring aromatic species and aromatic species containing heteroatoms as the stabilized shale oil (gray/black) is mildly hydrotreated (red dash), and fully hydrotreated (green dot). Representative chemical structures are shown for each spectral region and stage of upgrading.

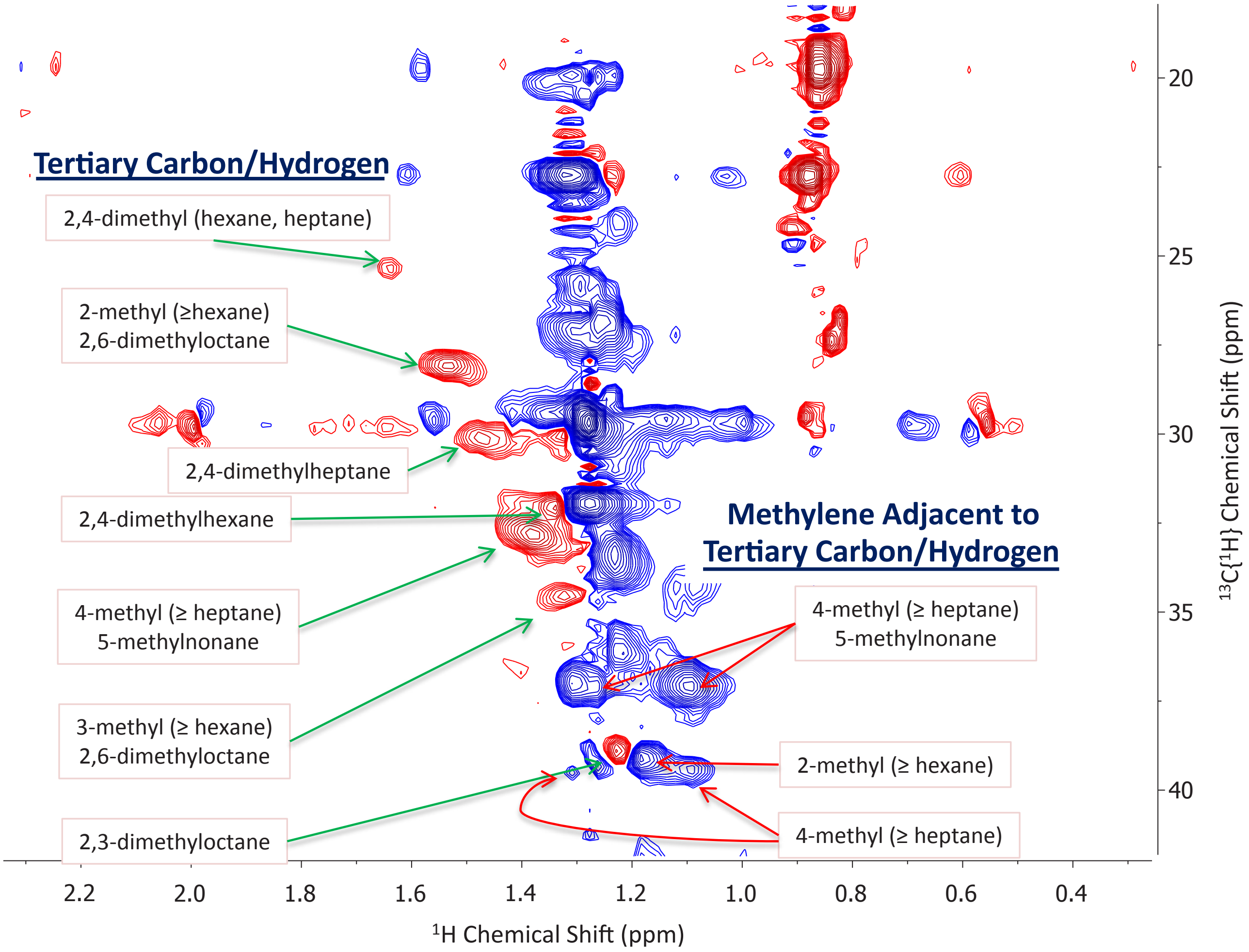

**FIGURE 2.** Aliphatic region of an HSQC spectrum for a GTL diesel fuel. This two-dimensional NMR spectrum is a contour plot showing the correlation of protons attached directly to carbons of the fuel components in the aliphatic region of each spectrum. The horizontal axis represents the $^{1}$H NMR and the vertical axis represents the $^{13}C\{^{1}H\}$ NMR. Carbons directly bound to a single hydrogen or three hydrogens (CH or $CH_3$) are in red to indicate positive contours and carbons directly bound to two hydrogens ($CH_2$) are in blue to indicate negative contours. HSQC and other two-dimensional NMR techniques are particularly useful for resolving areas of overlapping NMR resonances. Identifying position and carbon type provides insight into molecular substructures associated with a specific or chemical or class of chemicals.

to molecular substructures in the fuel correlate with wear scar diameter (WSD)? Second, can these features be used to predict WSD of the fuels? Fuels having widely variant properties were used to probe these relationships, including finished diesel fuels having combinations of high-, low-, and ultra-low sulfur content, and combinations of high and low diaromatic content. These fuels were fractionated into boiling point cuts to isolate viscosity effects on lubricity. Correlation analysis shows that certain spectral regions do correlate with the WSD of the test fuel set. These correlated NMR resonances lie in spectral regions for compounds known to impact the lubricity of diesel fuels, compounds such as hydroaromatics, such as substituted tetralins and naphthenes, and methylene groups at least four carbons away from a methyl group or branch point. Partial least squares (PLS) regression using these peaks as x-variables and the WSD as the y-variable show that the NMR data can be used to predict lubricity. Figure 3 shows the results of the PLS regression. The measured WSD value is plotted on the x-axis. The WSD predicted from PLS regression is plotted on the y-axis. The data values follow the line, with an R-squared value of 0.84 and a validation root mean squared error (σ) of 71.2 µm. This error is lower than the ASTM-specified reproducibility value of 90 µm, suggesting this PLS model can be used to predict wear scar diameter with accuracy sufficient for practical application.

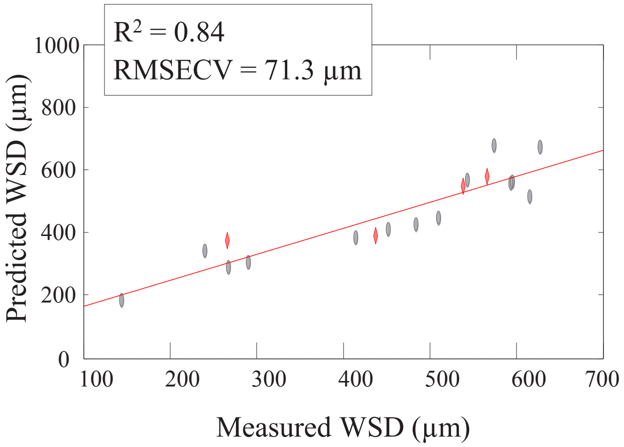

**FIGURE 3.** Predicted versus measured WSD. Using PLS regression, WSD is predicted from $^{13}C\{^1H\}$ and $^1H$ NMR spectral regions corresponding to molecular substructures of interest having either strong positive or negative correlations, including hydroaromatics, such as tetralins and naphthenes, and methylene groups four or more carbons away from a terminal methyl group or branch point. Gray ovals represent training data and red diamonds represent cross validation data used to test the correlation.

## CONCLUSIONS

- PNNL has continued developing 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 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.
- Clear advantage for structural and sub-structural speciation can be seen from the results of two-dimensional NMR studies. These results are being translated into actionable correlations.

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# IV.3 Emissions and Operability of Gasoline, Ethanol, and Butanol Fuel Blends in Recreational Marine Applications

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## 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) 2014 Objectives

- Assess engine cold-start capability operating on 16 vol% blend of iso-butanol in gasoline (iB16) compared to 10 vol% ethanol in gasoline (E10)
- Complete engine tear-down inspections and compare iB16 and E10 engine components
- Perform end-of-season emissions and performance testing on engines operated on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends comprised of 5 vol% ethanol, 8 vol% iso-butanol, and 87 vol% gasoline
- Perform additional field testing of vessels operated on tri-fuel blends

## FY 2014 Accomplishments

- Engine cold-start performance was found to be nearly identical between iB16 and E10 fuel blends at 24°C. The data indicate a reduction in time to start at -1°C for the Mercury four-stroke outboard engine operating on iB16 compared to E10 fuel.
- Engine tear-down inspections performed after full useful life durability testing indicate similar wear characteristics between control engines operated on E10 and test engines operated on iB16.
- End of season testing performed on field test engines operated on tri-fuel blends indicate similar gaseous emissions and engine performance as E10 test fuels. All engines remained below the Environmental Protection Agency (EPA) emissions standards for hydrocarbons plus oxides of nitrogen and carbon monoxide, and no engine runability or durability issues were encountered during the testing program.
- An additional 100 hours of field testing of two vessels operating 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.

## Future Directions

- Determine critical blend level for iso-butanol in laboratory test engines
- 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
- Perform end-of-season testing on recreational marine engines operated on 3.5 wt% oxygen (E10 equivalent) tri-fuel blends

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## INTRODUCTION

The Renewable Fuel Standard under the Energy Independence and Security Act of 2007 mandates an increase in the volume of renewable fuel to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022 [1]. 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 (E15) in model year 2001 and newer light-duty motor vehicles [3].

The impact of extended ethanol blends and other alcohol fuels on recreational marine engines and vessels is widely unknown. However, given the dominant engine 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.

## RESULTS

Recreational marine engines produced by several different engine manufacturers covering a range of technologies, engines sizes and power ratings were included in the test program in order to ensure a comprehensive assessment. An overview of the engine specifications and area of focus for the tests is presented in Table 1.

### Engine Cold-Start Assessment

Three outboard engines were selected for cold-start assessment which include a 200-HP Evinrude direct fuel injection two-stroke, a 90-HP Mercury electronic fuel injection four-stroke, and a 10-HP Tohatsu carbureted pull-start four-stroke. The engines were instrumented to record engine block temperature, air intake temperature, battery voltage and engine RPM. Each engine was preconditioned for 45 minutes across several operating points from idle to midrange loading on the respective test fuel to ensure the test fuel was fully flushed through the fuel system. After the conditioning was complete, the engine was shut off and remained at the test temperature for 24 hours.

Block temperature was verified prior to each start event. A battery maintainer was used to ensure consistent battery voltage and charge prior to the start event. For each start event for the electric start models, the starter solenoid was energized continuously until the engine started. If the engine did not start within 45 seconds of continuous cranking, the start event was considered a failure. The data was processed and the time to start was determined. For the pull-start engine, the choke was set on the carburetor and the starter rope was pulled until the engine started. The number of pulls to start was recorded. If the engine did not start within 10 pulls, the start event was considered a failure.

**TABLE 1.** Overview of the Test Engines and Respective Test Scope

| Engine Manufacturer | Mercury | BRP Evinrude | Tohatsu | BRP Evinrude | Yamaha |
|---|---|---|---|---|---|
| Engine Model Number | 1F90413ED | E200DHX | F9.8A3 | E135DPX | F90XA |
| Combustion Cycle | Four-Stroke | Two-Stroke | Four-Stroke | Two-Stroke | Four-Stroke |
| Cylinder Configuration | I-4 | V-6 | I-2 | V-6 | I-4 |
| Fuel Induction | EFI | DFI | Carbureted | DFI | EFI |
| Displacement (L) | 1.7 | 3.3 | 0.2 | 2.6 | 1.6 |
| Power (HP) | 90 @ 5,500 | 200 @ 5,500 | 9.8 @ 5,500 | 135 @ 5,500 | 90 @ 5,500 |
| Bore x Stroke (mm) | 82 x 82 | 98 x 73 | 55 x 44 | 91 x 66 | 79 x 81 |
| Test Scope | Cold-Start<br>Teardown | Cold-Start<br>Teardown | Cold-Start<br>Teardown | Tri-Fuel | Tri-Fuel |

EFI – electronic fuel injection; DFI – direct fuel injection

The engines were cold started at 24°C and at -1°C using E10 and iB16. Each alcohol was splash blended with Indolene certification fuel. The cold-start event was performed three times at each temperature set-point, and the average time to start in seconds or average pulls to start is presented. The engines were equilibrated for a minimum of 12 hours between each start event. The seconds to start for the Mercury and Evinrude outboard engine are indicated in Figure 1. As shown, the time to start (seconds) for the Mercury and Evinrude are nearly identical between E10 and iB16 test fuels at 24°C, and at -1°C for the Evinrude. The time to start for the Mercury at -1°C on iB16 was reduced by approximately 40% compared to the ethanol test fuel. It is unclear as to why the time to start was reduced using the iB16 fuel. Additional testing will need to be performed to further validate the results of the -1°C cold start on the four-stroke engine.

Pulls to start for the Tohatsu engine are indicated in Figure 2. As shown, the pulls to start at 24°C were similar for both test fuels. The engine failed to start within 10 pulls on either fuel at -1°C.

## Engine Tear-Down Assessment

Six engines from three different engine manufacturers were tested for the full useful life of the engine. One engine from each set of two matching engines was run for the full useful life on E10 fuel as a control, and the other engine run for the full useful life on iB16. Gaseous emissions were recorded throughout the test program and the data reported in the FY 2013 annual report [5]. All engines remained below the U.S. EPA standards on both fuels. After hour accumulation was completed, the engines were torn down for side-by-side comparisons between the E10 control engine and iB16 test engine. Engine components such as pistons, cylinder heads, cylinder bores, intake/exhaust valves, intake/exhaust ports, connecting rods and rod bearings were inspected.

Tear-down inspection reports indicate similar wear characteristics between E10 and iB16 engines. Carbon buildup on the cylinder heads and pistons (Figure 3) generally appear to be very similar between the E10 and

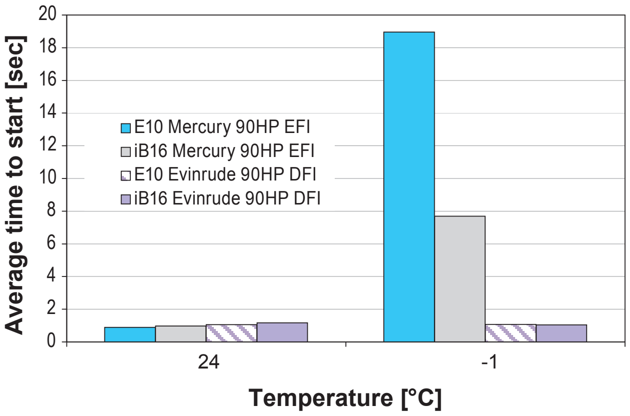

**FIGURE 1.** Average Time to Start for Evinrude and Mercury Engines at 24°C and -1°C on E10 and iB16 Test Fuels

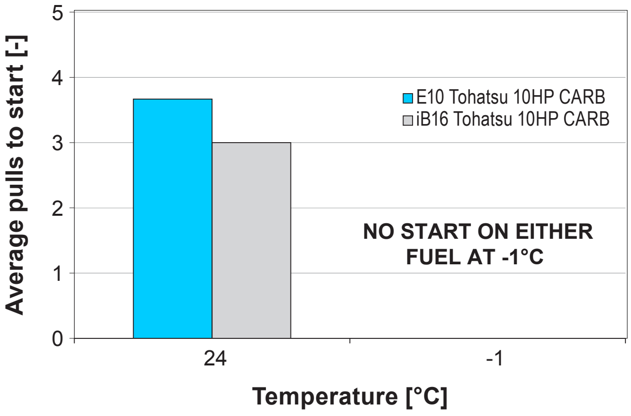

**FIGURE 2.** Average Pulls to Start for the Tohatsu Engine at 24°C and -1°C on E10 and iB16 Test Fuels

**FIGURE 3.** Comparison of Pistons (cylinder number 1) for the Evinrude and Mercury Engines Operated on E10 and iB16

iB16 engines. As indicated in Figure 4, the cylinder bore #1 cross hatch for the Evinrude engines are clearly visible and in good condition between the E10 and iB16 engines. The Tohatsu piston #1 and cylinder head #1 for the E10 and iB16 engine are shown in Figure 5. As indicated, deposits are nearly identical for both engines.

### End-Of-Season Testing

Three engines successfully completed 100 hours of field operation on boats. Two Evinrude 135-HP engines were in service on a 27' Premier pontoon boat located in Washington, D.C., and one 90-HP Yamaha was in service on a 17' Angler boat located in Annapolis, MD. Each vessel operated during the boating season on a tri-fuel blend comprised of 5 vol% ethanol, 8 vol% iso-butanol and 87 vol% gasoline. No engine runability or performance issues were encountered during the 100-hour test program. It is important to note that based on the EPA useful life for recreational marine engines, 100 hours represents approximately three years of operation for a typical boater. All engines remained below the EPA emissions standards on the tri-fuel blend. Engine wide open throttle corrected brake horsepower for one Evinrude 135-HP and the 90-HP Yamaha operating on E10 and tri-fuel blend is shown in Figure 6. As indicated, engine power is nearly identical between the two test fuels.

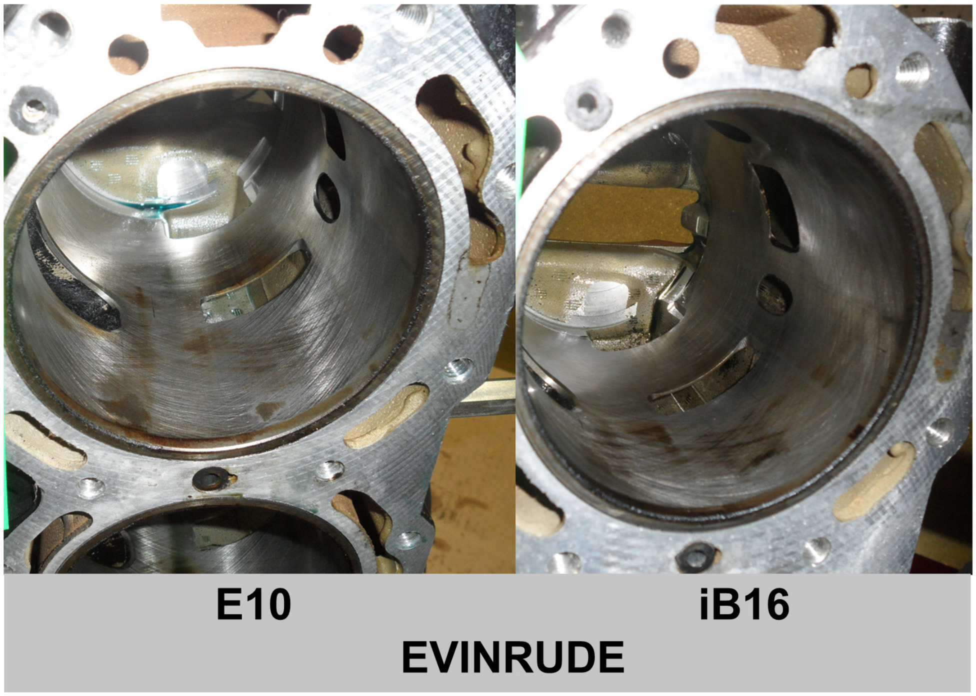

**FIGURE 4.** Comparison of Cylinder Bore (cylinder number 1) for the Evinrude Engines Operated on E10 and iB16

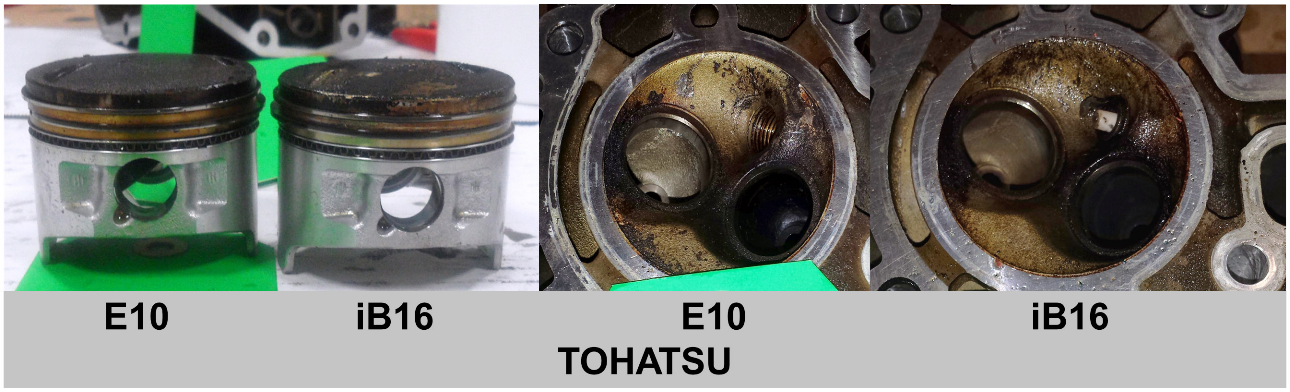

**FIGURE 5.** Comparison of Pistons and Cylinder Heads (cylinder number 1) for the Tohatsu Engines Operated on E10 and iB16

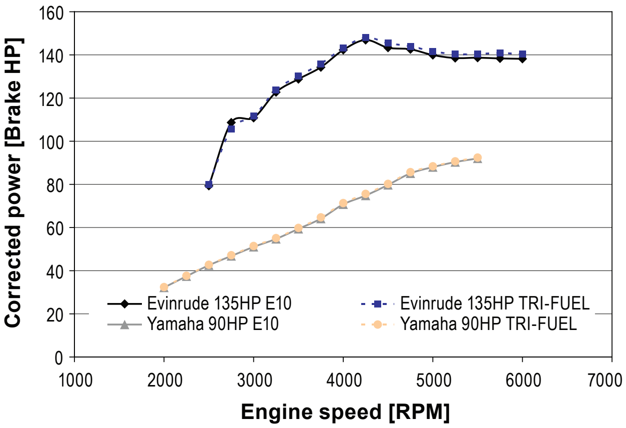

**FIGURE 6.** Corrected Wide Open Throttle Brake Horsepower (CBHP) for Field Test Engines Operated on E10 and Tri-Fuel Blends

## CONCLUSIONS

- Engine cold-start data indicate similar seconds/pulls to start for E10 and iB16 fuel blends at 24ºC for all engines tested. Engine cold start at -1ºC showed little difference between E10 and iB16 fuels for the Evinrude, and a 40% reduction in seconds to start for the mercury on iB16 fuel compared to E10. Additional testing is required to understand the difference in start times between E10 and iB16 fuels at -1ºC for the Mercury engine.
- Full useful life engine tear down and inspection on pistons, cylinder heads, cylinder bores, intake/exhaust valves, intake/exhaust ports, connecting rods and rod bearings indicate similar wear between the E10 control engines and iB16 test engines. No unusual wear, carbon build-up or durability issues were observed with either fuel during the 350-hour (equivalent 10-year useful life) testing.
- Two field test engines were operated on a tri-fuel blend comprising of 5 vol% ethanol, 8 vol% iso-butanol and 87 vol% gasoline. End-of-season exhaust emissions and performance testing was performed at 100 engine hours which represents nearly three years of operation for a typical boater. All engines remained below the EPA exhaust emissions standards and no engine issues were encountered. Engine power and performance remained very similar between E10 and the tri-fuel blend.
- Three field test engines successfully completed an additional 100 hours of operation (for a total of 200 engine hours) on tri-fuel blends. No engine runability or durability issues were encountered. Exhaust emissions and engine performance testing will be completed in due course.

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**2.** Wallner, T., Ickes, A., Wasil, J., Sevik, J. et al., “Impact of Blending Gasoline with Isobutanol Compared to Ethanol on Efficiency, Performance and Emissions of a Recreational Marine 4-Stroke Engine,” SAE Technical Paper 2014-01-1230, 2014, doi:10.4271/2014-01-1230.

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**5.** Wasil, J. McKnight, J., ‘Marine Isobutanol Testing Update’ International Council of Marine Industry Associations - International Marine Engine Committee. October, 2014.

**6.** Wasil, J. and Wallner, T., “Gaseous and Particulate Emissions Using Isobutanol-Extended Fuel in Recreational Marine Two-Stroke and Four-Stroke Engines,” SAE Int. J. Fuels Lubr. 7(3):1062-1068, 2014, doi:10.4271/2014-32-0087.

## SPECIAL RECOGNITIONS & AWARDS/PATENTS ISSUED

**1.** Wisconsin Business Friend of the Environment Award in recognition of the unique emissions sampling equipment developed in support of the U.S. Department of Energy’s search for a more environmentally friendly gasoline alternative. Wisconsin Manufacturing and Commerce May, 2014

**2.** Press release announcing Gulf Racing Fuels supplying three new fuels for marine and all-terrain vehicle use containing 16.1 vol-% iso-butanol (iso-butanol sourced from Gevo) http://

www.biofuelsdigest.com/bdigest/2014/10/02/gevo-sells-isobutanol-to-gulf-racing-fuels-for-marine-and-off-road/

# IV.4 CFD Simulations and Experiments to Determine the Feasibility of Various Alternate Fuels for Compression Ignition Engine Application

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## Overall Objectives

- Biodiesel is a lucrative alternative fuel for compression ignition engines. However, differences in physical and chemical properties of biodiesel and petrodiesel are significant.
  - Development of physics-based nozzle flow and spray models for biodiesel from different feedstocks
  - Development of chemical kinetic models for biodiesel from different feedstocks which are validated against experimental ignition delay data from literature such as the Ignition Quality Tester (IQT$^{TM}$)
  - Develop computational fluid dynamics (CFD) tools to perform engine simulations to gain further insights into biodiesel performance and emission characteristics
- Perform "in-house" engine experiments to support the CFD activity by providing combustion and emission data for biodiesel from different feedstocks.

## Fiscal Year (FY) 2014 Objectives

- Determine temperature dependent physical properties of biodiesel from different feedstocks such as soy, cuphea, rapeseed, jatropha, and karanja, and compare them against diesel fuel and hydro-treated vegetable oil (HVO).
- Perform nozzle flow simulations with these fuels and determine the differences in in-nozzle flow and cavitation characteristics.
- Develop a biodiesel chemical kinetic mechanism for soy-based feedstock in collaboration with Lawrence Livermore National Laboratory (LLNL) and compare with other published mechanisms in the literature.
- Perform engine experiments with cuphea methyl ester obtained from the U.S. Department of Agriculture and karanja- and jatropha-based biodiesel from India to provide data for validation of CFD simulations.

## FY 2014 Accomplishments

- Seven different fuels (five methyl esters, diesel, and HVO mentioned previously) with different physical properties were simulated and in-nozzle characteristics such as cavitation, injection velocity and turbulence levels were determined. Significant differences were observed between the methyl esters and diesel fuel were noted.
- A new chemical kinetic mechanism to represent combustion characteristics of soy-based methyl ester was developed for CFD applications and this mechanism has been made available to the industry and academia. This chemical kinetic mechanism was also observed to perform better than other published mechanisms in the literature.
- A comprehensive experimental campaign was performed to determine the combustion and emission characteristics of cuphea methyl ester and compared against diesel fuel. This study determined the feasibility of cuphea fuel as a potential alternate or blending agent for diesel fuel.

## Future Directions

- Complete the engine experimental campaign with cuphea, jatropha, and karanja fuels in the single-cylinder Caterpillar engine at Argonne and compare against diesel fuel for combustion and emission characteristics. Publish the experimental data to aid in CFD model development at Argonne and world-wide.
- Develop a CFD model to simulate nozzle flow, spray, combustion, and emission characteristics for cuphea methyl ester for comparison with diesel fuel.
- Develop a "work-flow" to efficiently develop comprehensive CFD models for different biofuels that may be of interest to this project which will involve collaborations with experimentalists at

Argonne, Sandia National Laboratories, and the National Renewable Energy Laboratory (NREL) and the chemical kinetics group at LLNL.

- Further improve the authors' previously published soy-based methyl ester mechanism for wide-range of speed, load, and other engine conditions by validating the mechanism against experimental data from the IQT$^{TM}$. This will be done through a three-laboratory collaboration (Argonne-LLNL-NREL).

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## INTRODUCTION

Internal combustion engine (ICE) processes are multi-scale and highly coupled in nature and characterized by turbulence, two-phase flows, and complicated spray physics. Furthermore, the complex combustion chemistry of fuel oxidation and emission formation makes engine simulations a computationally daunting task. Given the cost for performing detailed experiments spanning a wide range of operating conditions and fuels, CFD modeling aided by high-performance computing has the potential to result in considerable cost savings. Development of physics-based CFD models for nozzle flow, spray, turbulence, and combustion are necessary for predictive simulations of the ICE with different alternate fuels of interest. High-performance computing can play an important role in ICE development by reducing the cost for design and optimization studies. This is largely accomplished by being able to conduct detailed simulations of complex geometries and moving boundaries with high-fidelity models describing the relevant physical and chemical interactions, and by resolving the relevant temporal and spatial scales. These simulations provide unprecedented physical insights into the complex processes taking place in these engines, thus aiding designers in making judicious choices. High-fidelity experimental data for alternate fuels of interest is necessary for preliminary validation of the CFD approaches for different fuels before the CFD model can be used as a design tool for further co-optimizing fuel and engine together.

## APPROACH

During the past year, we have focused on performing nozzle flow simulations with biodiesels from different feedstocks, developing a chemical kinetic model for soy-based biodiesel and comparing it with existing models in the literature. Experiments were also performed with cuphea methyl ester for providing additional data for validation. Our approach is highlighted here:

1. Transient in-nozzle flow simulations were performed using FLUENT software. The software employs a mixture-based approach [1], comprised of fuel in liquid phase, vapor phase, and a non-condensable gas phase. A no-slip condition between the liquid and vapor phases was assumed. The mixture properties were computed using Reynolds-averaged continuity and momentum equations. In order to account for large pressure gradients, the Re-Normalization Group $k-\in$ turbulence model was incorporated, along with non-equilibrium wall functions. Vapor generation and condensation were calculated using the simplified solution of the Rayleigh-Plesset equation [1]. Further details about the physical model and governing equations can be found in the referred study [1,2]. Fuel properties such as density, viscosity, surface tension, and vapor pressure for the different fuels of interest were measured and formed input to the nozzle flow simulations.
2. Methyl decanoate, methyl 9-decenoate and n-heptane were identified as chemical surrogates to represent soy-based biodiesel fuel. A detailed mechanism was obtained from LLNL [3] which was further reduced using mechanism reduction techniques such as directed relation graph and isomer lumping, etc. More details about this can be found in the authors' previous publication [4].
3. The previously mentioned mechanism was further compared against three other published mechanisms in the literature. These mechanisms use two different sets of surrogates: (a) methyl decanoate, methyl 9-decenoate, and n-heptane, (b) methyl butanoate and n-heptane. The mechanisms include: {Mechanism 1} 115 species and 460 reactions [4] developed by the authors using surrogate mixture (a); {Mechanism 2} 77 species and 209 reactions [5] using surrogate mixture (a); {Mechanism 3} 145 species and 869 reactions [6] using surrogate mixture (b); {Mechanism 4} 41 species and 150 reactions [7] using surrogate mixture (b).
4. Engine experiments were performed on a single-cylinder Caterpillar 3400 engine. Various fuels were used including diesel, neat cuphea, neat jatropha, neat karanja, and 30 percent (by volume) blends of karanja and jatropha with diesel (K30 and J30). Three injection timings were selected to explore the differences in the fuel. Full emissions and performance parameters were measured. Further details about the experimental setup can be found in other published work [9].

## RESULTS

Some critical findings associated with the different objectives highlighted before are discussed here. Further details can be obtained from the authors' publications in FY 2014.

Figure 1 plots the vapor fraction contours for diesel, soy-methyl ester (SME), rapeseed methyl ester (RME), cuphea methyl ester (CuME), tallow methyl ester (TME) and HVO. A vapor fraction of 1 implies pure vapor and 0 means pure liquid. These simulations are performed at 1,500 bar injection and 30 bar back pressure. Cavitation inception is observed at the inlet to the orifice as the flow field encounters a sharp bend from the needle-seat and sac region into the orifice. For diesel, HVO, and CuME the cavitation contours are observed to reach the exit of the nozzle which is expected to have a profound influence on the spray behavior. Other fuels like SME, TME, and RME also show cavitation at the orifice inlet but the cavitation bubbles seem to implode within the orifice and do not reach the nozzle exit. The presence of cavitation at the nozzle exit is known to enhance atomization and breakup of the jet [2]. Also clear from this plot is that CuME and HVO behaves quite similar to diesel fuel (for other flow features also which are not shown here), at least inside the nozzle. For other methyl esters the differences are quite significant inside the injector compared to the standard diesel fuel and are expected to persist and compound outside the injector as well.

Figure 2 plots velocity contours at the nozzle orifice exit for diesel fuel compared to pure jatropha biodiesel

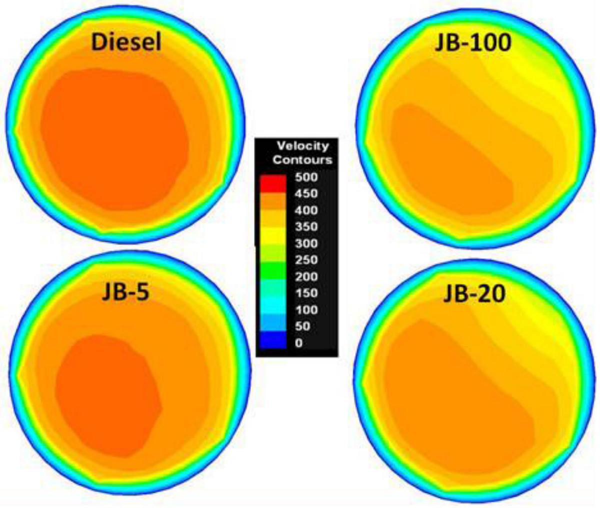


**FIGURE 2.** Three-dimensional transient simulation of a multi-hole injector with specified needle lift. The differences in mass flow rate are shown at the nozzle exit plane for diesel, jatropha, and its different blends with diesel fuel.

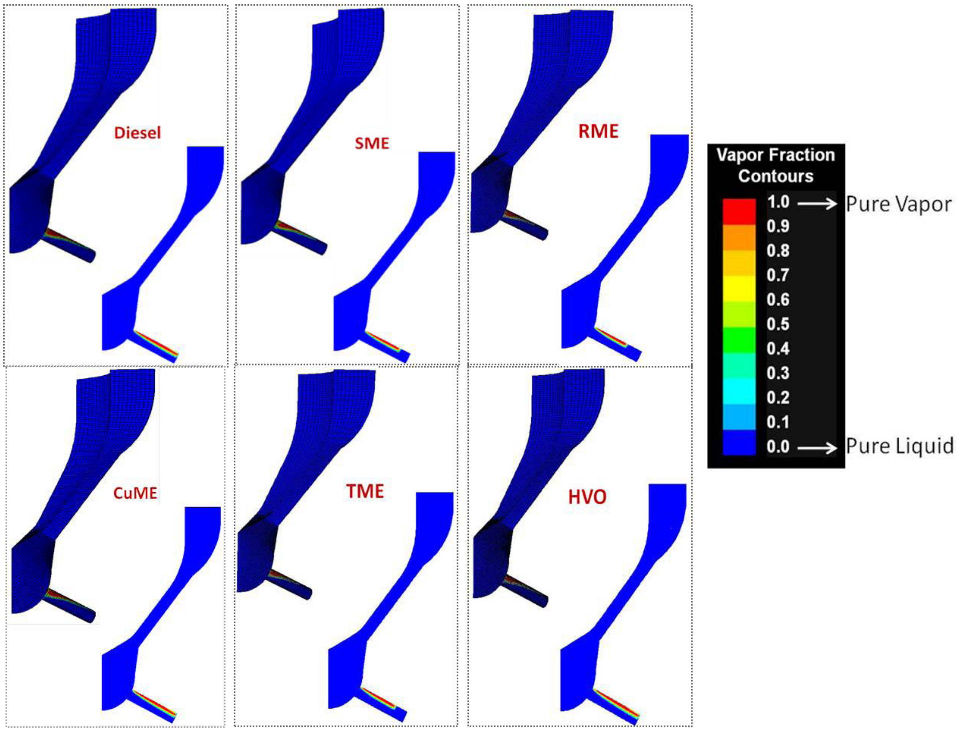


**FIGURE 1.** Three-dimensional transient simulation of a multi-hole injector with specified needle lift. The differences in mass flow rate are shown at a specific cut plane through the center of the orifice for different fuels of interest.

and its blends with diesel fuel. For e.g., JB5 denotes 5% (by volume) jatropha fuel is added to diesel fuel and the mixture properties are simulated for in-nozzle flows. Significant differences are observed at the nozzle exit between pure jatropha and diesel fuel. Nozzle exit velocities are at least 50 m/s lower for pure jatropha which is due to its higher kinematic viscosity compared to diesel fuel. JB5 is observed to behave quite similar to diesel fuel while JB20 resembles JB100. The results indicate that up to 5% blending of jatropha to diesel fuel may have only a small influence on the spray behavior.

Figure 3 plots OH and soot contours from simulations compared against experimental data from Nerva et al. [8] for soy-based biodiesel in a constant volume combustion chamber. The spray-flame simulations are performed using the reduced mechanism developed by the authors' in Ref. [4]. OH contours are plotted on the top and compared to OH chemiluminescence data. The comparison shows that the spray and chemical kinetic model can capture the lift-off length location and flame shape and size quite well. Although not shown here the simulations were also able to capture the ignition delay very well. Additionally, the average equivalence ratio at lift-off location is also well captured in the simulations. The bottom part of the figure plots the soot contours which are predicted using a Hiroyasu soot model [1] which uses $C_2H_2$ as a precursor for soot. The simulations again show that the location of soot can be well predicted by the simulations.

Figure 4 compares the location and contours of soot for the four different mechanisms discussed above against experimental data for soy-derived biodiesel from Nerva et al. [8]. The dashed lines show the location of the stabilized lift-off length. Mechanism 1 was developed as part of this funded activity and is observed to mimic the experimental soot contours and locations very well. Although not shown here, other quantitative parameters such as ignition delay and lift-off length for variety of conditions were also better predicted by mechanism 1.

Figure 5 shows the measured cylinder pressure curve and a zoomed plot of heat release rate for the 5 degree before top-dead center start of injection (SOI) timing case with the six fuels. Little difference is visible in the cylinder pressure plot. The heat release curve shows variance in the start of combustion behavior between diesel and the alternative fuels. The K30 blend performs closest to the diesel during this initial stage, with the cuphea, K100, J30, and J100 showing earlier reaction with lower premix heat release rate peak. While in all of the cases the diesel has the highest premix heat release

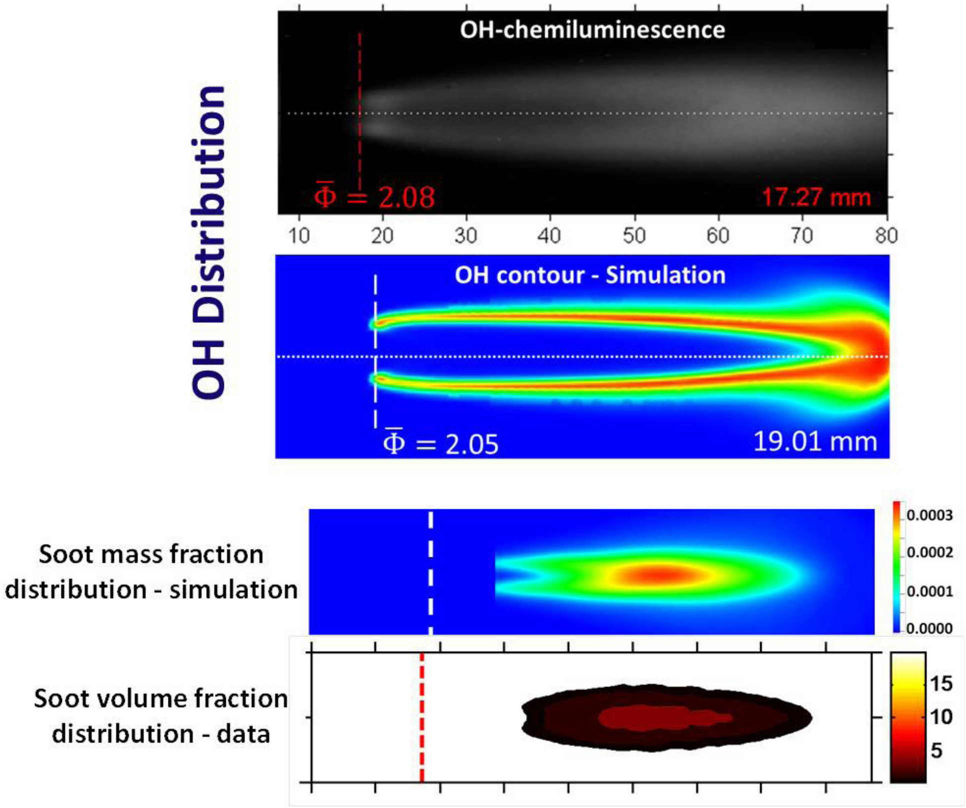


**FIGURE 3.** Comparison of flame structure and soot contours between simulations and experiment done at Sandia National Laboratories [8].

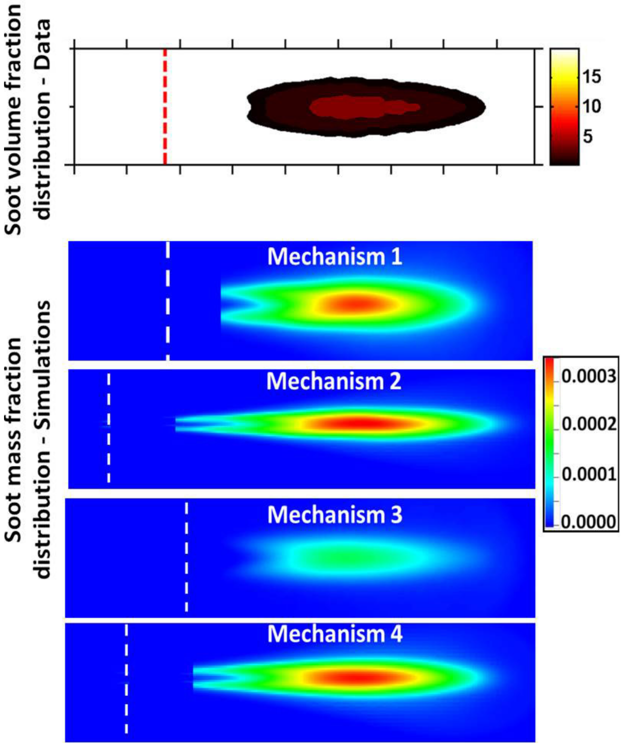


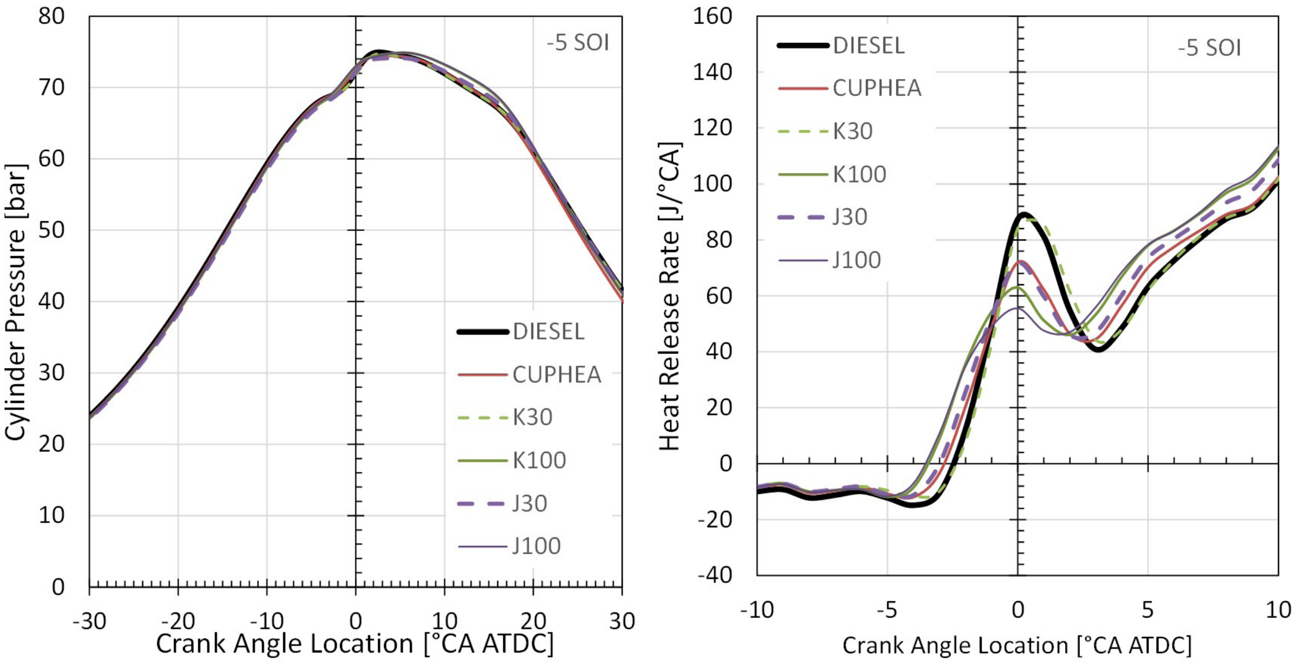
**FIGURE 4.** Comparison of soot contours predicted by different mechanisms for soy-based biodiesel compared against experimental data from Sandia National Laboratories [8].

peak, as start of injection timing is retarded, this earlier start of combustion from the biofuels is not visible (plots not shown).

Figure 6 shows the brake mean effective pressure (BMEP) and brake specific oxides of nitrogen (NOx) values for all of the fuels at the varied SOI timings. While the jatropha and karanja fuels show closer power output to the diesel they produce higher NOx at all of the SOI timings. Cuphea has a lower brake mean effective pressure value with lower penalty in NOx emissions.

## CONCLUSIONS

- Seven different fuels (five methyl esters, diesel, and HVO mentioned above) with different physical properties were simulated and in-nozzle characteristics such as cavitation, injection velocity and turbulence levels were determined. Significant differences were observed between the methyl esters and diesel fuel which were attributed to the differences in physical properties such as viscosity, density, and vapor pressure.
- A chemical kinetic mechanism to represent combustion characteristics of soy-based methyl ester was developed and reduced for engine simulations and this mechanism has been made available to the industry and academia. This new chemical kinetic



ATDC - after top-dead center

**FIGURE 5.** Cylinder pressure and heat release rate experimental curves for diesel, cuphea, karanja, jatropha, K30, and J30 at the 5 degree before top-dead center SOI case. Earlier heat release rate and lower premix peaks can be observed for the alternate fuels.

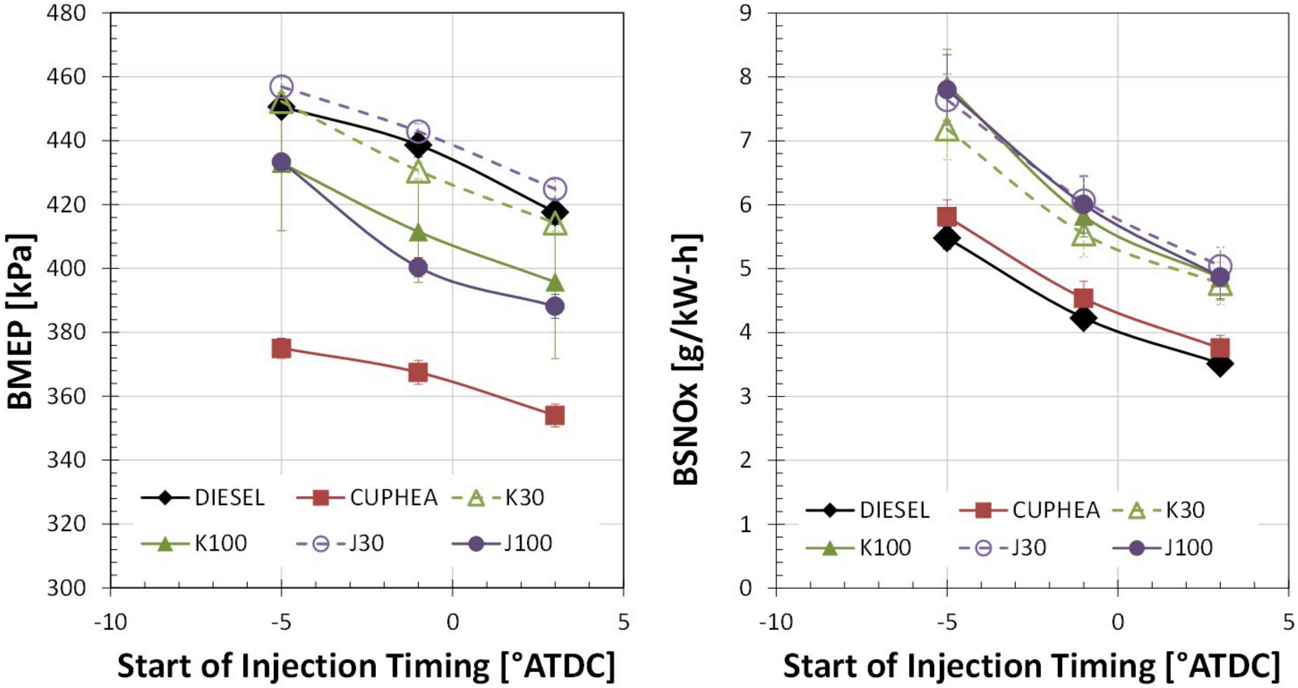


**FIGURE 6.** Brake mean effective pressure and specific NOx emissions for diesel, cuphea, karanja, jatropha, K30, and J30 for all injection timings. Biofuels show lower power output with higher NOx emissions.

mechanism was also observed to perform better than other published mechanisms in the literature. This is mainly due to the fact that a three component surrogate was chosen. Even though the mechanism is reduced, it is still quite large for engine simulations.

- Based on the experiments, jatropha, karanja, and cuphea are suitable alternate fuels as well as blending agents with diesel fuel. Differences in combustion characteristics, especially early in the cycle, require further investigation. Additional experiments can be performed to get a further understanding of the effects of the differences in fuel properties on the combustion and performance in the engine.

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**1.** A.I. Ramirez, S.K. Aggarwal, S. Som, T. Rutter, D.E. Longman, "Effects of blending a heavy alcohol ($C_{20}H_{40}O$) with diesel in a heavy-duty compression ignition engine," *Fuel*, 10.1016/j.fuel.2014.06.039, 2014.

**2.** P. Kundu, Y. Pei, S. Som, M. Wang, R. Mandhapati, "Evaluation of Turbulence Chemistry Interactions under Diesel Engine conditions with a Multi-Flamelet RIF model," *Atomization and Sprays*, 24 (9): 779-800, 2014.

**3.** Z. Luo, S. Som, S.M. Sarathy, M. Plomer, W.J. Pitz, D.E. Longman, T. Lu, "Development and validation of an n-Dodecane skeletal mechanism for diesel spray-combustion applications," Combustion Theory and Modeling, doi:10.1080/13647830.2013.872807, 2014.

**4.** Y. Pei, W. Liu, M. Mehl, S. Som, T. Lu, W.J. Pitz, "A multi-component blend as a diesel fuel surrogate for compression ignition engine applications," *Spring Technical Meeting of the Central States Section of the Combustion Institute*, Tulsa, OK, March 2014.

## SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

**1.** Dr. Sibendu Som: High Performance Computing Innovation Excellence Award from International Data Corporation, June 2014.

**2.** Dr. Sibendu Som: Invitee to US-Frontiers of Engineering workshop organized by National Academy of Sciences (only 100 people under the age of 45 were invited).

# IV.5 Evaluation of Cellulosic Biomass-Derived Oxygenates as Drop-In Fuel Blend Components

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## Overall Objectives

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

## Fiscal Year (FY) 2014 Objectives

- Complete measurement of physical and fuel performance properties for pure component oxygenates representing those found in partially hydroprocessed biomass pyrolysis oil
- Evaluate the performance properties of the pure component oxygenates blended into gasoline or diesel
- Set up gasoline direct-injection (GDI) engine system for fine particulate matter (PM) measurements and complete particle number and mass emissions measurements for oxygenate blends

## FY 2014 Accomplishments

- For biomass pyrolysis oxygenates boiling below the $T_{90}$ of gasoline (185 to 190°C):
  - Showed that furans and methyl aryl ethers (MAEs) such as anisole have excellent gasoline properties because of their insolubility in water, minimal impact on vapor pressure, and high blending octane numbers.
  - However, 2,5-dimethylfuran oxidized to form gum on an oxidation stability test.
  - Phenol (and also the higher boiling cresol and guaiacol) cannot be used as drop-in fuel components because of their solubility in water and impact on phase separation temperature.
  - Ketones (represented by hexanone) have low octane number but did not negatively impact gasoline performance properties when blended at low levels.
  - Measurement of fine PM emissions from a GDI engine showed that particle number emissions could increase by up to a factor of three upon blending of the aromatic oxygenates, indicating no impact of the oxygen atom on PM formation.
- Biomass pyrolysis oxygenates boiling in the diesel range are primarily phenolic and MAE compounds. While these generally have low cetane number (ranging from 7 to 26) they had no other negative effects on diesel fuel performance properties. The phenolic compounds improved lubricity and oxidation stability.

## Future Directions

- Evaluate particle mass and number emissions from a broader range of oxygenate structures and fuel properties
- Analyze the cause of dimethylfuran oxidative instability and determine if simple antioxidant additives can mitigate this issue for this promising high octane gasoline oxygenate
- Research the knock resistance properties of biomass oxygenates in more detail including temperature effects on autoignition and kinetics
- Perform more extensive combustion and emissions characterization of diesel oxygenates

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## INTRODUCTION

Processes being investigated for conversion of biomass to liquid fuels include fast pyrolysis, acid depolymerization, and base depolymerization. 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 [1], there is a clear economic advantage to removing only 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. In FY 2014 we evaluated oxygenates observed in partially hydroprocessed biomass pyrolysis oils [2]. Critical fuel properties were measured for pure component oxygenates, as well as their blends with gasoline and diesel fuel. Blends were then tested in a GDI engine to examine fine PM emissions.

## 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). The blends were characterized using standard test methods and previously published in-house methods [3]. Gasoline fuels were tested in a single-cylinder engine developed from a 2009 model year General Motors Ecotec 2.0-L LNF-series engine, with a wall-guided direct-injection combustion system. The dynamometer, engine control, air handling, fuel supply, and combustion analysis systems have all been previously described [4]. The PM emission measurement system consists of a Dekati FPS-4000 two stage exhaust dilution system that feeds into a Dekati Thermodenuder and then supplies the diluted sample to a TSI Fast Mobility Particle Sizer model 3091 for particle size distribution measurements.

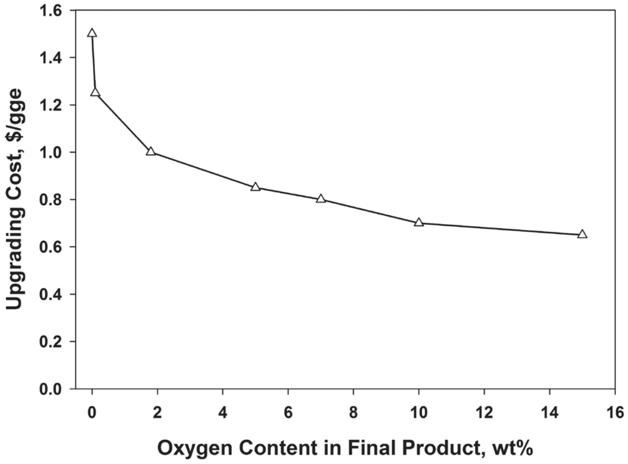

**FIGURE 1.** Cost for upgrading of biomass pyrolysis oil by hydrotreating as a function of product oxygen content (adapted from reference 7).

## RESULTS

### Fuel Properties

Representative oxygenates are listed in Table 1, which is a compilation of fuel property data from literature sources and in-house measurements. Looking at the gasoline boiling range (boiling points below the $T_{90}$ of gasoline: 185 or 190°C), both furans and anisoles show high octane number, relatively high net heating value and density combined with low melting point and low solubility in water; suggesting that compounds of these types could function as drop-in gasoline blendstocks. 2-hexanone also appears to be compatible with gasoline but its octane number is unknown and there may be potential for gum formation by condensation reactions. Methyltetrahydrofuran and phenol have significant water solubility suggesting their use as drop-in fuel components would be challenging. In addition, phenol has a high melting point. Cresol, guaiacol, xylenol, 4-propylanisole, 2-phenylethanol (2-PE) and 4-methylguaiacol all boil above the $T_{90}$ but below the end point (225°C) of gasoline. This significantly limits the level at which these can be blended, regardless of other properties.

Dimethylfuran (DMF), 4-methylanisole (4-MA), and 2-PE were blended into a BOB at 13, 10, and 20 vol%, respectively, while other oxygenates were blended at lower levels. All three oxygenates slightly lowered vapor pressure. Effects on the distillation curve were small for DMF and 4-MA, while blending with 2-PE caused the $T_{90}$ to increase by more than 50°C such that the blend failed the ASTM D4814 limit. The oxygenates tested at lower levels had little or no impact on distillation parameters. Blending of the oxygenates also had little impact on gasoline density, viscosity, or heating value. DMF, 4-MA and 2-PE significantly increased Research Octane Number (RON) and Motor Octane Number (MON) when blended with the suboctane BOB. The volumetric blending RON and MON of 4-MA were 134.8 and 100.2. Blending RON and MON for DMF were 156.6 and 108.9. Blending RON and MON of 2-PE were 141.6 and 109.1, respectively. We also estimated blending RON for 2-hexanone (90.8) and p-cresol (187.5) using the 6 vol% blend level data.

ASTM D525 is a pass/fail test of stability under oxidizing conditions, showed only that at the concentrations measured, all of the oxygenate blends passed. The results of ASTM D873, which provides a more quantitative measure of the tendency for fuels to form gums under accelerated thermal and oxidative

**TABLE 1.** Fuel Relevant Properties of Pure Oxygenates Identified in Hydroprocessed Pyrolysis Oils (shaded compounds not included in gasoline/diesel blending)

| Class/ Compound | | Boiling Point (°C) | Blending RON and MON | Cetane Number (or DCN) | Net Heating Value (MJ/L) | Flash Point (°C) | Density at 25°C (g/ml) | Melting Point (°C) | Solubility in Water at 20°C (wt%) |
|---|---|---|---|---|---|---|---|---|---|
| 2-Methylfuran | a | 64[a] | 155, 92[b] | 8.9[e] | 27.60[a] | -17[d] | 0.910[m] | -89[d] | 0.3[l] |
| Methyltetrahydrofuran | b | 79[a] | 85, 76[b] | 22[e] | 28.18[a] | -11[d] | 0.86[d] | -136[a] | 12.1[l] |
| 2,5-Dimethylfuran | c | 94[a] | 153, 109[b] | 10.9[e] | 30.13[a] | 7[d] | 0.903[d] | -62[d] | 0.26[l] |
| 2-Hexanone | d | 127[a] | --[*] | -- | 28.35[g] | 23[d] | 0.812[d] | -57[a] | 2[n] |
| Anisole | e | 154[a] | 112/108[h] | 6[f] | 33.19[g] | 52[d] | 0.995[d] | -23[a] | Insoluble[d] |
| 4-Methylanisole | f | 177[a] | 166, 148[c] | 7[f] | 33.38[f] | 59[d] | 0.969[d] | -32[a] | Insoluble[d] |
| Phenol | g | 182[a] | -- | -- | 33.34[g] | 79[d] | 1.071[d] | 41[a] | 8.8[p] |
| p-Cresol | h | 202[a] | 153, 149[k] | -- | 33.73[g] | 85[d] | 1.034[d] | 34[a] | 2.1[o] |
| Guaiacol | i | 205[a] | -- | 19[f] | 31.06[f] | 82[d] | 1.129[d] | 28[a] | 1.7[m] |
| 2,4-Xylenol | j | 211[a] | 140, 113[k] | -- | 34.21[g] | 94[d] | 1.011[d] | 25[a] | 0.79[o] |
| 4-Propylanisole | k | 215[a] | -- | 7[f] | 34.22[f] | 90[d] | 0.941[d] | -5[f] | Slight[r] |
| 2-Phenylethanol | l | 218[a] | 110/90[h] | 8[f] | 34.78[f] | 102[d] | 1.02[d] | -19[a] | 2[n] |
| 4-Methylguaiacol | m | 221[a] | -- | 20[f] | 31.57[f] | 99[d] | 1.092[d] | 5[d] | Slight[q] |
| 4-Methylacetophenone | n | 226[a] | -- | -- | 34.15[f] | 82[d] | 1.005[d] | -64[a] | 0.04[i] |
| 4-Propylphenol | o | 232[a] | -- | 9[f] | 34.16[f] | 106[d] | 0.983[d] | 22[a] | Insoluble[n] |
| 4-Propylguaiacol | p | 250[d] | -- | 18[f] | 32.66[f] | 113[d] | 1.038[d] | 16[a] | Slight[r] |
| 2,6-Dimethoxyphenol | q | 263[a] | -- | 26[f] | 28.63[f] | 140[d] | 1.134[j] | 55[d] | 2[i] |
| 4-Methyl-2,6-dimethoxyphenol | r | 268[i] | -- | 25[f] | 29.09[f] | 113[d] | 1.105[i] | 40[d] | Insoluble[d] |

[*] Indicates value unknown. [a] National Institute of Standards and Technology (NIST) Webbook. [b] Christensen, E. et al. [3]. [c] Singerman, G. [5]. [d] Material Safety Data Sheet from www.sigmaaldrich.com. [e] Sudholt, A., et al. [6]. [f] ASTM D6890, this study. [g] Calculated from density and higher heating value in the NIST Webbook. [h] Molar blending values reported in Zhou et al. [7]. [i] www.lookchem.com. [j] www.guidechem.com. [k] Buether, et al. [8]. [l] Yanowitz, et al. [9]. [m] Material Safety Data Sheet from www.acros.com. [n] www.chemicalbook.com. [o] Donhal and Fenclova [10]. [p] Narasimhan, et al. [11]. [q] www.fao.org/ag/agn/jecfa-flav/.
DCN – derived cetane number

aging conditions, show significant effects for some oxygenates. Blending of 2-hexanone at the 6 vol% level caused a small increase in gum formation. Most notably, the 13% DMF blend produced a large amount of gum, over 700 mg/100 mL (insoluble gum). We are currently investigating this reaction in more detail, as well as the potential of antioxidant additives to control or eliminate it.

Both phenol and p-cresol (and by extension, the two other cresol isomers) significantly increase phase separation temperature at low blending levels indicating limited solubility in gasoline hydrocarbons. Given the water extractability and uptake properties of phenol and cresols, it seems unlikely that these molecules could be present at above trace levels in drop-in fuels.

Because of the relatively low cetane number of all of the diesel boiling range (160 to 340°C) biomass oxygenates they were tested at relatively low blend levels. Consequently, many properties including net heating value, viscosity at 40°C, density at 15°C, distillation $T_{90}$, and carbon residue show little or no impact from oxygenate blending. Only very small impacts on cloud point were observed, in spite of the high melting point of most of the oxygenates used for blending. The oxygenates had no effect on acid value, copper corrosion, or thermal stability. Many of the oxygenates increased conductivity. The phenolic compounds all caused an improvement in fuel lubricity and acted as antioxidants, improving stability.

## GASOLINE DIRECT-INJECTION ENGINE STUDY

In FY 2014 particle emission studies were completed for BOB blended with ethanol, isobutanol, DMF, 4-MA, and 2-PE. The correlation between particle number and particle mass concentrations at 2,500 rpm and 13 bar is shown in Figure 2. The strong correlation is expected for particles that are predominantly elemental carbon, accumulation mode particles [4,14]. The highest emission levels were for 4-MA and 2-PE, and were two to three times higher than observed for 10% ethanol in gasoline. Researchers at Honda have shown that for both port fuel injection and direct injection engines PM emissions are

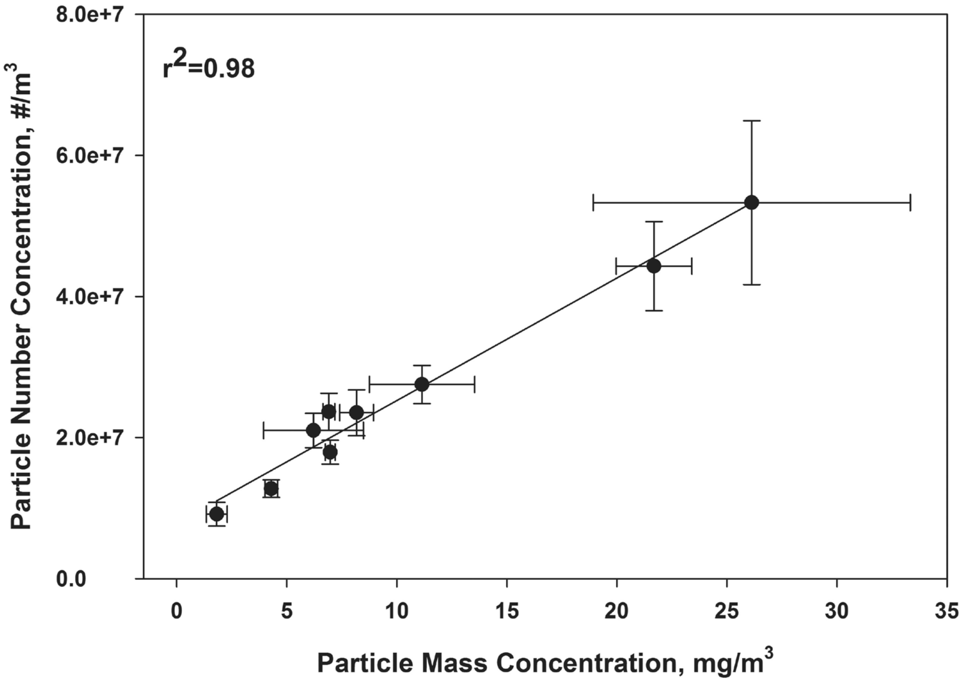

**FIGURE 2.** Correlation between PM mass concentration and particulate number concentration for all eight fuels at 2,500 rpm, 13 bar net mean effective pressure.

correlated with a particulate matter index (PMI) that can be calculated based on a detailed hydrocarbon analysis for a gasoline. PMI is a function of weight fraction, vapor pressure, and double bond equivalent (DBE) value for each component in the fuel [12,13]. Fuel components with high vapor pressure will evaporate quickly even if the fuel spray impinges on the cylinder wall or piston, avoiding diffusion flame or pool fire combustion. The DBE is the number of hydrogen molecules required to saturate the double bonds and open rings present in a fuel molecule. Figure 3 shows the correlation between particle mass concentration, particle number concentration and PMI. Because 2-PE has such a high boiling point (causing the gasoline blend to fail the $T_{90}$ limit) and low vapor pressure its combustion may not have been complete. 2-PE has a distinctive odor and observation suggested that this compound accumulated in the engine lubricant. Elimination of 2-PE from the particle emissions-PMI correlation significantly improves the correlation. 2-PE produced significantly more particulate matter than its isomer 4-MA, yet it seems unlikely that the shift in the location of the oxygen atom would lead to a reduction in PM emissions. However, the lack of a hydroxyl group in the structure of 4-methylansiole significantly reduces its capability for hydrogen bonding relative to 2-PE, thus resulting in higher volatility and a much lower PMI. Because there appeared to be no effect of the aromatic oxygenates oxygen atom on PM emissions, any effect of increasing local air-fuel ratio is outweighed by their low vapor pressure and high DBE values.

## CONCLUSIONS

Oxygenates present in partially hydroprocessed biomass pyrolysis oils were examined for their impact on performance properties of gasoline and diesel. These included: methyltetrahydrofuran, DMF, 2-hexanone, 4-MA, 2-PE, phenol, p-cresol, 2,4-xylenol, guaiacol, 4-methylguaiacol, 4-methylacetophenone, 4-propylphenol, and 4-propylguaiacol. Based on the available data, 4-MA and by extension other MAE appear to be the best drop-in fuel components for gasoline because they significantly increase RON and slightly reduce vapor pressure without significant negative fuel property effects. The low solubility of phenol and p-cresol (and likely the two other cresol, the two other cresol isomers) in hydrocarbons and the observation that phenol is also highly extractable into water suggests that these molecules cannot likely be present at above trace levels in drop-in fuels. The diesel boiling range oxygenates all have low cetane number which presents challenges for blending into diesel fuel. There were some beneficial properties observed for the phenolic oxygenates in diesel, including increasing conductivity, lubricity, and oxidation stability of the diesel fuel.

Research was also performed to determine the effect of a small group of oxygenated molecules on GDI engine particle emissions. Particle emission effects of fuels were revealed at the highest load condition employed

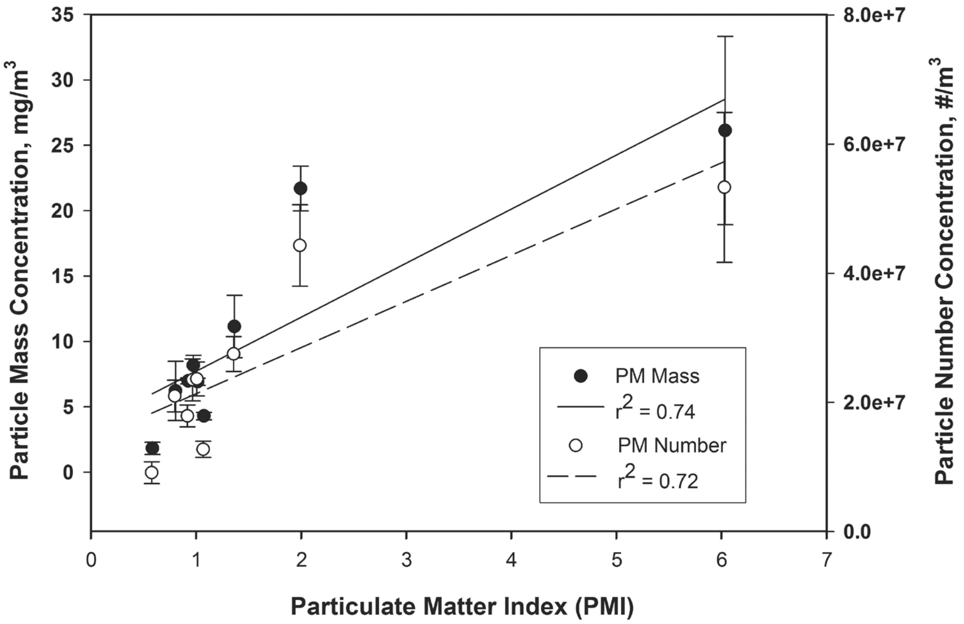

**FIGURE 3.** PM Index correlation with PM mass and particulate number count for 2,500 rpm and 13 bar conditions.

of 2,500 rpm and 13 bar net mean effective pressure. Isobutanol and DMF had only a small or even negligible effect on both particle mass and number emissions under the engine operating conditions investigated here. This is consistent with these molecules relatively low boiling point, high vapor pressure, and lack of unsaturated structures for isobutanol. 4-MA and 2-PE both caused a significant increase in particle mass and number emissions (by a factor of approximately two to threee) relative to 10% ethanol in gasoline. Thus any effect of their oxygen atom on increasing local air-fuel ratio is outweighed by their low vapor pressure and high DBE values. The boiling point of 2-PE (220°C) and its very low vapor pressure may have significantly altered performance properties that are critical to GDI engine performance.

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# IV.6 Performance of Biofuels and Biofuel Blends

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## Overall Objectives

Develop a fundamental understanding of how saturated monoglycerides (SMGs) may influence the co-crystallization of minor components in biodiesel and how this may affect the cloud point (CP) and cold weather performance (fuel filter clogging) of both the biodiesel and blends with diesel.

## Fiscal Year (FY) 2014 Objectives

- Measure the solubility of SMGs in several pure solvents that represent different components of both biodiesel and diesel fuel and determine how these components influence their solubility.
- Develop a fundamental understanding of how SMGS affect the crystallization of other minor components in biodiesel and how this influences the CP of the fuel as well as crystal size and shape and how this relates to fuel filter clogging.
- Determine if SMGs can cause other components in the fuel to come out of solution at higher temperatures than expected based on single component solubility.

## FY 2014 Accomplishments

- Determined that the solubility of SMGs can vary greatly in different components of diesel fuel.
- Demonstrated that SMGs can cause other components found in biodiesel to come out of solution at higher temperatures than expected by providing a surface for the compounds to co-crystallize on.
- Demonstrated that SMGs in conjunction with other minor components leads to increased filtration times.
- Crystals containing monoolein (MO) physically appeared to stack higher on the filters than when only SMGs were present.

## Future Directions

- Additional characterization of crystals containing co-crystallized components.
- Expansion of the test matrix to include other fuel minor components, notably water.
- Evaluate the influence of SMGs on gel formation and rheology in biodiesel blends.
- Determine how additives could prevent or alter crystallization of SMGs and other components to reduce the CP of the fuel and prevent fuel filter clogging.

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## INTRODUCTION

Low temperature operability of biodiesel and especially biodiesel blended with diesel fuel remains a concern. While not common, unexpected issues of fuel filter clogging are still observed in winter months [1]. Development of a fundamental understanding of how minor components in biodiesel can influence cold weather behavior is still needed in order to prevent these unexpected issues.

## APPROACH

The solubility of monostearin (a saturated monoglyceride) was measured in several pure solvents. Solvents that represent different components of biodiesel and diesel fuel were chosen for this study. Solvents used were: decane, dodecane, isocetane, isobutyl benzene, toluene, and methyl oleate. The solvents were saturated with monostearin and held at several different temperatures for 24 hours each. At the end of 24 hours, an aliquot of the solvent was removed and filtered and the amount of monostearin dissolved in the solvent was measured by gas chromatography.

In order to obtain a more fundamental understanding of the influence of SMGs on other minor components in the fuel, surrogate fuel blends were prepared and spiked with various combinations of components. The surrogate blends were made with either methyl oleate or methyl linoleate as a biodiesel component at 5 volume % and dodecane and a mixed blend of decane, undecane, dodecane, tridecane, and tetradecane as a diesel fuel component. Monopalmitin, monostearin, and MO were then spiked into these surrogate fuels in various combinations and the CP was measured. The samples were held in an environmental chamber at the temperature of the unspiked surrogate fuel for 16 hours. After the cold soak, the time to filter was measured and the composition of the collected precipitate was determined by differential scanning calorimetry (DSC) and gas chromatography. Microscope images of the crystals on the filters were taken digitally.

## RESULTS

The CP of a biodiesel or biodiesel blend is used to determine the low temperature operability of the fuel. It is assumed that the fuel can be used down to that temperature without causing any fuel filter clogging. Fundamentally, the CP measures the temperature at which the first component crystallizes out of solution and a component will come out of solution once its solubility limit has been reached. In previous work [2] we have shown that SMGs are the most significant factor that influences the CP, therefore knowledge of the solubility of SMGs in different fuel components is beneficial. Figure 1 shows the solubility of monostearin in various pure solvents. At 20°C, the solubility of monostearin increases by about 10 times in methyl oleate and 20 times in toluene. This is significant because it shows that the addition of biodiesel (methyl oleate) and aromatics (toluene) in the fuel would increase the solubility of SMGs and in turn could decrease the CP of the fuel (when SMGs are present).

It is well known [3] that once a component crystallizes out of the solution that the thermodynamics of the entire system are affected and that the presence of crystals could cause other components of the system to come out of solution above their solubility limit. This occurs through co-crystallization, where other components can crystallize on the surface of the component that has come out of solution. Because SMGs can readily crystallize out of biodiesel and biodiesel blends, it is important to understand if additional minor components can co-crystallize with SMGs as these may contribute significantly to the mass of material on a fuel filter. One common minor component found in biodiesel is MO. MO is an unsaturated monoglyceride that has a much lower melting point [4] than monopalmitin or monostearin (typical SMGs found in biodiesel). MO is also found at higher concentrations than SMGs in the fuel. In order to determine if MO can co-crystallize with SMGs and also if SMGs themselves can co-crystallize with each other, various surrogate fuels were prepared and spiked with different combinations of monopalmitin, monostearin, and MO (see Table 1). The CP as well as the time to filter was measured. The composition of the collected precipitate was also analyzed to determine if MO came out of solution with the SMGs.

Table 1 contains a list of all the blends prepared, the measured CP and the time it took for each solution to filter after being held in an environmental chamber for 16 hours. Dodecane blends were held at -10°C and

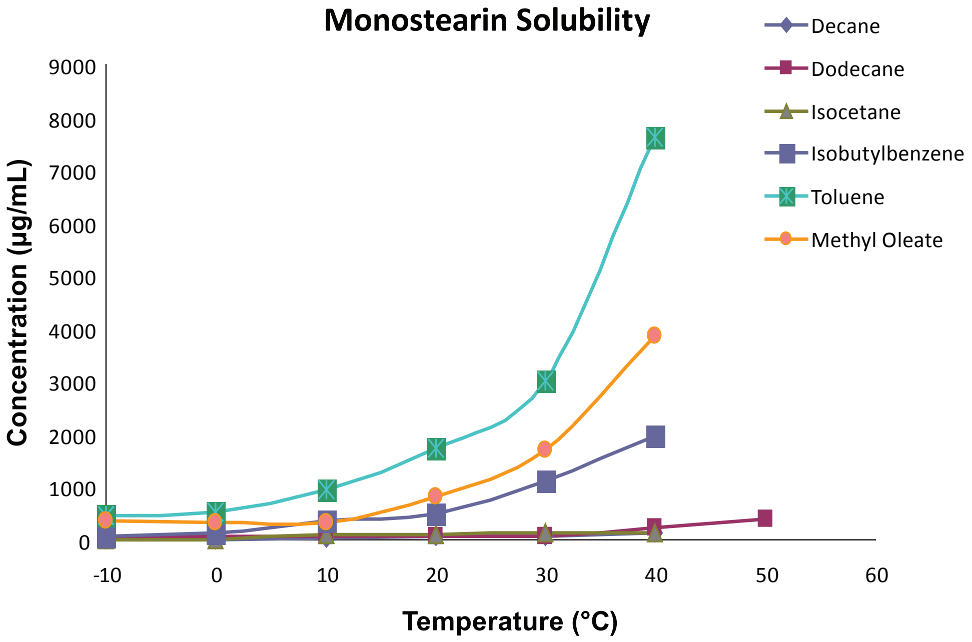

**FIGURE 1.** Monostearin Solubility in Various Pure Components

mixed hydrocarbon blends (mixture of decane, undecane, dodecane, tridecane, and tetradecane) were held at -15°C. From the CP measurements, it can be seen that SMGs (monopalmitin and monostearin) greatly affected the CP of the solutions. Significantly, it can be seen how SMGs increased the CP over values measured for blends that only contained MO. Looking at the time it took for each sample to filter, the longest filtration times were for the samples that contained all three components. This could indicate that the MO was coming out of solution with the SMGs. We performed analysis of the collected precipitate to test the hypothesis that MO was in fact co-crystallizing with SMGs at temperatures well above its solubility limit.

**TABLE 1.** List of Prepared Fuel Blends

| Sample | CP (°C) | Time to Filter (Sec) |
|---|---|---|
| Methyl Oleate (MeO)/Dodecane | -15.9 | 7.4 |
| 0.025% Stearin MeO/Dodecane | 12 | 44.8 |
| 0.025% Palmitin MeO/Dodecane | 8 | 122.2 |
| 0.025% Palmitin/Stearin MeO/Dodecane | 6.4 | 62.9 |
| 0.1% MO MeO/Dodecane | -14 | 67.0 |
| 0.025% Palm/Stear 0.1% MO MeO/Dodecane | 10 | 231.1 |
| Methyl Linoleate (MeLin)/Dodecane | -14.6 | 7.6 |
| 0.025% Stearin MeLin/Dodecane | 10 | 43.0 |
| 0.025% Palm MeLin/Dodecane | 8 | 53.0 |
| 0.025% Palm/Stear MeLin/Dodecane | 9 | 75.3 |
| 0.1% MO MeLin/Dodecane | -14.7 | 56.0 |
| 0.025% Palm/Stear 0.1% MO MeLin/Dodecane | 1.5 | 111.6 |
| MeO/Custom | -21.6 | 8.0 |
| 0.025% Stearin MeO/Custom | 12 | 44.4 |
| 0.025% Palmitin MeO/Custom | 9 | 95.2 |
| 0.025% Palm/Stear MeO/Custom | 11 | 105.0 |
| 0.1% MO MeO/Custom | -21.6 | 116.0 |
| 0.025% Palm/Stear 0.1% MO MeO/Custom | 6.5 | 142.6 |
| MeLin/Custom | -21.8 | 8.4 |
| 0.025% Stearin MeLin/Custom | 16 | 52.6 |
| 0.025% Palm MeLin/Custom | 10 | 88.0 |
| 0.025% Palm/Stear MeLin/Custom | 15 | 64.4 |
| 0.1% MO MeLin/Custom | -21.4 | 108.0 |
| 0.025% Palm/Stear 0.1% MO MeLin/Custom | 13.8 | 150.2 |
| Custom = Mixed hydrocarbon blend | | |

Analysis of the collected precipitate by gas chromatography and DSC determined that MO did in fact come out of solution with the SMGs. Gas chromatography showed that the precipitates could include up to 40% MO when all three components were in solution. DSC indicates that the MO has co-crystallized with the SMGs as well. Figure 2 shows thermograms of MO alone, palmitin/stearin, and palmitin/stearin/MO in the methyl oleate and dodecane blend. From the melting peaks it can be seen that the melting points are drastically different as the combination of components is changed. Also, only one melting peak is present for each of the samples indicating that all of the components are able to co-crystallize together into one mixed crystal. As more components are included in the crystal, the melting point is reduced [5]. The monnoolein has reduced the melting of the monopalmitin/monostearin co-crystal by about 7°C. Another indication of a co-crystal is the broadening of the melting peak with the addition of more components as the material becomes less "pure." This is a significant finding showing that much lower melting point components can come out of solution when SMGs are present, perhaps causing a larger volume of material on a fuel filter.

Lastly, we took images of the crystals on the filters with a digital microscope with 100 times magnification. In looking at the images, it does appear that the samples containing all three components were able to "stack up" higher on the filter. This could be the main reason for the slower filtration times (other than increased mass due to more material crystallizing out of solution). Figures 3 and 4 contain images of the combined monopalmitin/monostearin crystals and all three components from the methyl linoleate/custom hydrocarbon blends respectively. It can easily be seen that the crystals from all three components looks to be stacked up higher in height than with just monopalmitin and monostearin present.

## CONCLUSIONS

- It was found that the solubility of monostearin could vary greatly in different components of biodiesel and diesel fuel. In particular, methyl oleate, a biodiesel component and toluene (representing aromatics in diesel) could provide a 10 to 20 times solubility benefit, indicating that an increase in biodiesel content or aromatic content in diesel used for blending could reduce the CP of the final blend.
- Both DSC and gas chromatography showed that MO, a lower melting, and more highly soluble component of biodiesel could co-crystallize with SMGs, causing precipitation of this component above its solubility limit. This could lead to an increased mass on fuel filtration filters.
- The time to filter was increased for samples that contained all three components due to co-crystallization of MO with SMGs.
- Crystals containing MO physically appeared different in shape and mass than those containing just SMGs.

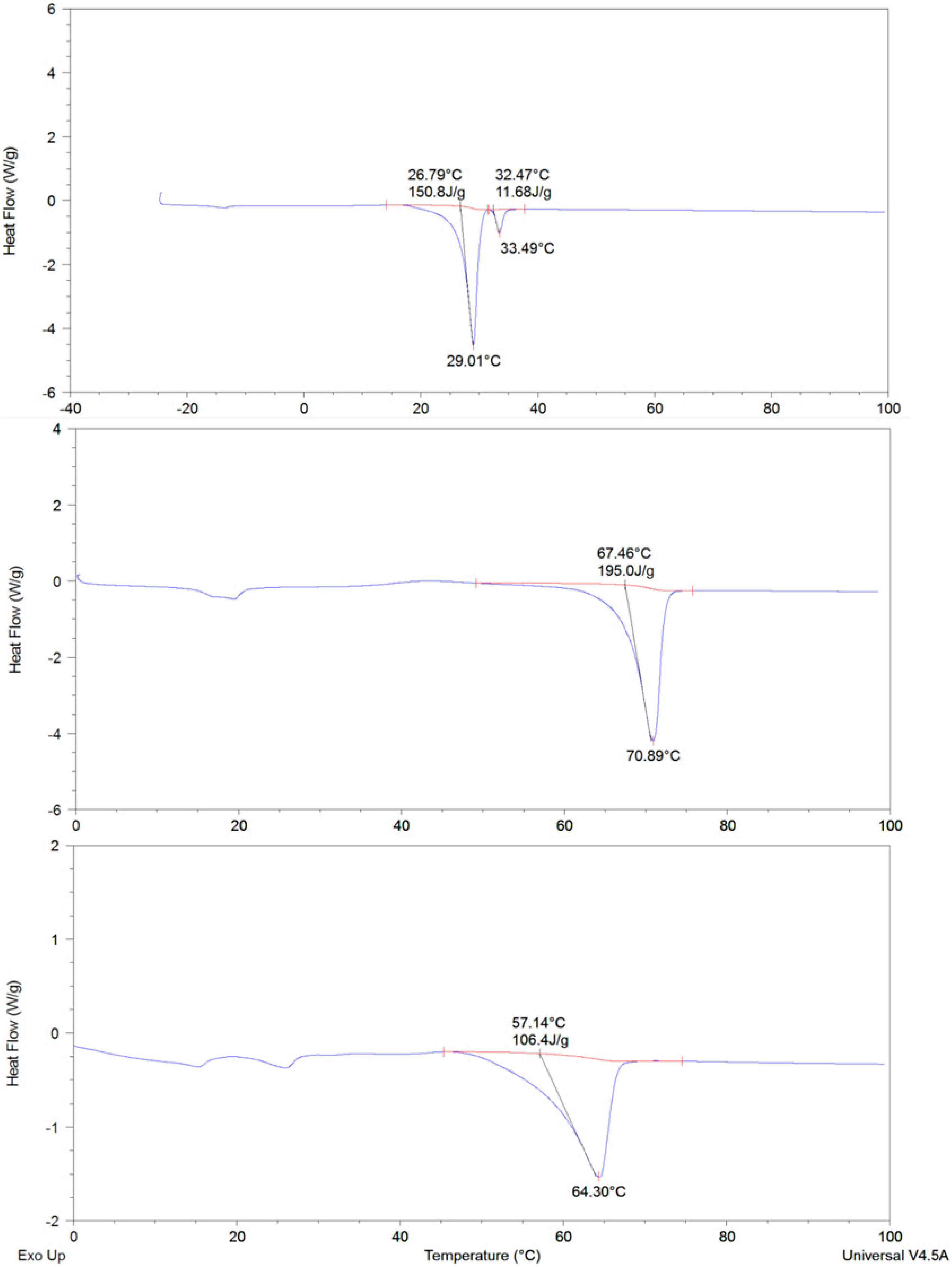

**FIGURE 2.** DSC Thermograms of Monoolein, Monopalmitin/Monostearin, and all Three Monoglycerides

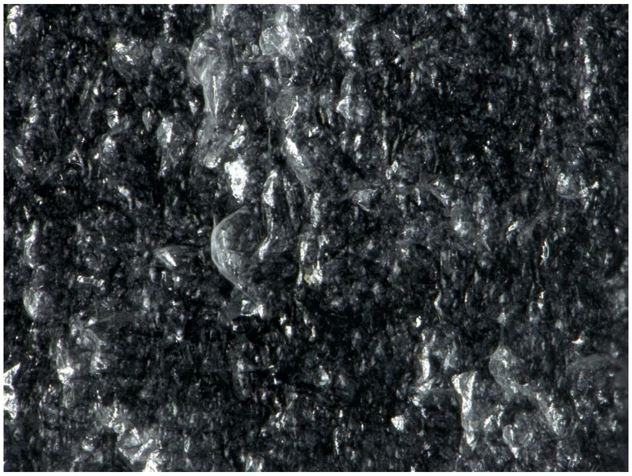

**FIGURE 3.** Digital Microscope Image of Mixed Monopalmitin/Monostearin Crystal on Filter Paper

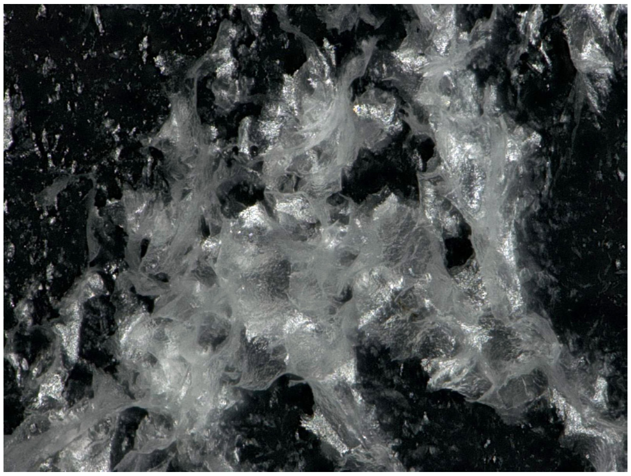

**FIGURE 4.** Digital Microscope Image of Mixed Monopalmitin/Monostearin/MO Crystal on Filter Paper

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**2.** Chupka, G.M., McCormick, R.L. “Effect of Biodiesel Composition on Cold Weather Operability of Biodiesel Blends” presented to USCAR Fuels Working Group, Golden, CO, July 29, 2014.

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# IV.7 Impact of Fuel Metal Impurities on the Performance and Durability of Diesel Emission Control Systems

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## Overall Objectives

- Quantify the impact of fuel metal impurities on the performance and durability of engine exhaust aftertreatment components.
- Conduct accelerated aging tests to simulate full useful life of operation while exposed to fuel metal impurities.
- Test multiple light-duty and heavy-duty catalyst systems.
- Help overcome technical barriers to more widespread use of biofuels for petroleum displacement.

## Fiscal Year (FY) 2014 Objectives

- Conduct an accelerated aging test on a heavy-duty engine and catalyst system to simulate full useful life exposure to a biodiesel at the allowable ASTM standard for Na.
- Quantify the emissions performance degradation by periodically operating the engine over the Federal Test Procedure (FTP) cycle and measuring tailpipe oxides of nitrogen ($NO_x$) emissions to track performance degradation after exposure to fuel metal impurities.
- Conduct post mortem analysis to determine the location and elemental nature of deposits found on the surface and within catalyst substrates after exposure to fuel metal impurities.

## FY 2014 Accomplishments

- A heavy-duty aftertreatment system was aged for 1,001 hours, simulating the full useful life (435,000 miles) using a 20% blend of biodiesel in diesel fuel (B20) which was doped with Na to represent the allowable ASTM standard limit with a 14x acceleration factor.
- Tailpipe $NO_x$ emissions were tested periodically throughout the aging process over the FTP composite and shown to increase to 0.41 g/bhp-hr with the fully aged system, exceeding the family emission limit of 0.33 g/bhp-hr for engine and aftertreatment certification.
- Diesel particulate filter (DPF) weights were also taken periodically throughout the aging process and it was determined that ash from the Na dopant was a significant contributor, estimated to account for over 80% of the total ash load (50 g/L).
- Analysis of the aged components using electron probe microanalysis (EPMA) showed Na to be deposited throughout the thickness of the washcoat and along the entire diesel oxidation catalyst (DOC) length. However, no Na was detected within the selective catalytic reduction (SCR) catalyst.
- Individual components of the aged system were replaced by new degreened parts and hot-start FTP tests showed 65% of the increased $NO_x$ emissions could be attributed to the aged DOC/DPF and 35% was due to the degraded SCR.

## Future Directions

- Further investigation of the influence from accelerated testing is needed and should be explored by repeating testing at a lower acceleration factor or potentially without acceleration to determine a deterioration factor.
- Aging conditions and test cycle selection need to be evaluated to determine if they are representative of real world engine operation.

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## INTRODUCTION

In order to advance the use of biofuels to displace petroleum use, it is important to understand the impact these fuels may have on modern exhaust aftertreatment systems and work to ensure compatibility. Alkali and alkaline earth metals can be present in small quantities as a byproduct of the biofuel production and processing [1,2]. These metal impurities can be converted to oxides, sulfates, hydroxides, or carbonates in the combustion process and form an inorganic ash that can be deposited onto the surface of modern diesel exhaust emissions control devices. Alkali metals are well known poisons for catalysts and therefore, these deposits have the potential to adversely affect the performance of an exhaust aftertreatment system [3,4]. The following work aims to examine the impact on the performance and durability of a heavy-duty diesel exhaust aftertreatment system with accelerated full useful life exposure to biodiesel at the allowable ASTM specification limit for Na.

## APPROACH

The full production exhaust system from a Cummins ISL diesel engine was selected for this work. The system was aged on a Caterpillar C9 engine but was periodically returned to the Cummins ISL, approximately every 250 hours, for emission testing on certification diesel throughout the aging process. The full useful life requirement for diesel engines certified for intended service class heavy-heavy-duty is 435,000 miles or 22,000 hours. Assuming a line haul fuel economy of 6 mpg and using an acceleration factor of 14x based on previous work [5] it was determined that 5,179 gallons of B20 fuel would need to be consumed. The ASTM D6751 specification currently allows a maximum of 5 ppm Na+K and 5 ppm Ca+Mg in a 100% biodiesel fuel (B100). Assuming the worst case of 5 ppm metal impurities in a B100, this would result in 1 ppm for a B20 fuel. However, since an acceleration factor of 14x was chosen the B20 fuel was doped with 14 ppm Na using dioctyl sodium sulfosuccinate. A three-mode cycle was developed consisting of 25 minutes at 260°C (DOC outlet), 25 minutes at 380°C and 15 minutes at 550°C. This cycle simulates the full useful life thermal aging exposure by assuming a DPF regeneration occurs approximately every 24 hours and lasts for 15 minutes over a 22,000-hour lifetime, exposing the system to 230 hours of high temperature operation.

## RESULTS

After the exhaust system was initial degreened, a baseline FTP composite emissions test initially was run. The system was subsequently returned for emissions testing after 280, 553, 756 and 1,001 hours of aging. Figure 1 shows the FTP composite tailpipe $NO_x$ results at each interval. Each bar represents the composite of six hot starts and one cold-start test. The red dashed line represents the engine family emission limit of 0.33 g/bhp-hr, which the system is intended to conform to over the full useful life. Figure 2 shows these same

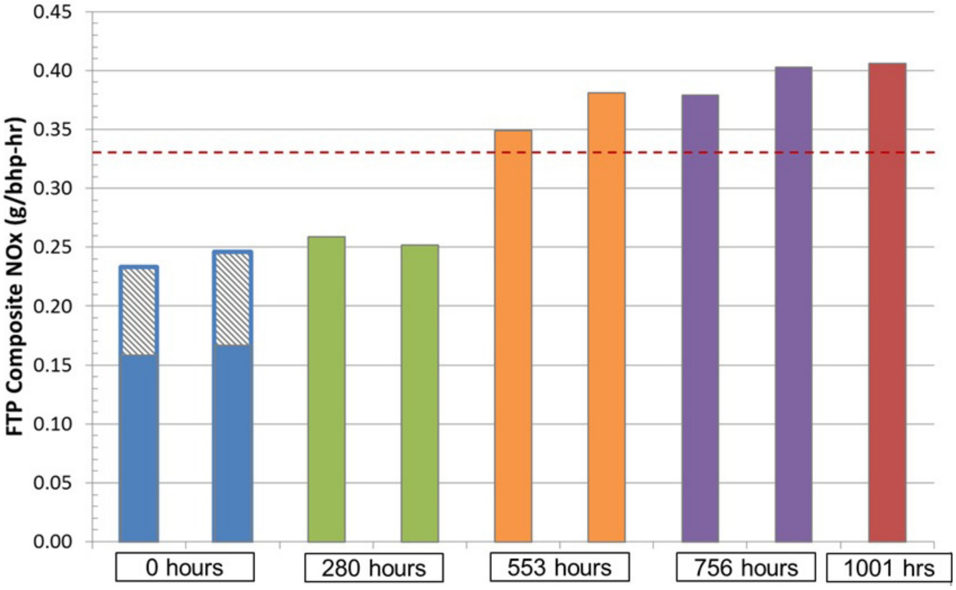


**FIGURE 1.** FTP Composite $NO_x$ Emissions after the Designated Hours of Aging with Doped Fuel

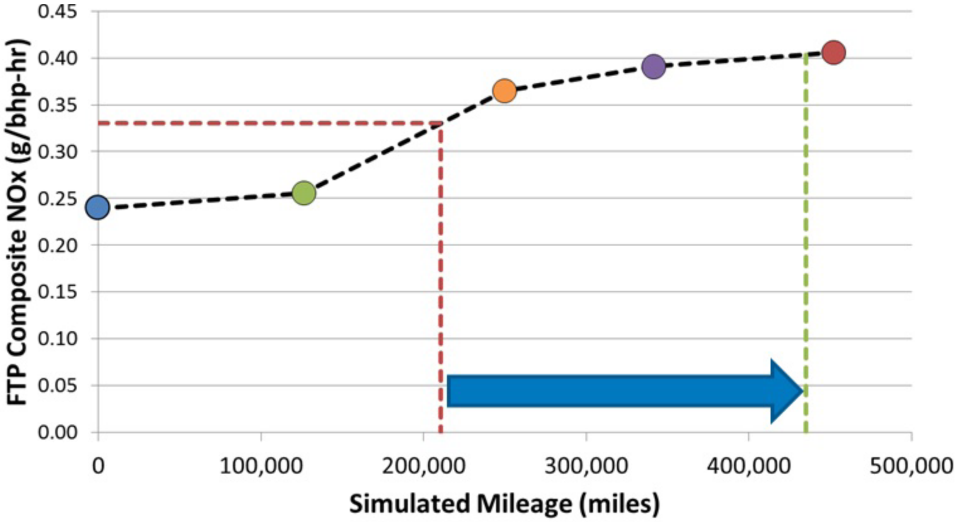


**FIGURE 2.** FTP Composite $NO_x$ Results as a Function of Simulated Miles

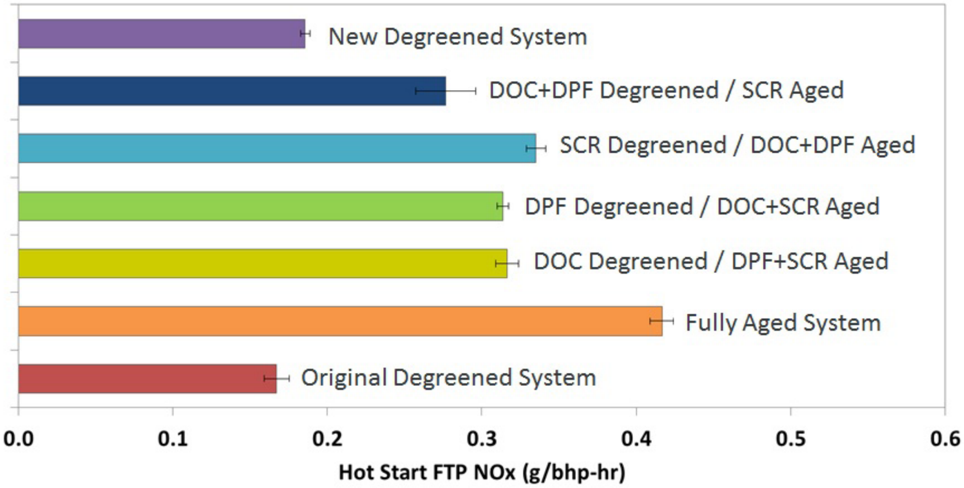


**FIGURE 3.** Hot-Start FTP Results with Various Combinations of Aged and New Degreened Components

emissions results expressed as a function of simulated miles and that the system falls out of compliance around ~210,000 miles, far short of the 435,000 mile goal. After completing the aging, a second, new system was degreened and individual components of the aged system were swapped out for new degreened ones. Figure 3 shows the hot-start FTP composite emissions for various combinations. The DOC and DPF actually have a stronger effect on the tailpipe $NO_x$ emissions over the test cycle compared with the aged SCR. This is likely due to a degraded capacity to oxidize NO to $NO_2$ upstream of the SCR system.

Each time the system underwent emissions testing, micro-core samples were taken from the front face of the DOC and SCR bricks for further analysis using Brunauer, Emmett and Teller surface area analysis, energy dispersive X-ray spectroscopy, electron probe microanalysis (EPMA), X-ray diffraction and bench flow reactor studies. No evidence of severe thermal aging was detected from BET surface analysis. Figure 4 shows optical images of a white powder deposited on the front face of the DOC within the first 1-2 mm. X-ray diffraction and energy dispersive X-ray spectroscopy analysis have identified the powder to be a Na-Ca sulfate mixture. It is speculated that the powder is related to the lower temperatures in this region. Figure 5 shows EPMA maps of Na collected from cross-sections near the inlet and outlet of the DOC. Na was found at similar levels across the washcoat thickness and down the entire DOC length. The decrease of $NO_x$ oxidation function

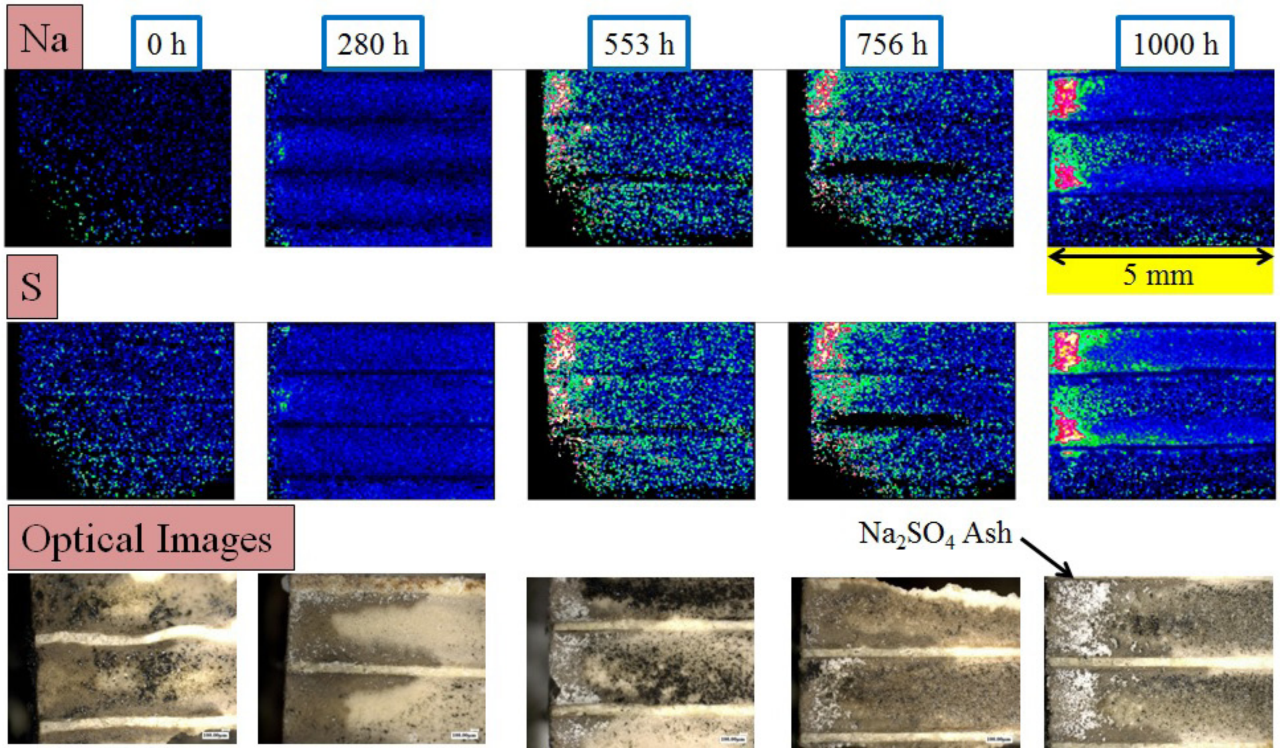


**FIGURE 4.** White Ash Deposits Observed on the Front Face of the DOC

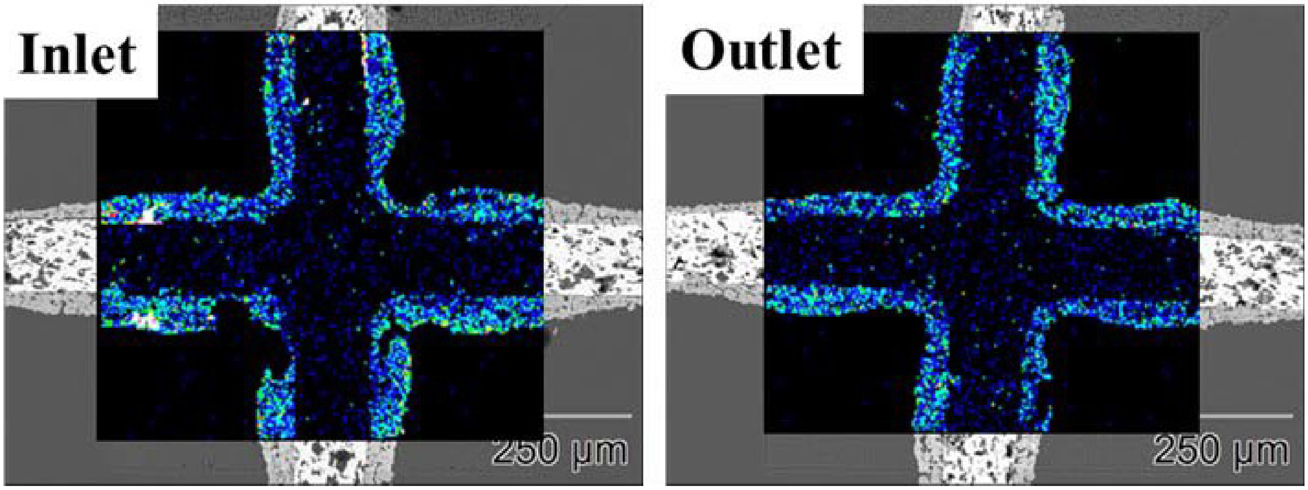


**FIGURE 5.** EPMA Maps of Na Collected from Cross-Sections of the Fully-Aged DOC 1 cm from the Inlet (left) and Outlet (right).

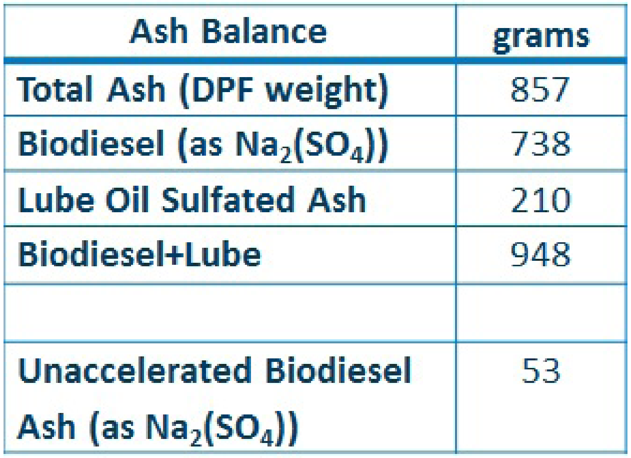
following aging is likely related to the accumulation and stabilization of Na contamination in the DOC.

Throughout the aging process the DPF was weighed periodically to track total ash accumulation. Table 1 shows the total measured ash, 857 g (50 g/L) and estimates of it constituents based on the known quantities of fuel and oil consumed throughout the test. At these levels the biodiesel derived ash has the potential to shorten the DPF ash cleaning interval, possibly below the Environmental Protection Agency mandated 150,000 miles.

## CONCLUSIONS

- Metal impurities present in biofuels at the current ASTM specification limit, introduced in an accelerated manner, have the potential to limit the

**TABLE 1.** DPF Ash Balance



| Ash Balance | grams |
|---|---|
| Total Ash (DPF weight) | 857 |
| Biodiesel (as $Na_2(SO_4)$) | 738 |
| Lube Oil Sulfated Ash | 210 |
| Biodiesel+Lube | 948 |
| | |
| Unaccelerated Biodiesel Ash (as $Na_2(SO_4)$) | 53 |

ability of modern heavy-duty aftertreatment devices to meet the EPA requirements for tailpipe $NO_x$ emissions.

- The suspected cause is the impact of Na on the catalytic reactivity of the DOC hindering its ability to oxidize NO to $NO_2$. However, questions remain about the degree to which test acceleration by doping the fuel with high levels of Na have affected the result.

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**4.** Cavataio, G., Jen, H., Dobson, D., and Warner, J., "Laboratory Study to Determine Impact of Na and K Exposure on the Durability of DOC and SCR Catalyst Formulations," SAE Technical Paper 2009-01-2823, 2009, doi:10.4271/2009-01-2823.

**5.** Williams, A., McCormick, R., Lance, M., Xie, C. et al., "Effect of Accelerated Aging Rate on the Capture of Fuel-Borne Metal Impurities by Emissions Control Devices," SAE Int. J. Fuels Lubr. 7(2):2014, doi:10.4271/2014-01-1500.

## FY 2014 PUBLICATIONS/PRESENTATIONS

**1.** Williams, A., McCormick, R., Lance, M., Xie, C. et al., "Effect of Accelerated Aging Rate on the Capture of Fuel-Borne Metal Impurities by Emissions Control Devices," SAE Int. J. Fuels Lubr. 7(2):2014, doi:10.4271/2014-01-1500.

**2.** Preliminary results were presented at the National Biodiesel Technical Workshop.

# V. Acronyms, Abbreviations and Definitions

| | |
|---|---|
| $\eta_{th}$ | Thermodynamic cycle efficiency |
| $\gamma$ | Ratio of specific heats |
| µl | Micro-liter |
| $\phi$ | Fuel/air-equivalence ratio |
| $\eta_{f,ig}$ | Gross indicated fuel-conversion efficiency |
| °F | Degrees Fahrenheit |
| % w/w | % weight/weight |
| 1-D | One-dimensional |
| 2-D | Two-dimensional |
| 2D-GC | 2-dimensional gas chromatograph |
| AC&F | Advanced Combustion and Fuels |
| AEO | Annual Energy Outlook |
| A/F | Air/fuel ratio |
| $AFR_{st}$ | Stoichiometric air/fuel ratio |
| AHRR | Apparent heat release rate |
| AISI | American Iron and Steel Institute |
| AKI | Anti-knock index |
| ASTM | ASTM International, a standards setting organization |
| atdc, ATDC, aTDC | After top-dead center |
| $aTDC_f$ | After firing top-dead center |
| a.u. | Arbitrary units |
| AVFL | Advanced Vehicles Fuels and Lubricants |
| AW | Anti-wear |
| B5 | 5% biodiesel |
| B6 | 6% biodiesel |
| B20 | 20% biodiesel |
| B100 | 100% biodiesel |
| BDC | Bottom dead center |
| BET | Named after Brunauer, Emmett and Teller, this method for determining the surface area of a solid involves monitoring the adsorption of nitrogen gas onto the solid at low temperature and, from the isotherm generated, deriving the volume of gas required to form one monolayer adsorbed on the surface. This volume, which corresponds to a known number of moles of gas, is converted into a surface area though knowledge of area occupied by each molecule of adsorbate. |
| BEV | Battery electric vehicle |
| BEV-100 | Battery electric vehicle with 100-mile range |
| BL | Boundary lubrication |
| BMEP | Brake mean effective pressure |
| BOB | Blendstock for oxygenate blending |
| BSFC | Brake specific fuel consumption |
| BTDC | Before top-dead center |
| BTE | Brake thermal efficiency |
| Bxx | Biodiesel blend containing xx volume percent biodiesel |
| $^{13}C\{^{1}H\}$ | Proton-decoupled, carbon-13 |
| CA | Crank angle |
| 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 |
| CLCC | Closed-loop combustion control |
| CLEERS | Cross-Cut Lean Exhaust Emissions Reduction Simulations |
| CME | Canola methyl ester |
| CN | Cetane number |
| CNG | Compressed natural gas |
| CNT | Carbon nano-tube |
| COV | Coefficient of variation |
| CP | Cloud point |
| CR | Compression ratio |
| CRADA | Cooperative Research and Development Agreement |
| CRC | Coordinating Research Council |
| CSM | Colorado School of Mines |
| CuME | Cuphea methyl ester |
| DBE | Double bond equivalent |
| DCN | Derived cetane number |
| DEER | Diesel Engine Emissions Reduction |
| degCA | Degrees crank angle |
| DEPT | Distortionless enhancement of polarization transfer |
| DI | Direct injection |
| DISI | Direct-injection spark-ignition |
| DLC | Diamond-like carbon |
| DLS | Dynamic light scattering |

| | |
|---|---|
| DME | Dimethyl ether |
| DMF | Dimethylfuran |
| DOC | Diesel oxidation catalyst |
| DOSY | Diffusion-ordered spectroscopy |
| DPF | Diesel particulate filter |
| DRIFTS | Diffuse reflectance infrared Fourier-transform spectroscopy |
| DSC | Differential scanning calorimetry |
| E0 | Gasoline with no ethanol |
| E10 | 10% ethanol, 90% gasoline fuel blend |
| E15 | 15% ethanol, 85% gasoline fuel blend |
| E20 | 20% ethanol, 80% gasoline fuel blend |
| E30 | 30% ethanol, 70% gasoline fuel blend |
| E50 | 50% ethanol, 50% gasoline fuel blend |
| E70 | 70% ethanol, 30% gasoline fuel blend |
| E85 | Nominally 85% ethanol/15% gasoline blend which can actually range from 51–83% per ASTM D5798 |
| ECM | Engine control module |
| ECS | Emission control system |
| ECU | Electronic control unit |
| EDAX | Energy-dispersive X-ray spectroscopy |
| EDXS | Dispersive X-ray spectroscopy |
| EGO | Exhaust gas oxygen |
| EGR | Exhaust gas recirculation |
| EHN | Ethyl hexyl nitrate |
| EISA | Energy Independence and Security Act of 2007 |
| EIVC | Early intake valve closing |
| ELOC | Extended lift-off combustion |
| EOI | End of injection |
| EP | Extreme pressure |
| EPA | Environmental Protection Agency |
| EPMA | Electron probe microanalysis |
| $\eta_{th}$ | Thermodynamic cycle efficiency |
| Exx | xx% ethanol, 100-xx% gasoline fuel blend |
| FACE | Fuels for Advanced Combustion Engines |
| FAME | Fatty acid methyl ester |
| FE | Fuel economy |
| FFV | Flexible-fuel vehicle; flex-fuel vehicle |
| FID | Flame ionization detector |
| FMC | Ford Motor Company |
| FMEP | Friction mean effective pressure |
| FSN | Filter smoke number |
| FTP | Federal Test Procedure |
| FTP-75 | Federal Test Procedure for LD vehicles |
| FUL | Full-useful life |
| G15 | 15%v TPGME blended with n-hexadecane |
| G33 | 33%v TPGME blended with n-hexadecane |
| G50 | 50%v TPGME blended with n-hexadecane |
| GC | Gas chromatography |
| GC-FID | Gas chromatography/flame ionization detector |
| GC-FIMS | Gas chromatography field ionization mass spectrometry |
| GCI | Gasoline compression ignition |
| GC-MS | Gas chromatography–mass spectrometry |
| GDI, GDi | Gasoline direct injection |
| GGE | Gasoline gallon equivalent |
| GHG | Greenhouse gas |
| GISFC | Gross indicated specific fuel consumption |
| GPF | Gasoline particulate filter |
| GTDI | Gasoline turbocharged direct injection |
| GTL | Gas to liquid |
| HBAE | Hyperbranched aromatic esters |
| h-BN | Hexagonal boron nitride |
| HC | Hydrocarbon |
| HCCI | Homogeneous charge compression ignition |
| HD | Heavy-duty |
| HECC | High-efficiency clean-combustion |
| HETCOR | Heteronuclear correlation |
| HEV | Hybrid electric vehicle |
| HFET | Highway Fuel Economy Test |
| HFRR | High frequency reciprocating rig |
| HMN | Heptamethylnonane (2,2,4,4,6,8,8-heptamethylnonane, a diesel primary reference fuel) |
| $^1$HNMR | Proton nuclear magnetic resonance spectroscopy |
| HPLC | High-performance liquid chromatography |
| HRR | Heat release rate |
| HRTEM | High-resolution transmission electron microscopic |
| HSDI | High-speed direct injection |
| HSQC | Heteronuclear single quantum coherence |
| HTHL | High temperature, high load |
| HTHS | High temperature, high shear |
| HVA | Hydraulic valve actuator |

| | |
|---|---|
| HVO | Hydro-treated vegetable oil |
| iB16 | 16 vol% blend of iso-butanol in gasoline |
| iB24, IB24 | 24 vol% blend of iso-butanol in gasoline |
| iBu48 | 48 vol% blend of iso-butanol in gasoline |
| ICE | Internal combustion engine |
| ICOMIA | International Council of Marine Industry Associations |
| ICP | Inductively coupled plasma mass spectrometry |
| ID | Ignition delay |
| IL | Ionic liquid |
| ILSAC | International Lubricants Standardization and Approval Committee |
| $IMEP_g$ | Indicated mean effective pressure, gross |
| $IMEP_{net}$ | Indicated mean effective pressure, net over all four strokes |
| IQT™ | Ignition Quality Tester |
| ISCO | Indicated specific carbon monoxide |
| ISFC | Indicated specific fuel consumption |
| ISHC | Indicated specific hydrocarbons |
| $ISNO_X$ | Indicated specific emissions of nitrogen oxides |
| ITE | Indicated thermal efficiency |
| IVD | Intake valve deposit |
| J30 | 30 volume% jatropha in diesel fuel |
| K30 | 30 volume% karanja in diesel fuel |
| kDa | Kilodalton |
| KIVA | Combustion analysis software developed by Los Alamos National Laboratory |
| kPa | Kilopascals |
| LC/MS | Liquid chromatography with mass spectrometric detection |
| LD | Light-duty |
| LED | Light-emitting diode |
| LEV | Low Emission Vehicle |
| LFT | Learned fuel trim (or long-term fuel trim) |
| LHV | Lower heating value; latent heat of vaporization |
| LII | Laser-induced incandescence |
| LIVC | Late intake valve closing |
| LL | Liquid length |
| LLFC | Leaner lifted flame combustion |
| LNG | Liquefied natural gas |
| LPG | Liquefied petroleum gas |
| LSPI | Low-speed pre-ignition |
| LTC | Low-Temperature Combustion |
| LTFT | Low temperature flow test; long-term fuel trim |
| LTHR | Low-temperature heat release |
| MA | Methylanisole |
| MAE | Methyl aryl ether |
| MBT | Maximum (spark advance) for best torque |
| MCE | Multi-cylinder engine |
| MD | Methyl decanoate; Molecular dynamic |
| µl | Micro-liter |
| MFB | Mass fuel burned |
| MFB50 | Crank angle where 50% of heat release has occurred |
| MIT | Massachusetts Institute of Technology |
| MO | Monoolein |
| MON | Motor Octane Number |
| MOUDI | Micro-orifice uniform deposit impactor |
| MTM | Mini traction machine |
| ng | Nano-gram |
| NHD | N-hexadecane |
| NIST | National Institute of Standards and Technology |
| NMHC | Non-methane hydrocarbon |
| NMOG | Non-methane organic gases |
| NMR | Nuclear magnetic resonance |
| $NO_2$ | Nitrogen dioxide |
| NOx | Oxides of nitrogen |
| NVO | Negative valve overlap |
| OEM | Original equipment manufacturer |
| OSC | Oxygen storage capacity |
| PAH | Polycyclic aromatic hydrocarbon |
| PAO | Polyalphaolefin |
| PCCI | Pre-mixed charge compression ignition |
| PE | Phenylethanol |
| % w/w | % weight/weight |
| PFI | Port fuel injection, port fuel injected |
| PGM | Platinum group metal |
| PHEV | Plug-in hybrid electric vehicle |
| PHEV-10 | Plug-in hybrid electric vehicle with 10-mile electric range |
| PHEV-40 | Plug-in hybrid electric vehicle with 40-mile electric range |
| PIV | Particle image velocimetry |
| PLIF | Planar laser induced fluorescence |
| PLS | Partial least squares |
| PM | Particulate matter |

| | |
|---|---|
| PMEP | Pumping mean effective pressure |
| PMI | Particulate matter index |
| PN | Particulate number |
| ppb | Parts per billion |
| PRR | Pressure rise rate |
| Q2 | Second quarter |
| RCCI | Reactivity controlled compression ignition |
| RCM | Rapid compression machine |
| RFS | Renewable Fuel Standard |
| RME | Rapeseed methyl ester |
| RON | Research Octane Number |
| RoPR | Rate of pressure rise |
| RPM, rpm | Revolutions per minute |
| RVP | Reid vapor pressure |
| SA | Spark assist, spark assisted |
| SA-HCCI | Spark-assisted homogeneous charge compression ignition |
| SANS | Small angle neutron scattering |
| SAPS | Sulphated ash, phosphorus and sulphur |
| SCE | Single-cylinder engine |
| SCORE | Sandia Compression-ignition Optical Research Engine |
| SCR | Selective catalytic reduction |
| SEM | Scanning electron microscopy |
| SI | Spark ignition; Spark ignited |
| SIDI | Spark ignition direct injection |
| SME | Soy methyl ester |
| SMG | Saturated monoglyceride |
| SOC | Start of combustion; soluble organic compound |
| SOF | Soluble organic fraction |
| SOI | Start of injection |
| SRR | Slide-roll ratio |
| ST | Spark timing |
| SULEV | Super Ultra-Low Emissions Vehicle |
| SwRI® | Southwest Research Institute® |
| T50 | Temperature for 50% evaporated |
| T50 | 50%v TPGME blended with ULSD |
| TAN | Total acid number |
| $T_{bdc}$ | Bottom-dead-center temperature |
| TDC | Top-dead center |
| $TDC_{exc}$ | Top-dead center (of gas-exchange strokes) |
| TDP | Thermal desorption/pyrolysis |
| TEM | Transmission electron microscopy |
| TGA | Thermo-gravimetric analysis |
| THC | Total hydrocarbon |
| THF | Tetrahydrofuran |
| TME | Tallow methyl ester |
| TOF/SIMS | Time-of-flight secondary ion mass spectrometry |
| TOST | Turbine oxidation stability test |
| TPD | Temperature-programmed desorption |
| TPGME | Tri-propylene glycol methyl ether |
| TPO | Temperature-programmed oxidation |
| TSF | Toluene standardization fuel |
| TWC | Three-way catalyst |
| UHC | Unburned hydrocarbon |
| UI | Upstream injection |
| ULEV | Ultra-Low Emission Vehicle |
| ULG 91 RON | Unleaded gasoline 91 Research Octane Number |
| ULG 95 RON | Unleaded gasoline 95 Research Octane Number |
| ULSD | Ultra-low sulfur diesel (fuel) |
| UTG | Unleaded test gasoline |
| VI | Viscosity index |
| VM | Viscosity modifier |
| VOF | Volatile organic fraction |
| vol% | Volume percent |
| V-P | Viscosity-pressure |
| VTO | Vehicle Technologies Office |
| VVA | Variable valve actuation |
| WGS | Water-gas shift |
| WOT | Wide-open throttle |
| WSD | Wear scar diameter |
| XPS | X-ray photo-electron spectroscopy |
| XRD | X-ray diffraction |
| XRF | X-ray fluorescence |
| ZDDP | Zinc dialkyl-dithiophosphate |

# VI. Index of Primary Contacts

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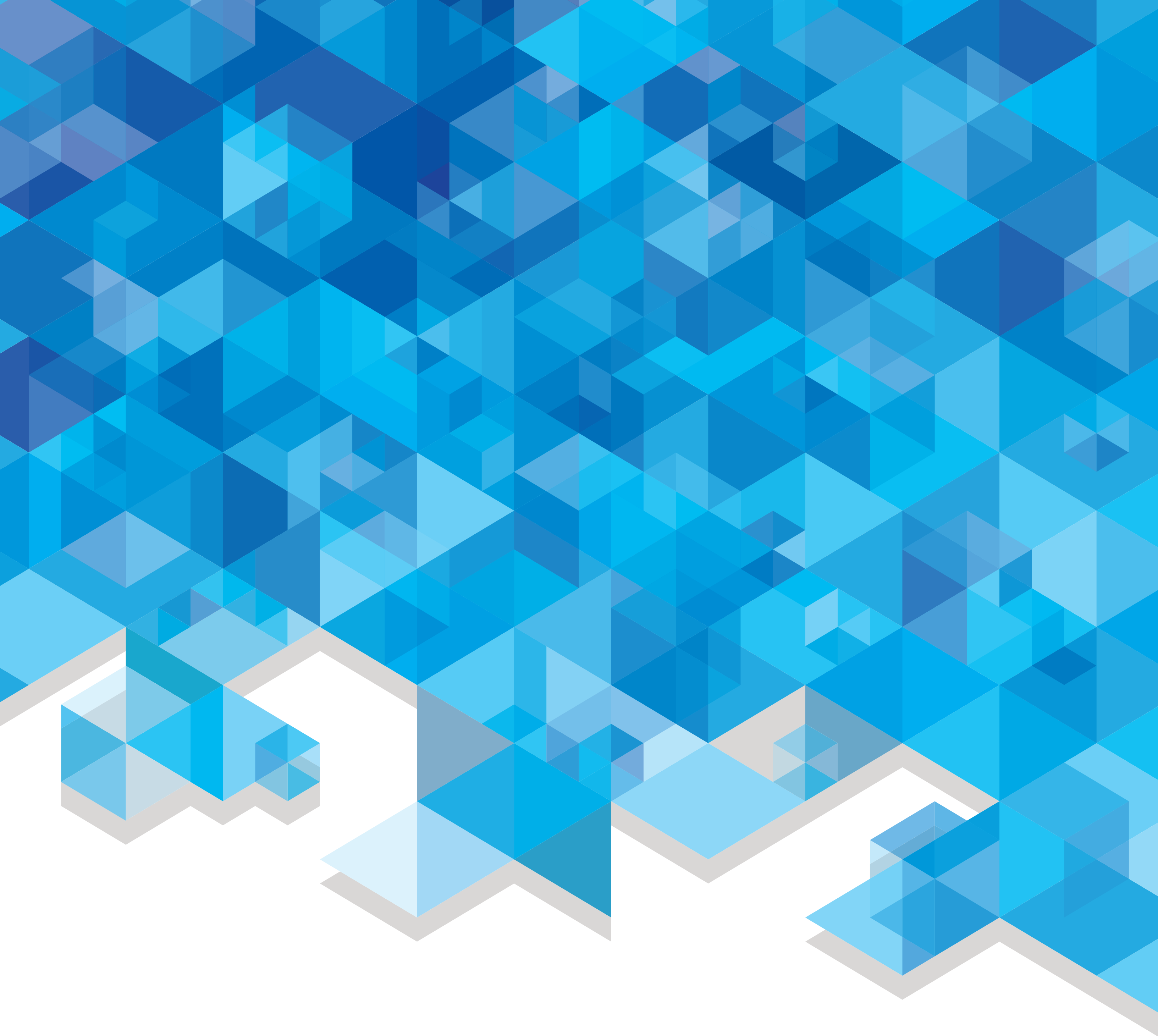

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