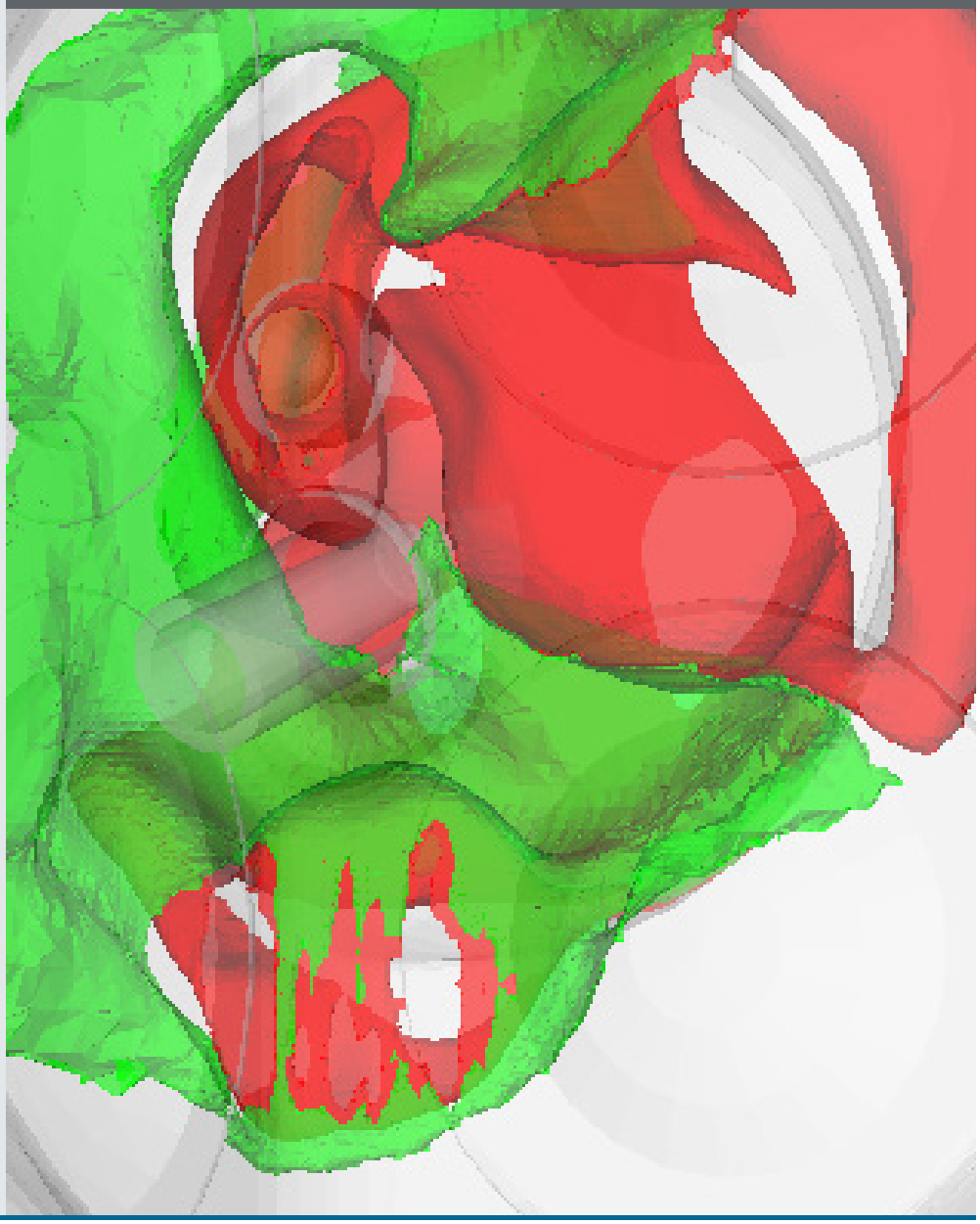
U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

Fuel and Lubricant Technologies

2015 Annual Report

Vehicle Technologies Office



Disclaimer

Acknowledgments

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Nomenclature or List of Acronyms

List of Acronyms, Abbreviations, and Nomenclature

$^{13}C\{^{1}H\}$	proton-decoupled, carbon-13 nuclear magnetic resonance
1MN	1-methylnaphthalene
2MHPD	2-methylheptadecane
2-PE	2-phenylethanol
3D	three-dimensional
4-MA	4-methylanisole
AART	adjustable-angle reciprocating tribometer
ACEC	Advanced Combustion & Emission Controls
ACI	advanced compression ignition
Add	additive
AEC	Advanced Engine Combustion
AF	antifoaming
Ag	silver
AHRR	apparent heat release rate
AKI	Anti-Knock Index
Al_2O_3	aluminum oxide
Alt	alternative
amu	atomic mass unit
ANL	Argonne National Laboratory
AO	antioxidant
ATDC	after top dead center
$ATDC_f$	after top dead center firing
ATF	automatic transmission fluid
atm	atmospheres
AVFL	Advanced Vehicle/Fuel/Lubricants
AW	antiwear
Bench.	benchmark
BHT	butylated hydroxy toluene
BL	boundary lubrication

BMEP	brake mean effective pressure
BOB	blendstock for oxygenate blending
BOV	base oil viscosity
BP	boiling point
BPE	branched polyethylene
bsDPM	brake specific diesel particulate matter
bsfc, BSFC	brake specific fuel consumption
bsHC	brake specific hydrocarbon
bsNOx	brake specific NO_x
BTDC	before top dead center
BTE	brake thermal efficiency
C_3H_6	propene
CA	capping agents
CA50	crank angle at which 50% of the heat has been released or mass fraction burned
CAD	crank angle degrees
CAP	Clean Air Power
CCV	cold crank viscosity
CDC	conventional diesel combustion
CF	#2 ULSD emissions-certification fuel
CFD	computational fluid dynamics
CI	compression-ignition
CN	cetane number
CNP	capping agents functionalized nanoparticle
Co	cobalt
CO_2	carbon dioxide
COF	coefficient of friction
Comb.	combustion
Conv.	conventional
COV	coefficient of variation
COV_{IMEP}	coefficient of variation of indicated mean effective pressure
cP	centipoise

CPN	cyclopentanone
CRADA	Cooperative Research and Development Agreement
CRAFT	Complete Reduction to Amplitude-Frequency Table
CRC	Coordinating Research Council
cSt	centistoke
Cu	copper
dB	decibel
DI	direct injection
DLS	dynamic light scattering
DOC	diesel oxidation catalyst
DP	dispersant
E0	100% gasoline
E10	fuel mixture of 10% ethanol, 90% gasoline
E100	100% ethanol
E30	fuel mixture of 30% ethanol, 70% gasoline
E50	fuel mixture of 50% ethanol, 50% gasoline
E85	fuel mixture of 85% ethanol, 15% gasoline
EDPCI	E85–Diesel Premixed Compression Ignition
EDS	energy dispersive X-ray spectroscopy
EF	experimental formulation
Eff.	efficiency
EGR	exhaust gas recirculation
EHL	elasto-hydrodynamic lubrication
EMD+	engine manufacturer diagnostics enhanced
EMS	engine management system
EOT	end of test
EP	extreme pressure
eV	electronvolt
Da	dalton
DCN	derived cetane number
det.	detergent

DFI	ducted fuel injection
DISI	direct-injection spark ignition
DLC	diamond-like carbon
DME	dimethyl ether
DMF	2,5-dimethylfuran
DT	detergent
e.g.	*exempli gratia* (for example)
et al.	*et alli* (and others)
etc.	*et cetera* (and so forth)
FACE	Fuels for Advanced Combustion Engines
Fe	iron
FE	fuel efficiency
FEI	fuel economy improvement
FMC	Ford Motor Company
FPT	first pulse timing
FREI	flame with repetitive extinction and ignition
FSN	filter smoke number
FTP	Federal Test Procedure
FM	friction modifier
FUL	full useful lifetime
FY	fiscal year
g/bhp-hr	grams per brake horsepower-hour
GCI	gasoline compression ignition
GEFORCE	Gasoline Engine and Fuels Offering Reduced Fuel Consumption and Emissions
Gen I	Generation 1
Gen II	Generation 2
GDI	gasoline direct injection
GIE	gross indicated efficiency
g/kWh	grams per kilowatt-hour
GM	General Motors
GPa	gigapascal
h	hour

H_2O	water
HBPE	hyperbranched polyethylene
HC	hydrocarbon
HCCI	homogeneous charge, compression ignition
HD OBD	heavy-duty on-board diagnostics
HFS	heavy fuel stratification
HL	hydrodynamic lubrication
HO_2	hydroperoxyl
HoV	heat of vaporization
hp	horsepower
HSQC	heteronuclear single quantum coherence
HTHS	high temperature high shear
Hz	hertz
iBu100	100% isobutanol
iBu24	blend containing 24% isobutanol, 76% gasoline
iBuOH	isobutanol
ICPS	in-cylinder pressure sensor
ID	ignition delay
i.e.	*id est* (that is)
IL	ionic liquid
IMEP	indicated mean effective pressure
$IMEP_g$	gross indicated mean effective pressure
IMT	intake manifold temperature
IQT	ignition quality tester
ITE	indicated thermal efficiency
ITHR	intermediate temperature heat release
J	joule
K	Kelvin
kDa	kilodalton
KLSA	knock limited spark advance
KOH	potassium hydroxide
kPa	kilopascal

ksi	kilopound per square inch
KV	kinematic viscosity
L	liter
lb·ft	pound-foot
LLFC	leaner lifted-flame combustion
LLNL	Lawrence Livermore National Laboratory
LNF	General Motors Generation II Ecotec engine
LSPI	low speed pre-ignition
LTG	General Motors Generation III Ecotec engine
LTGCI	low temperature gasoline compression ignition
LTHR	low temperature heat release
Max	maximum
MBT	maximum brake torque
MD	molecular dynamics
MFB	mass fraction burned
MFS	moderate fuel stratification
min	minute
ML	mixed lubrication
mm	millimeter
mm^3	cubic millimeter
mm/s	millimeter per second
Mn	number average molecular weight
MoDTC	molybdenum dialkyldithiocarbamate
MoN	molybdenum nitride
MON	Motor Octane Number
MPa	megapascal
mPa·s	millipascal-second
mpg	miles per gallon
m/s	meters per second
ms	milliseconds
MS	milestone

MSOIc	main start of injection
MTM	Mini Traction Machine
MY	model year
N	newton
Nat	naturally
NBCX	N-butylcyclohexane
NDA	non-disclosure agreement
NEI	N-eicosane
NG	natural gas
NH_3	ammonia
Ni	nickel
NL	natural luminosity
nm	nanometer
N·m	newton meter
NMEP	net mean effective pressure
NMR	nuclear magnetic resonance
NO_2	nitrogen dioxide
NO_x	oxides of nitrogen
NOD	N-octadecane
NP	nanoparticle
NREL	National Renewable Energy Laboratory
NTC	negative temperature coefficient
O	oxygen
$[O_2]$	mole fraction of oxygen
OCP	olefin co-polymer
OEM	original equipment manufacturer
OH	hydroxide
ORNL	Oak Ridge National Laboratory
OSP	oil soluble polyalkylene glycol
oxi.	oxident
$[P_{66614}][DEHP]$	trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate

$[P_{8888}][DEHP]$	tetraoctylphosphonium bis(2-ethylhexyl) phosphate
PAG	polyalkylene glycol
PAMA	polyalkyl methacrylates
PAO	polyalphaolefin
PFI	port fuel injection
PFS	partial fuel stratification
PHP	perhydrophenanthrene
PM	particulate matter
PMA	polymethacrylate
PMI	particulate matter index
PN	particle number
PNNL	Pacific Northwest National Laboratory
PoE	polyolester
PPD	pour point depressant
ppm	parts per million
Pres.	pressure
PRF	primary reference fuel
PRR	pressure rise rate
psi	pounds per square inch
PSOIc	pilot start of injection
Q1	first quarter
RCCI	reactivity controlled compression ignition
RCF	rapid compression facility
RCM	rapid compression machine
RD387	fully blended research gasoline
Ref	reference
Rg	radius of gyration
RMSECV	root mean squared error cross validation
RMSEP	root mean squared error predicted
RON	Research Octane Number
R_p	flow similarity parameter

rpm	revolutions per minute
s	second
S	octane sensitivity (Research Octane Number - Motor Octane Number)
SANS	small-angle neutron scattering
SCR	selective catalytic reduction
SD	standard deviation
SET	Supplemental Emissions Test
SI	spark-ignition
SINL	spatially integrated natural luminosity
SOI	start of injection
STEM	scanning transmission electron microscopy
SwRI	Southwest Research Institute
SWRS	software requirements specification
T	temperature
T50	A blend of 50 vol% certification fuel with 50 vol% tri-propylene glycol methyl ether (an oxygenate)
$T_{50\%}$	temperature at 50% conversion
$T_{90\%}$	temperature at 90% conversion
T_{90}	90% distillation temperature
TEM	transmission electron microscopy
$T_{end\text{-}gas}$	end-gas reactant temperature
TET	tetralin
TDC	top dead center
THC	total hydrocarbon
T_{in}	intake temperature
TIPB	1,3,5-triisopropylbenzene
TIPCX	1,3,5-triisopropylcyclohexane
TPGME	tri-propylene glycol methyl ether
TRZ	top ring zone
TSF	toluene standardization fuel
TWC	three-way catalyst
V0a	four-component diesel surrogate fuel for target certification fuel

V0b	five-component diesel surrogate fuel for target certification fuel
V1	eight-component diesel surrogate fuel for target certification fuel
V2	nine-component diesel surrogate fuel for target certification fuel
VI	viscosity index
VM	viscosity modifier
VN	vanadium nitride
vol%	volume percent
VP	vapor pressure
w/	with
w/o	without
WOT	wide open throttle
WSD	wear scar diameter
wt%	weight percentage
X_{O2}	Mole fraction of oxygen in engine intake mixture
XPS	X-ray photoelectron spectroscopy
Y4	Yubase 4
ZDDP	zinc dialkyldithiophosphate

List of Symbols

~	approximately
≈	approximately equal to
η_{th}	thermal efficiency
°C	degrees Celsius
°CA	degrees crank angle
°F	degrees Fahrenheit
$	dollars
>	greater than
≥	greater than or equal to
µ−FIT	micro-liter Fuel Ignition Tester
µg	microgram
µL	microliter
µm	micrometer
%	percent

ϕ	fuel/air equivalence ratio
ϕ_m	mass-based fuel/air equivalence ratio
+	plus
±	plus or minus

Executive Summary

On behalf of the Department of Energy's Vehicle Technologies Office, we are pleased to introduce the Fiscal Year 2015 Annual 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 crude oil and petroleum products, about 27% of which is currently imported (net). Advanced lubricants improve vehicle fuel efficiency, helping to reduce fuel consumption.
- Environmental sustainability: Cleaner fuels have the potential to reduce engine-out gaseous and particulate emissions and 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 objectives 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. The subprogram's activities asses the impacts of fuel and lubricant properties on the efficiency, performance, and emissions of current engines and enable emerging advanced internal combustion engines. From 2000–2011, this subprogram provided critical test data for both the Environmental Protection Agency's diesel sulfur rule (2006) and the 15% ethanol (E15) waiver (2011). The current Fuel-Engine Co-Optimization initiative broadens the research program to explore additional biofuels that are affordable, scalable, and sustainable, and can enable high-efficiency, low-emission engines.

The Fuel & Lubricant Technologies Program will continue to collaborate with DOE's national laboratories and universities to advance basic fuel and combustion science, as well as 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 (such as the Advanced Combustion Engine R&D program and the Biomass Energy Technologies Office) to ensure that engines and fuels resulting from their research and development are optimized to work in conjunction. This ensures maximum efficiency and durability with lowest possible greenhouse gas emissions.

The work being conducted in fuel and 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. In fiscal year 2016, we look forward to on-going and new cooperative efforts with the auto and energy industries to develop innovative fuel technologies for use in advanced transportation vehicles that are efficient, clean, and safe.

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Table of Contents

I. Introduction

I.1 Advanced Fuels and Lubricants for an Efficient, Clean, and Secure U.S. Vehicle Transportation System

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 while displacing petroleum. Over the long-term, it is expected that transportation fuels will be produced from future refinery feedstocks that may increasingly be from non-conventional fossil 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. This expectation brings new concerns for engine manufactures, regulatory bodies, and end users. While it may be seen as a challenge to make engines compatible with more diverse fuels, it is also an opportunity to change fuel composition and properties to enable emerging combustion strategies. The Fuel & Lubricant Technologies subprogram activities are primarily focused on the properties and quality of the finished fuels derived from non-conventional sources, not on their production.

The Fuel & Lubricant Technologies subprogram is an integral part of the United States Driving Research and Innovation for Vehicle Efficiency and Energy Sustainability (U.S. DRIVE) government–industry partnership. It provides a key means for pursuing the U.S. DRIVE mission to develop more energy-efficient and environmentally friendly highway transportation technologies. A U.S. DRIVE fuels technology team was initiated in 2013 and continued work in 2014, culminating in a plan to evaluate potential properties of new low-carbon fuels for future, high-efficiency engines and combustion regimes. The initial plan for precompetitive research includes an emphasis on low-carbon spark-ignition and compression-ignition 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 spark-ignition engines; and the determination of a new ignition delay metric for advanced low temperature combustion engines. Also, in 2015, in a collaboration with the Advanced Combustion Engines R&D subprogram and the Bioenergy Technologies Office, the Fuels & Lubricant Technologies subprogram formed a national laboratory consortium to look into the co-optimization of fuels and engines for higher efficiency and lower emissions. The goal of the consortium is to lower greenhouse gases (GHGs) from vehicles with both biofuel blending components and different combustion strategies. Lifecycle and techno-economic analyses will guide selection of new fuel candidates that can be scaled up and deployed rapidly, economically, and sustainably at the required scale of tens of billions of gallons per year.

Although fast-fill compressed natural gas stations are increasing every year and expected to reach over 1,400 in 2016, liquid fuels, primarily diesel, currently dominate the market for heavy over-the-road trucks. In 2015, the Fuel & Lubricant Technologies subprogram continued to advance gaseous fuels research through Funding Opportunity Announcements designed to remove barriers to the deployment of new, more efficient and enabling technologies for gaseous fuel use in medium- and heavy-duty applications. For example, one project is developing a robust dual-fuel engine control system to enable the use of natural gas and diesel in heavy-duty applications. While much of the ongoing fuels combustion research will benefit gaseous fuels as well, future program activities will continue to target new gaseous fuel technologies that can utilize assistance for commercial viability.

Program Goals

The Fuel & Lubricant Technologies Program has the following targets:

- By 2020, demonstrate expanded operational range of advanced combustion regimes covering >95% of the light-duty Federal Test Procedure.
- By 2020, demonstrate novel formulations for powertrain and driveline lubricants, compatible with new and legacy vehicles, to achieve at least a 4% real-world fuel economy improvement.

For these goals, the baseline 2015 vehicle powertrain will need to have combined sales in excess of 100,000 units per year. Fuel economy improvements will be demonstrated either through on-road testing, recognized vehicle cycles, or vehicle simulations. 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 R&D program and the Biomass Energy Technologies Office) to ensure that engines and fuels resulting from their research and development are optimized to work in conjunction with each other for maximum efficiency and durability with lowest possible greenhouse gas emissions.

Transportation Fuels and Energy Security

Petroleum-derived fuels account for 97% of all fuel used in the United States 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 restrict personal and commercial mobility in the United States. This was vividly illustrated during the summer months of 2005 when several hurricanes hit the Gulf Coast of the United States, interrupting, at one point, 28% of domestic crude oil production and 29% of the United States' 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 Organization of the Petroleum Exporting Countries (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. Oil prices never recovered in 2015 as expected. The continued production levels and current large market surplus will likely mean that oil prices will stay depressed through 2016, but there is a high degree of uncertainty in the predictions. Petroleum currently supplies about 36% of all the energy used in the United States, with 71% of this petroleum going to the transportation sector. The transportation sector alone consumes about as much petroleum as is produced in the United States. The increase in United States crude oil production in the Gulf of Mexico and from shale formations, combined with increasing biofuel 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, as well as 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 have played 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 continuing despite the lower price of petroleum worldwide. Since Canada is our largest supplier of crude oil and we import between 80% and 90% of its production, it is likely that oil sands liquids will represent an increasing portion of our transportation fuel. Natural gas is another resource that has increased significantly in the United States, which is near to reaching full natural gas independence with no net imports. Natural gas use in heavy-duty transportation continues to grow, and multiple research needs have been identified by industrial and trade groups.

The Energy Independence and Security Act (EISA) of 2007 mandates increasing production of biofuel for use in transportation vehicles. In terms of starch-based ethanol, the United States is close to the 15 M barrel limit imposed by EISA, but has not met the EISA goals for advanced biofuels. The Fuel & Lubricant Technologies subprogram is currently a major co-sponsor of a new DOE initiative to accelerate the introduction of affordable, scalable, and sustainable biofuels and high-efficiency, low-emission engines designed to work together in delivering maximum energy savings, emissions reduction, and on-road vehicle performance. The Fuel-Engine Co-Optimization initiative began in Fiscal Year 2015 and simultaneously tackles fuel and engine innovation to co-optimize performance of both elements and provide dramatic and rapid cuts in fuel use and emissions.

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 United States 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. An updated market survey of biodiesel will be carried out in 2016.

Transportation Fuels and Lubricants for 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, oxides of nitrogen (NO_x), particulate matter, volatile organic compounds, and sulfur dioxide. The Fuel & Lubricant Technologies subprogram is evaluating advanced petroleum and non-petroleum-based fuels for their impacts on engine-out emissions and emission control system efficiency and durability. For example, detailed research is currently being conducted on the use of biofuels to reduce NO_x emissions from lean-burn gasoline direct injection engines. Combustion of petroleum fuels also releases GHGs (primarily CO_2, plus nitrous oxide, black carbon, and methane) that are believed to contribute to climate change. 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. Detailed research has also demonstrated that black carbon emissions from gasoline direct injection engines can be reduced using biofuel blends.

The Fuel & Lubricant Technologies subprogram has historically led research that provides the basis for public policy. In 2000, a government–industry collaboration was formed and demonstrated that the sulfur content of diesel fuel had to be reduced to enable the use of advanced emission control systems required to meet the 2007 and 2010 heavy-duty diesel emissions regulations. Fuel & Lubricant Technologies subprogram-sponsored research led the Environmental Protection Agency (EPA) to require that all highway diesel fuel contain a maximum of 15 ppm sulfur, down from a maximum of 500 ppm. Similarly, in partnership with EPA and others, the Fuel & Lubricant Technologies subprogram conducted a verification program from 2009–2012 to enable the use of higher level ethanol blends in vehicles. This work was required to meet aggressive goals for renewable fuels established in EISA. The joint work resulted in EPA granting a partial waiver for E15 to be used on 2007 and newer light-duty vehicles (2010) and a second partial waiver for 2001 to 2006 light-duty vehicles (2011). The impact of E15 and E20 on vehicles and other engines, materials compatibility, evaporative emissions, and vehicle drivability were investigated.

In Fiscal Year 2015, the Fuel & Lubricant Technologies subprogram began the Fuel-Engine Co-Optimization initiative to pursue the goals of the Fuel & Lubricant Technologies sub-program through simultaneous fuel and engine innovation to accelerate the introduction of affordable, scalable, and sustainable biofuels along with high-efficiency, low-emission vehicle engines. This coordinated R&D effort brings together nine Department of Energy national laboratories and numerous industry and academic partners to integrate the research areas of biofuels, combustion, and analysis. The Co-Optimization initiative has three concurrent phases of R&D: optimizing spark ignition fuels and engines for near-term effect, developing fuels and engines to enable advanced compression ignition technologies needed for revolutionary long-term solutions, and developing and applying analysis tools to assess the economic and environmental impact of the proposed technologies.

Reducing friction losses in engines and drivelines can significantly reduce fuel consumption and the related greenhouse gas emissions. The Fuel & Lubricant Technologies subprogram is evaluating new approaches to lubrication that can reduce parasitic losses without adversely affecting component wear or the performance and emissions of the engine. To attain the ambitious goal of attaining 4% fuel economy improvement in both new and legacy vehicles, new approaches to lubrication must be explored, including novel base oils and additives and high-performance tribological coatings. To understand the efficiency and wear performance of novel formulations, correlations are being developed to relate benchtop testing to fuel economy, durability, and reliability in real vehicles. The Fuel & Lubricant Technologies subprogram supports universities, national labs, and industry to study many aspects of lubrication, from fundamental tribology to application of fully formulated lubricants in vehicles and engines.

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.

I.2 Summary of Program Accomplishments (FY 2015) and Future Activities (FY 2016)

The following presents highlights of the Fuel & Lubricant Technologies project accomplishments in FY 2015 and the activities that will be pursued in FY 2016.

Fuels Research to Enable High-Efficiency Engine Operation while Meeting Prevailing Emissions Standards

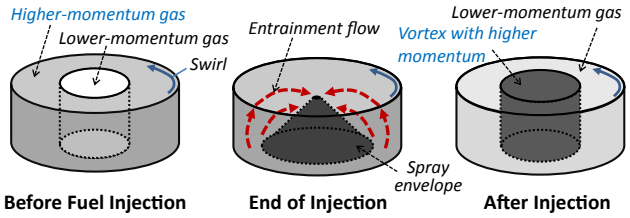
The goal of this program area is to explore fuel properties that can both result in lower carbon emissions and enhanced efficiency. An additional goal is to maintain compatibility with emissions control devices and prevent unwanted combustion byproducts. For FY 2016, the focus of this program area will be incorporated into the Fuel-Engine Co-Optimization initiative. The first research thrust will consider fuels with near-term impact on spark-ignited engine efficiency and emissions, and the second thrust will focus on fuels for advanced compression ignition engines that have both low NO_x and low particulate matter emissions.

- **Oak Ridge National Laboratory** is quantifying fuel efficiency benefits of increased octane fuels using multiple pathways towards octane improvement. **(Sluder, report II.1)**

  FY 2015 accomplishments: (1) completed engine maps for an 87 Anti-Knock Index E10 (blend of 10% ethanol, 90% gasoline) fuel at a compression ratio of 10.1 and for an E30 (blend of 30% ethanol, 70% gasoline) 101 Research Octane Number fuel at compression ratio of ~13; (2) developed initial vehicle model in Autonomie and compared the fuel economy of the vehicle for the two engine maps; and (3) examined data from three 97 Research Octane Number fuels to evaluate influences from heat of vaporization.

  FY 2016 activities: (1) explore more fuel formulations and compression ratio combinations, continue expansion of the data envelope to include additional fuels, and robustly examine the potential benefits and challenges of increasing octane rating; (2) examine hybrid powertrain strategies to explore potential synergistic effects from increasing the octane rating in a systems context; and (3) continue to actively engage with industry stakeholders to assess priorities in terms of the inclusion of different fuel formulations to assure alignment of the project with industry priorities in this research area.

- **Sandia National Laboratories** are providing the science base needed by industry to understand how emerging alternative fuels impact highly efficient direct injection spark ignition light-duty engines. In addition, they are exploring how engine design and operation can be optimized for most efficient use of future fuels. **(Sjöberg, report II.2)**



Conceptual model of spray-swirl interactions that create a repeatable vortex near the spark plug for stratified-charge operation. (Sjöberg, report II.2)

  FY 2015 accomplishments: (1) developed conceptual descriptions of both the spray-swirl interactions and flame-spread patterns that act to stabilize stratified combustion; (2) examined effects of fuel blend (E0 to E30 [blend of 30% ethanol, 70% gasoline]) on boosted, stratified operation with double injections; (3) quantified control authority over the ignition process, for both advanced multi-pulse transient plasma ignition and with partial fuel stratification; and (4) compared lean and dilute stability limits and fuel efficiency gains for E30, E85 (blend of 85% ethanol, 15% gasoline) and gasoline, using enhanced ignition to ensure repeatable end-gas autoignition for high combustion efficiency of ultra-lean deflagration-based SI operation.

  FY 2016 activities: (1) expand the conceptual model of swirl-spray stabilization mechanisms to include double injections of E0–E30 fuels for boosted stratified operation; (2) continue examination of well-mixed lean or dilute spark ignition operation while quantifying the relevance of Research Octane Number and Motor Octane Number for fuel reactivity under ultra-lean conditions; (3) incorporate new fuel components and blends in coordination with the Co-Optima initiative; and (4) refine partial fuel stratification technique to allow the use of a smaller pilot-fuel quantity and apply partial fuel stratification to examine fuel effects on limits of ultra-lean spark ignition combustion.

- **Oak Ridge National Laboratory** is establishing key engine technologies and fuel characteristics that enable very high fuel efficiency with very low emissions in future vehicles. **(Sluder, report II.3)**

  FY 2015 accomplishments: (1) executed a Cooperative Research and Development Agreement with Coordinating Research Council and a non-disclosure agreement with General Motors allowing the project to proceed; and (2) began test cell preparations for the advanced research engine and began development of the advanced research engine. The Coordinating Research Council selected Gage Products as a fuel supplier, putting in place a purchase order and releasing Gage Products to begin production of the entire matrix of fuels.

  FY 2016 activities: (1) work with the baseline engine to help guide calibration of the advanced engine for each fuel in the matrix; (2) install and commission advanced research engines; (3) begin calibration and mapping of the advanced engine for each fuel in the experimental matrix; and (4) utilize engine maps for each fuel to produce estimates of vehicle fuel economy and emissions to identify promising combinations of engine technology and fuel formulation that enable significant improvements in fuel economy and emissions performance.

- **Oak Ridge National Laboratory** is ensuring that new fuels and lubricants do not negatively impact emissions and emissions control systems and investigating unique characteristics of fuels that enable increased efficiency. **(Toops, report II.4)**

  FY 2015 accomplishments: (1) demonstrated isobutanol has similar lean NOx reduction performance to ethanol; (2) determined start-stop did not have a major impact on particulate matter formation on E0 (gasoline) or E30 (blend of 30% ethanol, 70% gasoline); however, when using iBu24 (blend of 24% isobutanol, 76% gasoline), particulate matter increased overall and during start-stop; (3) used a suite of laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate–orthophosphate interactions with catalysts; (4) showed that P-form on three-way catalyst was different when using ionic liquid additive compared to zinc dialkyl dithiophosphate, and aluminum phosphate formation was preferred with ionic liquid and cerium phosphate with zinc dialkyl dithiophosphate; and (5) completed long-term exposure of a heavy-duty truck emissions control system with full-useful life exposure of Na at ASTM-specified levels with collaborators.

  FY 2016 activities: study (1) emissions control opportunities when using biofuels and biofuel–gasoline blends; (2) fuel and lubricant formulation impacts on gasoline direct injection particulate emissions; (3) techniques for identifying lubricant and fuel species in emissions control devices; (4) compatibility of ionic liquid lubricant additives with three-way catalysts; and (5) compatibility of biodiesel with diesel emissions control devices.

Lubricants to Enable High Engine and Vehicle Fuel Efficiency

The goal of this program area is to identify new approaches to lubrication that result in higher engine and powertrain efficiency. Friction reduction, wear protection, and compatibility with the legacy fleet are key features of this research area. For FY 2016, the focus of this program area is novel additives to enable lower viscosity oils, high performance tribological coatings, and combustion and emissions control compatibility of advanced lubricants.

- **Argonne National Laboratory** is developing accurate and reliable correlations between friction data and wear mechanisms from a select set of benchtop and engine tests of fuel economy, durability, and reliability. **(Demas, report III.1)**

  FY 2015 accomplishments: (1) broadened the network of industrial collaborators; (2) procured a system able to deliver nanoliter quantities of lubricating oil to simulate starved conditions; (3) acquired engine components for evaluation; (4) initiated the development of test methodology to simulate scuffing, a major failure mechanism of concern to industrial collaborators; and (5) developed a new data acquisition program that can be used not only to perform a computer-controlled scuffing routine during which the load is increased in a step-wise fashion, but also to record friction and automatically stop the test when a specified high friction is reached.

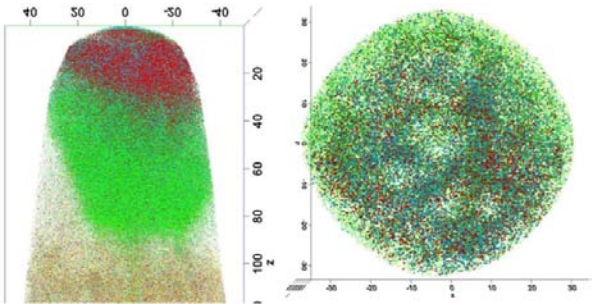
  FY 2016 activities: (1) improve existing friction test protocols to examine the effect of contact pressure, metallurgy, temperature, speed, and oil degradation; (2) develop test protocols to create scuffing reliably and compare to scuffing failures observed in engine surfaces; (3) design a wear test to accurately enable the screening of new-technology ring coatings and fully formulated oils; and (4) investigate the durability and reliability of journal bearings.

- **George Washington University** is developing a GF-6A (backward compatible) 0W-20 fuel efficient lubricant with at least 2% fuel economy improvement over a 5W-30 2014 GF-5 commercial oil (baseline oil) using the most up to date GF-6 specification engine test sequence available at the time (milestone due date). **(Hsu, report III.2)**

  FY 2015 accomplishments: (1) tested the lubricant in ASTM Engine Sequence VIE tests and showed 2.3% fuel economy improvement over the 2014 5W-30 GF-5 commercial oil; (2) evaluated various friction modifiers in industrial standard bench tests and in-house tests; (3) evaluated various antiwear additives under low viscosity formulations and high temperatures; and (4) successfully formulated a GF-6A lubricant based on these evaluations.

  FY 2016 activities: (1) formulate GF-6B 0W-16 ultra-low viscosity lubricants; (2) conduct engine tests to measure fuel economy of this oil; and (3) prepare surface texture and microcapsules for durability testing.

- **Oak Ridge National Laboratory** is developing oil-soluble ionic liquids (ILs) as engine oil additives, demonstrating 10% improvement in mechanical efficiency of internal combustion engines. It is also exploring potential advantages and disadvantages of this new category of additives through systematic lab experiments, modeling, engine dynamometer tests, and field tests. **(Qu, report III.3)**



Atom probe revealing the three-dimensional composition structure of the tribofilm formed by IL + ZDDP: a network of metal phosphates and oxides. Color scheme: P: red, Zn: light blue, O and FeO_x: green, and Fe: yellow. (Qu, report III.3)

  FY 2015 accomplishments: (1) highlighted the newly discovered synergism between IL and zinc dialkyldithiophosphate (ZDDP) by writing two media reports , three journal papers, and presenting at three conferences (one invited talk); (2) performed three-dimensional visualization of the tribofilm composition structure using atom probe; (3) determined compatibility of the top candidate IL with other engine oil additives, particularly detergents and dispersants; (4) fully formulated SAE 0W-16 engine oil containing a combination of IL and ZDDP as anti-wear additives was produced; and (5) evaluated prototype engine oil using Sequence VIE engine dynamometer test, with results demonstrating fuel economy improvement of 2.12% over the standard reference oil and 0.25% over a similar prototype engine oil in the same viscosity grade but using ZDDP only as the anti-wear additive.

  FY 2016 activities: (1) complete investigation of the effects of an ionic liquid plus zinc dialkyldithiophosphate combination on three-way catalyst using an accelerated small engine test and (2) end the Funding Opportunity Announcement/Cooperative Research and Development Agreement joint project between Oak Ridge National Laboratory and Shell.

- **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% (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. **(Wu, report III.4)**

  FY 2015 accomplishments: (1) demonstrated Federal Test Procedure cycle improvement of 1%; 1.7% improvement on the Supplementary Emissions Test cycle with Candidate 1 engine oil; (2) demonstrated Federal Test Procedure cycle improvement of 1.5%; 1.1% improvement on the Supplementary Emissions Test cycle with Candidate 2 engine oil; (3) showed that both axle oil candidates performed better than the baseline in all test conditions where temperature reduction was up to 16.4°C, and efficiency improvement was between 0.63% to 1.36% under demanding conditions; and (4) conducted nine SAE #2 friction tests with transmission fluid.

  FY 2016 activities: (1) reformulate two engine oil candidates per the learning from National Renewable Energy Laboratory's Cummins ISL 8.9 L engine fuel efficiency verification tests; (2) rerun the National Renewable Energy Laboratory's Cummins ISL 8.9 L fuel efficiency engine test on the same two engine oil candidates, anticipating

improvement of around 2% against the baseline; and (3) conduct SAE J1321 test on three types of lubricants at the Transportation Research Center Inc. in East Liberty, Ohio, expecting greater than 2% total fuel efficiency.

- **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. **(Cosimbescu, report III.5)**

  FY 2015 accomplishments: (1) synthesized several novel base oils that have built-in polarity for friction control and have an added advantage of being miscible with existing mineral oil base stocks for a drop-in oil package formulation; (2) determined pour point of the above base oils and four materials to meet industrial requirements; (3) completed simulations of a series of four model compounds that have structural similarities to the compounds subjected to dynamic light scattering studies; (4) established collaboration with researcher at the National Institute of Standards and Technology's (NIST) Small-Angle Neutron Scattering facility and a co-authored proposal for beam time at NIST user facility; (5) completed small-angle neutron scattering experiments which are in agreement with dynamic light scattering measurements; and (6) demonstrated temperature-induced conformational and size changes using simulations, dynamic light scattering and small-angle neutron scattering.

  FY 2016 activities: (1) evaluate at least three synthesized base oils for viscosity, wear, and friction against unadditized commercial base oils; (2) continue to investigate the potential of tribopolymers as a renewable in situ additive and expand beyond caprolactams and caprolactones; (3) conduct these investigations at Southwest Research Institute, which is set up with the proper rig for testing tribopolymers, since Pacific Northwest National Laboratory was unable to obtain meaningful data of known materials with its unidirectional tribometer; (4) explore the evaluation of friction and wear of generated materials at Southwest Research Institute; (5) demonstrate the value of modeling in predicting viscosity changes with temperature of viscosity modifiers; and (6) investigate shear thinning simulations to build a predictive model spanning various architectures and topologies.

- **Northwestern University** is developing novel lubricant formulations for improving vehicle fuel efficiency by at least 2% without adversely impacting vehicle performance or durability. **(Wang, report III.6)**

  FY 2015 accomplishments: (1) synthesized and characterized three major families of heterocyclic friction modifiers (FMs); (2) designed and conducted the synthesis of the first generation of di-block copolymers as viscosity modifiers; (3) identified excellent heterocyclic FMs that were capable of reducing boundary lubrication friction more than selected commercial products by means of laboratory scale tests; (4) functionalized the nanoparticles, demonstrated their good solubility in base oils and plausible friction reduction together with improvements in wear and scuffing resistances of mating surfaces; (5) conducted ultra-thin film measurements and verified reinforcement of lubricant film in the boundary lubrication regime; (6) investigated FMs' surface adsorption abilities and viscosity modifiers' shear-thinning transitions via molecular dynamics simulations; and (7) trained postdoctoral researchers, graduate, and undergraduate students, one of whom graduated with a master's of science and two (partially involved) with doctorates.

  FY 2016 activities: (1) finalize synthesis of the di-block copolymer viscosity modifiers (VMs); (2) comprehend the tribo-rheological properties of the newly synthesized VMs; (3) further improve the design of the heterocyclic friction modifiers (FMs) and functionalized nanoparticles; (4) develop a strategy for formulating additive packages (including FMs, VMs, and nanoparticles); (5) conduct an in-depth mechanism investigation for VMs and a physical/chemical surface study for FMs; (6) perform further laboratory tests at more severe conditions for oil aeration effects and oxidation stability; and (7) initiate Ricardo engine simulation and industrial verification tests.

- **Ford Motor Company** is formulating new modified PAG-based (polyalkylene glycol) engine oils, and evaluating fundamental material properties with respect to the new lubricant formulations. **(Gangopadhyay, report III.7)**

  FY 2015 accomplishments: (1) conducted friction evaluations on one PAG base oil and several formulated PAG oils and compared against GF-5 base oil and GF-5 SAE 5W-20 oil at 40°C and 100°C under sliding/rolling conditions using a Mini Traction Machine rig; (2) completed motored valvetrain wear assessments on two PAG oils (14-2 and 15-1) when fresh, PAG oil 15-1 following 10,000-mile aging, and GF-5 SAE 5W-20 oil under the same aging

conditions as PAG oil 15-1; (3) analyzed bucket tappet surfaces from motored valvetrain tests and Mini Traction Machine disks using Auger spectroscope and time-offlight secondary ion mass spectroscope to understand the mechanism of friction reduction; (4) completed ASTM Sequence VG testing on PAG oil 17-1 to understand its sludge and varnish protection capability; and (5) completed chassis roll dynamometer fuel economy and emission evaluations on PAG oil 15-1 and GF-5 SAE 5W-20 oil following 500-, 5,000-, and 10,000-mile aging on a vehicle with an I-4 engine.

FY 2016 activities: This project was completed on September 30, 2015.

- **Ford Motor Company** is formulating new PAG-based gear oils that will improve the fuel efficiency of light- and medium-duty applications by 2% over SAE 75W-140 grade axle oils without adverse impacts on vehicle performance or durability, and evaluating fundamental material properties with respect to the new lubricant formulations. **(Gangopadhyay, report III.8)**

  FY 2015 accomplishments: (1) completed system level industry standard load carrying capacity testing (ASTM D6121); (2) completed hardware and tribofilm analysis and hypothesized prospective deficiencies of the Gen I PAG and additive package with Dow Chemical; (3) selected two oil soluble PAG formulations and two Gen II formulations as the best candidates, showing wear and friction results comparable to SAE 75W-140; and (4) completed system level load carrying capacity testing and passed the requirements for post-test gear condition. Dow completed hardware, tribofilm, and lubricant analysis and confirmed that the adjustments made in oil soluble PAG formulations and additive package addressed the speculated deficiencies of the Gen I formulation.

  Sequence VG results

Parameters	17-1	GF-5 limits
Average Engine Sludge, Merits	8.76	8.0 minimum
Rocker Cover Sludge, Merits	9.32	8.3 minimum
Average Engine Varnish, Merits	8.19	8.9 minimum
Average Piston Skirt Varnish, Merits	5.17	7.5 minimum
Oil Screen Sludge, % Area	4.96	15 maximum
Number of Hot Stuck Rings	0	None

(Gangopadhyay, report III.7)

  FY 2016 activities: (1) complete laboratory bench rig tests on oil soluble PAG and Gen II formulations with hardware test pieces made from Ford hypoid gear steels; (2) complete additional industry standard axle system tests, including load carrying capacity, moisture corrosion, oxidative stability, and shock loading testing with oil soluble PAG and Gen II candidates; (3) complete Ford proprietary axle system (efficiency and gear wear) testing with oil soluble PAG and Gen II candidates; (4) define the best candidate formulation; and (5) complete chassis roll dynamometer tests for fuel economy and emission evaluations when oil is fresh and aged.

- **Pacific Northwest National Laboratory** is developing novel polymers with a branched or hyperbranched architecture as viscosity modifiers. **(Cosimbescu, report III.9)**

  FY 2015 accomplishments: (1) designed multiple polymers with dual performance function in the molecule (viscosity modifier and friction modifier); (2) developed structure–property relationships based on the friction data gathered from Oak Ridge National Laboratory; (3) identified three potential viscosity modifier candidates that meet viscosity and friction requirements; (4) selected one candidate based on performance and scalability; (5) synthesized ~1.4 kg of selected viscosity modifier; and (6) acquired dispersant inhibitor package and Yubase 4 oil for finished formulation.

  FY 2016 activities: (1) explore hybrid structures (comb, branched, and star polymers) as potential next generation additives; (2) investigate shear stability of several analogs; (3) design novel structures with potential to address several performance metrics, such as viscosity, friction, and wear; and (4) complete and submit several manuscripts to peer reviewed journals.

- **Argonne National Laboratory** is developing technologies (coatings, additives, and basefluids) that reduce parasitic friction losses in engines and drivetrains and maintain or improve component reliability and durability. **(Fenske, report III.10)**

  FY 2015 accomplishments: (1) measured the rheological and traction properties for several polyalphaolefin-ester hybrid basestock blends; (2) established friction benchmark for current advanced lubricant to be 0.08–0.13 under boundary lubrication regime; (3) identified, synthesized, and characterized with analytical transmission electron microscopy, five anti-wear, four friction modifier, and five extreme pressure particulate additives; (4) completed measurements of rheological properties and preliminary friction and wear performance of colloidal additives in polyalphaolefin under reciprocating sliding contact; (5) developed and optimized a range of non-ferrous coatings consisting of MoN and VN as the hard phases and Cu, Ni, Co as the soft catalyst phases; (6) optimized deposition parameters with respect to temperature, deposition rate, bias voltage, and sample rotation in order to achieve highly uniform coating thickness and structure; and (7) completed structural, chemical, and mechanical characterization of the optimized coatings and correlated conditions with the tribological performance.

  FY 2016 activities: (1) downselect the most advanced mineral oil-based fluid as a baseline for the mixed fluid development effort (Yubase 4 and Yubase 4+); (2) evaluate friction and wear performance of fluid mixtures with optimized rheological properties in comparison with the Yubase baseline fluids with and without additives; (3) evaluate scuffing performance of colloidal additive systems; (4) analyze nano-structure of tribo-chemical films formed from colloidal systems using transmission electron microscopy with a focused ion beam; (5) complete remaining bench tribological studies and develop friction and wear maps illustrating operational ranges of optimized coatings; (6) confirm durability and effectiveness under conditions that are typical of actual engine components; and (7) complete surface and structural characterization of carbon-based boundary films and elucidate their lubrication mechanism.

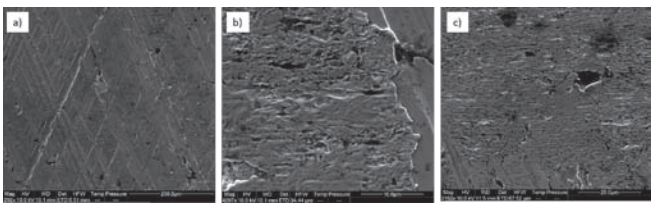
- **Oak Ridge National Laboratory** is improving the understanding of how engine lubricants and fuel properties affect the low speed pre-ignition (LSPI) phenomena with a fundamentally focused thermo-chemical parametric fuel and lubricant study. **(Splitter, report III.11)**

  FY 2015 accomplishments: (1) illustrated that liquid fuel species are proportional to fuel boiling point, with mass concentration measurements corresponding to approximately 20% fuel in the top ring zone under steady state operation; (2) determined that LSPI propensity and event frequency are directly proportional to fuel boiling point, where increased intermediate fuel boiling point increased LSPI tendency; (3) demonstrated that in-cylinder thermodynamic conditions and fuel–air mixing during charge preparation are critical to LSPI event promotion, where reduced mixing or increased top dead center temperature increased LSPI tendency; and (4) formed strategic partnerships with industry to isolate specific lubricant detergents, antioxidants, and anti-wear properties of interest for parametric lubricant property study of LSPI.

  FY 2016 activities: (1) evaluate parametric lubricant study of lubricant detergent types on LSPI with two fuels; (2) provide unused and used sump lubricant to National Renewable Energy Laboratory for IQT testing, and if successful, couple Ignition Quality Tester results with statistical LSPI results from engine studies; (3) develop an understanding of lubricant and fuel chemistry through batch reactor studies to explore aging and chemistry effects on lubricant and fuel formulations of interest, and couple aged liquid properties to engine studies with LSPI event count; and (4) fully formulate a test ionic liquid lubricant and evaluate ionic lubricant effects in LSPI.

- **Argonne National Laboratory** is developing better understanding of the nature (structure), composition, and the mechanisms of formation of tribochemical surface films. **(Ajayi, report III.12)**

  FY 2015 accomplishments: (1) observed peculiar frictional variation with temperature for low viscosity mineral and ester base fluids containing zinc



Scanning electron micrographs of wear track of liner components from laboratory tests: (a) boundary of wear track and (b) and (c) different levels of surface shear strain evolution during the scuffing process. (Ajayi, report III.12)

dialkyldithiophosphate antiwear and molybdenum dialkyldithiocarbamate friction modifier additives; (2) identified the possible mechanisms for the peculiar friction behavior for low viscosity base fluids using high-resolution transmission electron microscopy of tribochemical films; and (3) completed initial analysis of scuffing and wear mechanisms for ring and liner components in engines.

FY 2016 activities: (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 lubricated interfaces;(4) verify the peculiar friction behavior for low viscosity base fluid for other additive systems; and (5) develop an empirical relationship between base fluid viscosity and boundary regime frictional behaviors.

- **Oak Ridge National Laboratory** is investigating the compatibility of engine lubricant antiwear (AW) additives, specifically conventional zinc dialkyldithiophosphate (ZDDP) and newly developed ionic liquids (ILs), with selected commercial hard coatings, and providing fundamental understanding to guide future development of engine lubricants. **(Qu, report III.13)**

  FY 2015 accomplishments: (1) received the Oak Ridge National Laboratory Significant Event Award; (2) wrote journal papers and presented at five conferences; (3) discovered a new wear mechanism for the excessive material removal on the steel counterface against diamond-like carbon coating, diamond-like carbon-catalyzed tribocorrosion; and (4) revealed and correlated evolution of wear debris generation to the wear process and tribofilm formation.

  FY 2016 activities: Investigate the compatibility between AW additives and non-ferrous engine bearing alloys, specifically bronze and aluminum alloys

Petroleum Displacement Fuels/Fuel Blending Components

The goal of this program area is research on the incorporation of biofuels and other blending streams into petroleum gasoline and diesel. Biofuels can substantially lower greenhouse gas emissions as well as enhance energy security. For FY 2016, well-to-wheel analysis of greenhouse gas emissions and engine performance will continue to be pursued. Direct-injection, spark ignition engines will be emphasized due to their prevalence in the current and future United States light-duty fleet.

- **National Renewable Energy Laboratory** is determining if and at what levels biomass-derived oxygenates are scientifically and commercially feasible as drop-in fuels for both diesel and gasoline applications. **(McCormick, report IV.1)**

  FY 2015 accomplishments: (1) blended ethanol, isobutanol, anisole, 4-methylanisole, 2-phenylethanol, 2,5-dimethylfuran, and 2,4-xylenol into a blendstock for oxygenate blending at levels ranging from 10 to 25 volume percent; (2) measured knock-limited spark advance, particle mass, and particle number in a gasoline direct injection engine; and (3) confirmed and studied oxidation of the promising high-Research Octane Number oxygenate 2,5-dimethylfuran at 100°C in the presence of oxygen.

  FY 2016 activities: Work to evaluate fuel performance properties and combustion of a wider range of biomass-derived oxygenates and hydrocarbons will continue under the Co-Optimization of Fuels and Engines program in 2016.

- **Pacific Northwest National Laboratory** is facilitating the successful introduction of future fuel feedstocks which will help reduce the United States' dependence on foreign oil, while being compatible with future advanced combustion engines. It is also developing analytical approaches to correlating the molecular structure of fuel components to fuel properties and fuel performance. **(Bays, report IV.2)**

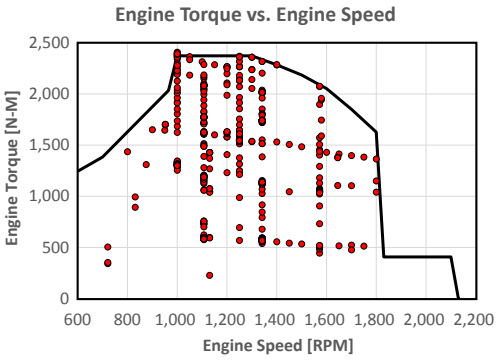
  FY 2015 accomplishments: (1) continued development of new nuclear magnetic resonance approaches for identifying structure–property relationships of diesel fuels, focusing on the two-dimensional nuclear magnetic resonance technique, single-bond proton–carbon correlation; (2) continued collaboration with CanmetENERGY to develop structure–property relationships for diesel fuel lubricity using nuclear magnetic resonance and gas

chromatography-field ionization mass spectrometry data; (3) developed a method for testing fuels at pressures up to 380 MPa (~55 ksi) to assess fuel phase behavior at pressures, which reflect those found in modern common rail diesel fuel injection systems; and (4) continued collaborative efforts with Coordination Research Council through participation in the Fuels for Advanced Combustion Engines Working Group, and contributions to Coordination Research Council Advanced Vehicle/Fuel/Lubricants Projects.

FY 2016 activities: (1) continue to develop signal processing and correlation approaches to relate fuel properties and chemical structures; (2) refine structure–property correlations for lubricity and develop additional structure–property correlations using current fuel sets; (3) identify key molecular structures in unconventional fuels, which have the greatest impact on fuel properties and performance; (4) introduce additional fuel sets, including diesel, gasoline, and bio-derived fuels/fuel components, to broaden the applicability of fuel structure–property correlations; (5) continue to coordinate the interaction with Natural Resources Canada (CanmetENERGY) on analytical correlation of fuel properties and material compatibility investigations; and (6) continue collaborative work with members of the Coordinating Research Council's Working Group and the Alternative and Surrogate Fuels projects.

- **Cummins** is using a dual-fuel engine to reduce the petroleum usage of a Class 8 vehicle by at least 50% and developing and demonstrating an advanced, highly integrated combustion/aftertreatment system to achieve 2010 heavy-duty emissions compliance. **(Kocher, report IV.3)**

  FY 2015 accomplishments: (1) demonstrated 54% petroleum reduction over Supplemental Emissions Test modes; (2) demonstrated a full torque curve and operation over the entire engine map; (3) successfully integrated port fuel injection system and in-cylinder pressure sensors into the cylinder head; and (4) designed a dual-fuel combustion system to meet program goals.

  Demonstrated E85-diesel premixed compression ignition operating range. (Kocher, report IV.3)

  FY 2016 activities: (1) validate analysis-led combustion system design through engine testing; (2) develop steady-state calibration to meet program goals on demonstration hardware; (3) develop transient calibration to meet program goals on demonstration hardware; and (4) complete vehicle build of a dual-fuel engine demonstrating 50% petroleum reduction.

- **Clean Air Power** is demonstrating a compressed or liquefied natural gas Class 8 heavy-duty Dual-Fuel 13 L compression ignition engine that utilizes an average of 60–75% natural gas, ignited by a pilot of 25–40% diesel for use in heavy-duty commercial on-road applications. **(Kerekes, report IV.4)**

  FY 2015 accomplishments: (1) procured a model year 2015 vehicle with a Volvo/Mack 13 L engine during the first quarter of 2015, completed the installation of the Dual-Fuel system, and commissioned the vehicle to operate on natural gas; (2) assessed the EMD+ requirements during the first quarter time period, which was used in the second quarter time period to form the basis of the software requirements specification; (3) completed the software requirements specification to update the existing software and ensure compliance with new EMD+ requirements for system monitoring; (4) developed concept-level countermeasures to avoid activation of the original equipment manufacturer heavy-duty on-board diagnostic system while operating in Dual-Fuel mode; and (5) produced a list of support (information, hardware, etc.) that will be requested from an original equipment manufacturer partner.

  FY 2016 activities: (1) procure a model year (MY) 2016 Volvo/Mack D13/MP8 engine and vehicle, install the Clean Air Power Dual-Fuel system on the engine and vehicle, investigate any differences between the MY 2016 configuration and previous MY engines, and implement required revisions to the Clean Air Power Dual-Fuel system; (2) complete the development and the calibration of the new EMD+ software using the MY 2016 engine and vehicle; and (3) conduct market readiness demonstration of the heavy-duty on-board diagnostics compliant Dual-Fuel system.

- **Argonne National Laboratory** is optimizing a combustion concept with targeted in-cylinder natural gas (NG)–gasoline blending to achieve 10% efficiency improvement over gasoline baseline and demonstrating 10% improvement in NG power density over NG port fuel injection (PFI). **(Wallner, report IV.5)**

  FY 2015 accomplishments: (1) successfully validated three-dimensional computation fluid dynamics simulations of the gaseous injection event against X-ray measurements and developed a best practice for engine simulations of the NG direct injection event; (2) demonstrated 39.1% indicated efficiency with NG direct injection exceeding the efficiency in gasoline PFI operation by 5.9%, a ~17.8% relative improvement; (3) achieved 11.3 bar indicated mean effective pressure at 1,500 rpm with NG direct injection, a 13% improvement in power density over NG PFI; and (4) showed a 0.5% efficiency benefit through blended operation at part load (1.3% relative improvement) due to improved exhaust gas recirculation dilution tolerance.

  FY 2016 activities: (1) determine evaluation criteria and develop an optimized combustion system configuration to maximize the benefits of the in-cylinder gasoline–NG blending concept; (2) experimentally evaluate the performance and efficiency potential of the optimized configuration; (3) develop a vehicle level strategy with the goal to maximize the global benefits of the in-cylinder blending strategy; and (4) perform vehicle level simulations and a cost analysis evaluating progress towards the 50% petroleum reduction and 36-month payback period goals.

Fuel Property Effects on Advanced Combustion Regimes

The goal of this program area is to identify fuel properties which can expand the operating range of kinetically controlled combustion regimes in engines. These research 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. For FY 2016, the focus of this program area will be incorporated into the Fuel-Engine Co-Optimization (Co-Optima) initiative. Ignition characteristics and other metrics will be researched that will enable small volume testing for suitability in kinetically controlled combustion regimes.

- **Oak Ridge National Laboratory** is investigating the potential for direct substitution of biofuels for petroleum in advanced combustion technologies. Additionally, it is addressing fundamental pathways for increasing the efficiency of alternative gasoline-like fuels using multiple combustion strategies as appropriate for each load and fuel. **(Curran & Szybist, report V.1)**

  FY 2015 accomplishments: (1) attained the 2015 technical target of demonstrating fuel effects enabling the 2020 U.S. DRIVE Advanced Combustion & Emissions Controls Tech Team goal of 36% brake thermal efficiency at 2,000 rpm and 20% peak load; (2) conducted comparison of reactivity controlled compression ignition with conventional fuels and GCI a variety of fuels spanning wide range in Research Octane Number for efficiency, load expansion, and controllability; and (3) concluded that exhaust gas recirculation tolerance limits can be attributed to stochastic cycle-to-cycle instabilities—fuels with faster flame speeds are more resilient to the stochastic turbulence and are able to tolerate more dilution.

  FY 2016 activities: Both aspects of this project are being brought into the Co-Optima initiative during the first quarter of FY 2016. Upcoming work will (1) examine fuel effects for a variety of advanced and renewable fuels on advanced combustion, including effects on transient operation, (2) improve understanding of fuel effects on dilution tolerance, and (3) test candidate fuels from the Optima project. Both of these projects will collaborate with other internal and external projects within Co-Optima.

- **National Renewable Energy Laboratory** is addressing technical barriers of inadequate data and predictive tools for fuel effects on combustion, engine optimization, and emissions. Focusing on biofuel, it is developing an understanding of the chemical and physical properties of fuel that enable furtherance of the DOE Vehicle Technologies Office Advanced Combustion Engines research and development program for high-efficiency engines with cost-effective emission controls. **(Zigler, report V.2)**

  FY 2015 accomplishments: (1) continued development of Ignition Quality Tester (IQT)-based experimental and simulation research platform to characterize fuel ignition performance, including IQT cooling and injection system upgrades to enable higher temperature operation while avoiding boiling of low-end fractions within the injection

system for gasoline range blends; (2) measured and distributed critical ignition characterization data for alternative and renewable fuels; these data support continual updates to the frequently cited NREL report, Compendium of Experimental Cetane Numbers; (3) characterized ignition performance of fuel compounds and simple blends to support development of kinetic mechanisms, including blend mechanisms and reduced mechanisms, with focus on ethanol/isooctane blends, primary reference fuel blends, toluene standardization fuel blends, and blends of ethanol into primary reference fuels and toluene standardization fuels; (4) evaluated and validated reduced kinetic mechanisms for key fuel surrogates; and (5) continued development of KIVA-based computational fluid dynamics linked to CHEMKIN simulation for the IQT.

FY 2016 activities: Fuel ignition research will continue within the Co-Optimization of Fuels and Engines program. Upcoming work will (1) study fuel components and blends, in coordination with the Co-Optima program; (2) will continue expanding IQT-based experimental and simulation research.

- **Argonne National Laboratory** is utilizing rapid compression machine experiments and modeling to develop new fuel quality metrics that are capable of characterizing fuels for low temperature combustion applications. This work will quantify the impacts of fuel properties (i.e., composition, distillation) on combustion performance in a prototype gasoline compression-ignition engine, extending the database available under low temperature combustion operation in order to validate the new metrics. **(Goldsborough, V.3)**

  FY 2015 accomplishments: (1) procured and fully characterized the chemico-physical properties of the baseline gasoline using ASTM standardized testing protocol; (2) acquired autoignition delay and heat release measurements for the baseline gasoline over a range of engine-relevant conditions; (3) acquired engine performance and emissions data for the baseline gasoline, covering a wide range of speed and load conditions; and (4) initiated development of correlations capable of comparing the rapid compression machine results with the engine measurements.

  FY 2016 activities: (1) blend and characterize the chemico-physical properties of a matrix of fuels containing the baseline gasoline and single-component surrogates representing various chemical classes found in conventional and non-conventional gasolines; (2) acquire autoignition delay and heat release measurements for the blended gasolines using Argonne's twin-piston RCM, covering a range of engine-relevant conditions; (3) acquire engine performance and emissions data for the blended gasolines, covering a range of operating conditions selected to highlight fuel differences; and (4) extend the correlations in order to account for fuel compositional effects.

- **University of Michigan** is demonstrating a combination of fuel selection, fuel injection strategy, and mixture preparation that enables meeting the DOE targets for brake thermal efficiency of greater than 40% for spark-ignited engines and greater than 50% for compression-ignited engines. **(Wooldridge, report V.4)**

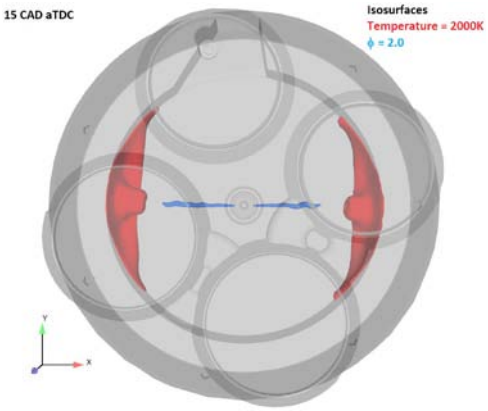
  FY 2015 accomplishments: (1) installed single-cylinder Ford Fox engine and determined baseline knock limits using dual fuels of ethanol and gasoline; (2) installed single-cylinder Ricardo Hydra engine and determined baseline knock limits using gasoline; (3) installed multi-cylinder Daimler M274 2.0 L; and (4) configured multi-cylinder General Motors 1.9 L turbodiesel for dimethyl ether/propane dual fuel combustion studies, completed dual fuel combustion studies, and reached a go/no-go decision point .

  FY 2016 activities: (1) develop ignition and fuel spray correlations that can be used to guide injection and spark timing strategies and can be used in the engine simulations; (2) continue to develop fuel injection strategies to achieve target efficiencies using the Fox and Hydra single-cylinder engines; and (3) demonstrate fuel injection strategies developed using the single-cylinder engine studies on the multi-cylinder engine.

- **Lawrence Livermore National Laboratory** is developing predictive chemical kinetic models for surrogate components and surrogate mixtures to represent next-generation fuels. These models will then be used in computational fluid dynamics simulations to optimize alternative fuel formulations and advanced engine combustion for maximum engine efficiency and very low pollutant emissions, thereby allowing the utmost petroleum displacement. **(Pitz, V.5)**

FY 2015 accomplishments: (1) performed Octane Number correlations for gasoline surrogate fuels, including ethanol; (2) computed flame speed correlations to help interpret dilute direct injection spark ignition engine experiments using gasoline–ethanol mixtures; (3) performed preliminary simulations of leaner lifted-flame engine combustion of methyl decanoate; and (4) performed preliminary fired simulations of lean/dilute direct injection spark ignition engine experiments at Sandia National Laboratories.

FY 2016 activities: develop chemical kinetic models for biofuel components and biofuel mixtures that enhance fuel octane



Isosurfaces of the equivalence ratio equal to 2.0 (blue) and temperature equal to 2,000 K (red) during leaner lifted flame combustion of methyl-decanoate at 15 degrees after top dead center (aTDC). (Pitz, report V.5)

- **Sandia National Laboratories** are facilitating the introduction of renewable, bio-derived, 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. **(Mueller, report V.6)**

FY 2015 accomplishments: (1) co-led a United States–Canadian team of researchers under the auspices of the Coordinating Research Council in modeling and measuring dozens of physical and chemical properties for a set of four ultra-low sulfur #2 diesel surrogate fuels with increasing compositional accuracies relative to a single target fuel; (2) conducted optical engine experiments showing that leaner lifted-flame combustion could be sustained, i.e., in-cylinder soot formation could be prevented throughout the combustion event, with a two-hole injector tip and the certification fuel–oxygenate blend, but not with neat certification fuel; and (3) demonstrated that ducted fuel injection can increase the degree of fuel/charge-gas premixing present in the autoignition zone, leading to the achievement of sustained leaner lifted-flame combustion over a range of conditions in constant-volume combustion vessel experiments.

FY 2016 activities: (1) conduct optical engine experiments on the certification fuel target and the set of corresponding diesel surrogate fuels described in this report to determine the level of surrogate fuel compositional accuracy required to adequately match the target fuel combustion performance; (2) further assess the feasibility of leaner lifted-flame combustion achieved via oxygenated fuels and/or ducted fuel injection as a means to enhance the degree of premixing in the autoignition zone and mitigate in-cylinder soot formation, to facilitate the deployment of renewable fuels and less expensive exhaust gas aftertreatment systems; and (3) collaborate with one or more computation fluid dynamics modeling groups to: (a) identify and overcome barriers to truly predictive computational engine simulations using the surrogate fuels described in the report, and (b) better understand and optimize leaner lifted-flame combustion–ducted fuel injection parameters for use in future engines.

I.3 Honors and Special Recognitions/Patents

Honors and Special Recognitions

1. "ORNL, Shell develop a less friction/wear hybrid lubricant additive," World Industrial Reporter, September 2, 2015. (Qu, report III.3)
2. "Reduce wear with synergistic lubricant pair," Materials Views, July 28, 2015. (Qu, report III.3)
3. Wang, Q., International Award, STLE, 2015. (Wang, report III.6)
4. Marks, T.J., Luigi Sacconi Medal, Italian Chemical Society, 2015. (Wang, report III.6)
5. Marks, T.J., Derek Birchall Award, Royal Society of Chemistry, 2015. (Wang, report III.6)
6. J. Qu, Y. Zhou, D.N. Leonard, H.M. Meyer, H. Luo, ORNL Significant Event Award, "Discovery and fundamental understanding of incompatibility between diamond-like-carbon coatings and lubricant additives provide new insights for future materials development," 2015. (Qu, report III.13)
7. Jim Szybist was awarded SAE Horning Award at the 2015 SAE World Congress in April in Detroit, MI for best paper demonstrating optimization of fuels and efficiency. (Curran & Szybist, report V.1)
8. Scott Curran was awarded the SAE 2015 Stefan Pischinger Young Industry Leadership Award at the SAE Foundation Annual Celebration in March in Detroit, MI. (Curran & Szybist, report V.1)
9. R&D 100 Award for Zero-order Reaction Kinetics software (Matt McNenly and Russell Whitesides). (Pitz, report V.5)

Invention and Patent Disclosures

1. J. Qu, W.C. Barnhill, H. Luo, B. Kheireddin, H. Gao, B.L. Papke, "Lubricant Formulations Containing Phosphonium-Organophosphate Ionic Liquids," ORNL Invention Disclosure #201503587, August 24, 2015. (Qu, report III.3)
2. J. Qu, H. Luo, "Ionic Liquids Containing Protic or Symmetric Aprotic Ammonium Cations and Phosphinate Anions as Lubricant Additives," ORNL Invention Disclosure #201503529, May 14, 2015. (Qu, report III.3)
3. Delferro, M., Chung, Y.W., Marks, T.J., Wang, Q., Densanker, M., He, X., "Cyclen friction modifiers for boundary lubrication." U.S. Patent (provisional) No. 62/179,564, May 2015. (Wang, report III.6)
4. A patent based on triazine compounds is under preparation. (Wang, report III.6)
5. Patent filed: Branched Polymers as Viscosity and/or Friction Modifiers For Lubricants; Application No. 14/823,838; Lelia Cosimbescu, Joshua W. Robinson, Priyanka Bhattacharya. (Cosimbescu, report III.9)
6. O.O. Ajayi, C. Lorenzo-Martin, and G.R. Fenske, "A Tribochemical Synthesis Method for Producing Low-Friction Surface Film Coatings," U.S. Patent: US20150087566A1. (Ajayi, report III.12)
7. U.S. Patent #8,967,129: "Ducted Combustion Chamber for Direct Injection Engines and Method." Issued March 3, 2015. (Mueller, report V.6)
8. U.S. Patent Application #14,789,782: "Ducted Fuel Injection." Filed July 1, 2015. (Mueller, report V.6)

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II. Fuels Research to Enable High-Efficiency Engine Operation while Meeting Emissions 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.

II.1 Improving Vehicle Fuel Economy through Increasing Fuel Octane Ratings

Overall Objectives

The overall objective of this project is to quantify fuel efficiency benefits of increased octane fuels using multiple pathways towards octane improvement. Increasing fuel octane rating provides additional knock resistance that is a key enabler of engine downsizing while maintaining vehicle performance and increasing fuel efficiency.

Fiscal Year (FY) 2015 Objectives

- Evaluate potential fuel economy differences between a 101 Research Octane Number (RON) E30 (30% ethanol, 70% gasoline) fuel at high compression ratio compared with an E10 (10% ethanol, 90% gasoline) 87 Anti-Knock Index (AKI) fuel using the original equipment manufacturer (OEM) compression ratio

FY 2015 Accomplishments

- Completed engine maps for an 87 AKI E10 fuel at a compression ratio of 10.1 and for an E30 101 RON fuel at compression ratio of ~13
- Developed initial vehicle model in Autonomie and compared the fuel economy of the vehicle for the two engine maps
- Examined data from three 97 RON fuels to evaluate influences from heat of vaporization (HoV)

Future Directions

- The project anticipates more fuel formulations and compression ratio combinations than can be achieved in one year. The near-term future direction of the project is to continue to expand the data envelope to include additional fuels. Expanding the data generated through this project will enable a robust examination of the potential benefits and challenges of increasing octane rating.
- Additionally, the project will examine hybrid powertrain strategies to explore potential synergistic effects from increasing the octane rating in a systems context.
- The project will continue to actively engage with industry stakeholders to assess priorities in terms of the inclusion of different fuel formulations to assure alignment of the project with industry priorities in this research area. ■

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Introduction

Engine downsizing is an important facet of increasing vehicle fuel efficiency while maintaining performance at a level that customers demand. As the OEMs have begun to increase the power density of smaller displacement engines, the onset of knock has emerged as an important challenge that currently limits the degree to which engine displacement (and fuel consumption) can be reduced in a practical automobile. A recent study by researchers from AVL, BP, John Deere, Ford Motor Company, and ICM has shown that increasing the fuel octane rating can allow substantial engine efficiency improvements at the knock limit [1]. Improvements were shown to be enabled through both a chemical octane effect as well as a charge cooling effect derived from the HoV of the fuel. The charge cooling effect was shown to be approximately the same order of magnitude improvement as the octane increase effect. Other studies have begun to show similar results.

The United States certification driving cycles on which fuel economy ratings are based typically result in engines operating well away from their peak efficiency values. Engine downsizing results in engines operating at higher loads more often during normal driving, thus reducing throttling and other losses and moving towards higher efficiency areas of their operating maps. However, in order to satisfy consumer demands, these engines must be able to deliver performance similar to non-downsized engines. These performance demands can cause downsized engines to operate in knock-limited regimes more frequently. In the past, some vehicles have utilized

"premium" fuel for its potential to improve performance, but these engines were not typically downsized to use the added anti-knock capability of the premium grade fuel to increase efficiency.

When engines reach the knock limit, one common technique that is used to protect the engine from damage is to retard the ignition timing. Retarding the timing has the effect of moving the onset of combustion to a cooler, lower pressure point, thus removing the knocking condition. However, this technique also results in a loss in fuel efficiency. Thus, when an engine reaches the knock limit, fuel efficiency is reduced in favor of engine durability. Increasing the knock limit through changes in fuel formulation, such as increasing the octane rating, offers the potential to improve fuel efficiency under these conditions and enable further engine downsizing.

Approach

ORNL will investigate the potential fuel economy impacts of the use of higher octane gasoline blends. At least three pathways for octane increase will be investigated. These paths include the use of ethanol, butanol, and a high-octane hydrocarbon blend.

ORNL is partnering with Ford Motor Company and will make use of their EcoBoost 1.6 L engine to examine the potential fuel efficiency benefits of octane improvement in areas of the engine map that will be relevant to a down-sized engine application. Ford has provided ORNL with the engine and engineering support. Models or other linkages will be used to estimate or measure the vehicle fuel economy in addition to brake specific engine measurements, and ORNL and Ford have established a collaboration in this area as well.

Hybridization presents opportunities to improve market penetration of engines designed to use high-octane fuels. These opportunities are possible through the use of hybridization strategies that can mitigate the performance penalties that occur when an engine designed for use with high-octane fuels is operated using a fuel with a lower octane rating. These strategies will be investigated alongside conventional vehicles using vehicle models to estimate the potential fuel economy benefits that are possible. In the studies for the project, fuels in the range of 90–100 RON will be investigated to characterize the amount of improvement that is possible using near-term engine hardware and fuel octane levels. The later stages of the project will investigate more aggressive use of octane increases, which are likely to require improved engine boosting, compression ratio increases, and other hardware changes.

Results

An E10 fuel with an AKI of 87 was selected as a baseline fuel. This fuel was obtained from Corrigan Oil Company in Ferndale, Michigan, in the retail marketplace to represent the gasoline formulations in use throughout the country. This fuel was used to conduct an engine performance map using the Ford EcoBoost 1.6 L engine with the OEM pistons installed. These pistons produce a geometric compression ratio of 10.1. Figure 1 shows the load and speed conditions where data was collected. The engine control unit controlled the spark timing for this baseline engine map, using its internal methods for knock avoidance.

An E30 fuel with RON of 101.5 was used to examine the potential for increasing compression ratio. For this study, the OEM pistons were replaced with custom manufactured pistons that produced a geometric compression ratio of approximately 13. Data collected in the baseline engine map were used to develop an external knock detection process that allowed the engine operator to retard spark timing to avoid knock, as recommended by staff at Ford Motor Company. The higher RON rating of the E30 fuel was anticipated to provide sufficient anti-knock performance to allow the engine to operate with the higher compression pistons and to achieve approximately the same combustion phasing as the baseline case. The conditions where data were collected in this map are shown in Figure 2. While the engine operability was comparable to baseline at low speeds, operation at high speeds required the combustion phasing to be retarded more than at baseline. This difference caused a loss of available torque at high speeds. This loss may be recoverable with additional calibration and development work, but suggests that the Motor Octane Number (MON)

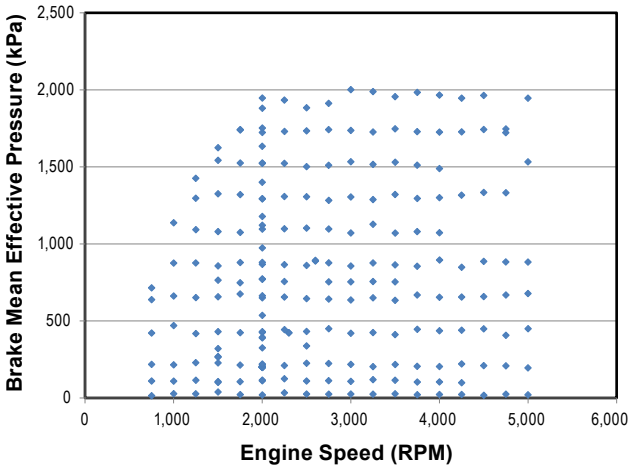

Figure 1. Load and speed points for 87 AKI E10 engine map with OEM pistons

of the E30 fuel was insufficient at high-speed conditions. Raising MON would likely improve this situation, but would detract from performance at lower speeds where most typical driving situations occur. Further investigation of this issue is planned for FY 2016.

Initial vehicle model results show that the E30 high compression ratio engine would produce between 4–13% fuel economy improvement on a volumetric basis, depending on the drive cycle used. Differences in the engine map resulting from the high-speed limitations discussed previously caused Autonomie to select gear shift points that confound the fuel economy improvement results significantly. Additional vehicle model development is planned to provide more robust improvement estimates in FY 2016.

The HoV of the fuel can potentially provide additional anti-knock benefits in direct injection engines such as the EcoBoost engine. Analyses of three fuels with well-matched RON and MON were undertaken to examine this potential. The three fuels were formulated using ethanol, isobutanol, and toluene to provide differing HoV values. Data from this study showed that engine performance trended with the fuel RON rating. A collaborative publication was initiated with staff at the National Renewable Energy Laboratory to collectively analyze these and other results in order to provide a more comprehensive answer concerning the anti-knock benefit of HoV. A joint publication is under development and planned for publication in FY 2016.

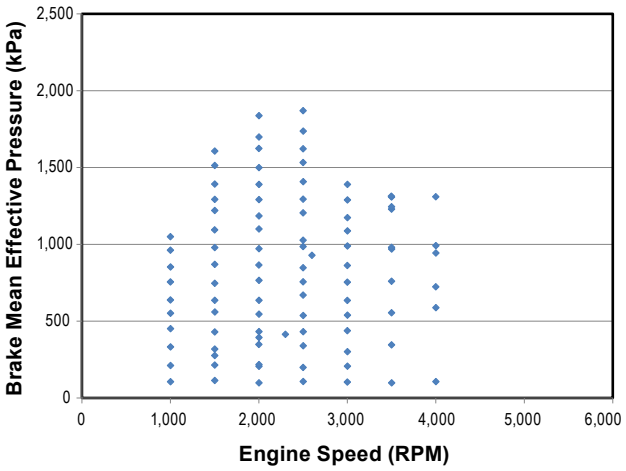

Figure 2. Load and speed points for 101 RON E30 engine map with compression ratio ≈13 pistons

Conclusions

Results show that use high-octane fuels as an enabler for increasing compression ratio can produce significant improvements in vehicle fuel economy. Early vehicle model results show improvement in fuel economy is achieved with the use of a high-octane fuel, but these results are limited by issues with gear shift algorithms and need further development to achieve a robust estimate of the potential gains available through increasing fuel octane ratings. These improvements, along with additional engine mapping, are planned in FY 2016.

References

1. Robert A. Stein, Dusan Polovina, Kevin Roth, Michael Fost, Michael Lynskey, Todd Whtiting, James E. Anderson, Michael H. Shelby, Thomas G. Leone, and Steve Vandergriend, "Effect of Heat of Vaporization, Chemical Octane, and Sensitivity on Knock Limit for Ethanol – Gasoline Blends," SAE Int. J. Fuels Lubr. 5(2):2012, doi: 10.4271/2012-01-1277.

FY 2015 Publications/Presentations

1. C. Scott Sluder, James P. Szybist, Brian C. Kaul, "Preliminary Investigation of Heat of Vaporization Effects in High-Octane Fuel Experiments at ORNL," presented to the U.S. DRIVE Advanced Combustion and Emissions Control Technical Team, July 16, 2015.

2. C. Scott Sluder and Derek A. Splitter, "Potential for Increasing Fuel Economy through Raising Octane Ratings," presented to the staff of Vehicle Technologies Office and Biomass Energy Technology Office, U.S. Department of Energy, December 15, 2014.

3. C. Scott Sluder, "An Overview of High-Octane Fuel Projects at ORNL," presented to the U.S. DRIVE Fuels Working Group, February 18, 2015.

4. James P. Szybist, Scott Curran, C. Scott Sluder, Derek A. Splitter, Adam B. Dempsey, and Robert M. Wagner, "Gasoline-Like Fuel Effects on Advanced Combustion Regimes," presented at the 2015 DOE Vehicle Technologies Annual Merit Review, June 11, 2015.

5. C. Scott Sluder, James P. Szybist, Robert McCormick, Matthew A. Ratcliff, and Brad Zigler, "Exploring the Relationship between Fuel Heat-of-Vaporization and Sensitivity," submitted for consideration of publication at the 2016 SAE World Congress.

II.2 Alternative Fuels DISI Engine Research

Overall Objectives

Provide the science-base needed by industry to understand:

- How emerging alternative fuels impact highly efficient direct injection spark ignition (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) 2015 Objectives

- Work towards developing a conceptual understanding of stratified spark ignition (SI) combustion that incorporates the effects of fuel on combustion 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

FY 2015 Accomplishments

- Based on particle image velocimetry and flame imaging, developed conceptual descriptions of both the spray-swirl interactions and flame-spread patterns that act to stabilize stratified combustion
- Examination of effects of fuel blend (E0 to E30 [blend of 30% ethanol, 70% gasoline]) on boosted, stratified operation with double injections
- Quantified control authority over the ignition process, for both advanced multi-pulse (MP) transient plasma ignition and with partial fuel stratification (PFS).
- Compared lean and dilute stability limits and fuel efficiency gains for E30, E85 (blend of 85% ethanol, 15% gasoline) and gasoline, using enhanced ignition to ensure repeatable end-gas autoignition for high combustion efficiency of ultra-lean deflagration-based SI operation
- Accomplishments address one of the barriers identified by the DOE Vehicle Technologies Office: inadequate data for fuel property effects on combustion and engine efficiency optimization

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Future Directions

- Expand conceptual model of swirl-spray stabilization mechanism to include double injections of E0–E30 fuels for boosted stratified operation
- Continue examination of well-mixed lean or dilute SI operation while quantifying the relevance of Research Octane Number (RON) and Motor Octane Number (MON) for fuel reactivity under ultra-lean conditions
- Incorporate new fuel components and blends in coordination with the Optima initiative
- Refine PFS technique to allow the use of a smaller pilot-fuel quantity and apply PFS to examine fuel effects on limits of ultra-lean SI combustion ■

Introduction

Climate change and the need to secure energy supplies are two reasons for a growing interest in engine efficiency and alternative fuels. 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. Our emphasis is on lean operation, which 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, we focus on techniques that can overcome these challenges. Specifically, fuel stratification is used to ensure ignition and completeness of combustion but has soot and NO_x emissions challenges. For ultra-lean well-mixed operation, turbulent deflagration can be combined with controlled end-gas autoignition to render mixed-mode combustion that facilitates high combustion

efficiency. However, the response of both combustion and exhaust emissions to these techniques depends on the fuel properties. Therefore, to achieve optimal fuel economy gains, the engine combustion control strategies must be adapted to the fuel being utilized.

Approach

The Alternative Fuels DISI Engine Lab at Sandia houses an engine that is capable of both performance testing and in-cylinder optical diagnostics. First, to characterize fuel efficiency and emissions behavior, performance testing with an all-metal engine configuration is conducted over a wide range 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 also provides insight into the 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 2015 are presented.

Stratified-Charge Operation – experiments have shown that intake-generated swirl promotes stable stratified combustion for both E30 and gasoline. To clarify the mechanism through which swirl stabilizes combustion, the in-cylinder flow was examined with particle image velocimetry for both swirling and non-swirling flows. The measurements show that swirl makes the flow patterns of individual cycles more similar to the ensemble-averaged cycle. Figure 1 quantifies this effect statistically through a "flow similarity" parameter (R_p), and shows that operation with swirl increases R_p from 0.77 to 0.90 at the time of spark ignition, reducing indicated mean effective pressure (IMEP) variability from 3.5% to 1.4%.

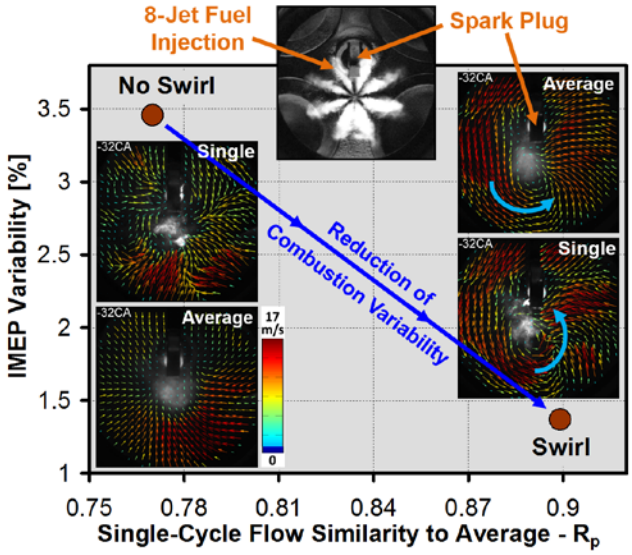


Figure 1. Effect of swirl on combustion and flow variability for stratified-charge operation.

Research during FY 2015 revealed that the interaction of the eight fuel sprays with the swirling gas flow strongly contributes to the flow stabilization at the time and location of the spark, as described conceptually in Figure 2. Flow measurements in both a horizontal and a vertical plane revealed that the fuel sprays displace low angular momentum gas downwards. In the wake of the spray, higher angular momentum gas from larger radii flows inward and increases its rotation rate due to conservation of momentum. This process creates a strong and very repeatable vortex near the spray centerline at the time of spark, as demonstrated by the vector fields on the right-hand side of Figure 1. It should be noted that the optimal spark timing for both gasoline and E30 coincides with the end of injection, so these descriptions apply to both fuels.

The increased flow similarity stabilizes the combustion process by reducing variability in both the ignition event

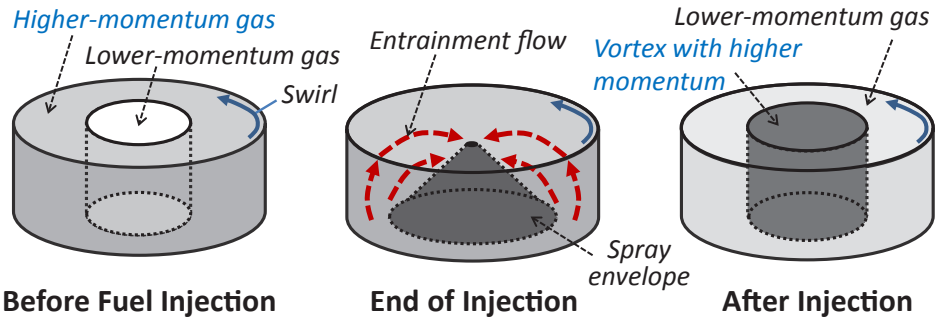


Figure 2. Conceptual model of spray-swirl interactions that create a repeatable vortex near the spark plug for stratified-charge operation.

and in the flame spread throughout the remaining charge. Analysis of a large number of flame images revealed that the flame-spread patterns are very repeatable for operation with swirl, as described by the schematic in the left-hand side of Figure 3. It shows that the strong vortex near the center of the combustion chamber promotes flame spread in the six o'clock direction. This avoids the occurrence of slow-burning cycles that may develop into partial burns. In contrast, the flow fields without swirl in the left-hand side of Figure 1 show no evidence of such a stabilizing vortex. Moreover, the single-cycle example without swirl is quite different from the average flow field, consistent with the observed higher combustion variability. Without swirl, the flame spread is occasionally very delayed in the six o'clock direction, as depicted on the right-hand side of Figure 3. This causes both combustion inefficiency and lower IMEP.

Based on this understanding of swirl-spray interactions and flame-spread patterns, combustion engineers can optimize injector and flow parameters to maximize combustion stability and enable high-efficiency operation. Moreover, the experiments show that the swirl-spray interaction and combustion stability characteristics are very similar for gasoline and mid-level ethanol blends, indicating that advanced stratified-charge combustion systems can be developed to accommodate potential future fuel changes.

Lean well-mixed operation – Lean or dilute operation can improve the thermal efficiency, but the fuel economy gains depend on several factors, including fuel type, dilution type, and intake temperature. This is exemplified in Figure 4. For both E30 and gasoline, there are two lean ϕ-sweeps where air is used as the oxidizer ($[O_2]$ = 20.9%), and two stoichiometric dilute ϕ_m- sweeps where $[O_2]$ is reduced by the addition of N_2. (To aid comparisons of the lean and dilute data sets, a mass-based equivalence ratio, ϕ_m, is used as a measure of the chemical energy per reactant mass, regardless of type of diluent [1]). For each type, two different intake temperatures are used; 30°C or 100°C (i.e., heated).

In Figure 4c, it can be seen that the fuel economy (FE) of gasoline improves by roughly 20% for ϕ = 0.52 - 0.55. In contrast, the best FE improvement is only 17% for E30, shown in Figure 4a. This difference can be attributed to the higher octane numbers of E30, which make it harder to achieve mixed-mode combustion for this operating point. This is illustrated in Figure 5, which plots the ensemble-averaged apparent heat release rate (AHRR) traces for gasoline, E30, and E85 operated lean with heated intake and ϕ = 0.55. The three fuels have nearly identical deflagration-based AHRR until top dead center, at which point the AHRR of gasoline deviates due to the onset of mild end-gas autoignition. As a result, the AHRR of gasoline keeps rising until a peak has been reached at 10°CA, and falls off rapidly thereafter. Due to this change of the AHRR profile, less heat is released during the later part of expansion stroke and this explains the larger gain of thermal efficiency (η_{th}). Both E30 and E85 display a slow burn-out process with substantial heat being released after 20°CA, making the conversion of heat to work less efficient.

Compared to heated lean operation, Figure 4 shows that the other modes of operation provide less η_{th} benefit, and are also more limited by onset of IMEP variability. Stoichiometric dilute operation offers the smallest η_{th} benefit for either fuel, with roughly 10% FE gain for heated dilute and 7% for non-heated dilute. The poor performance of dilute operation is largely explained by its slow early flame development and slower overall heat release.

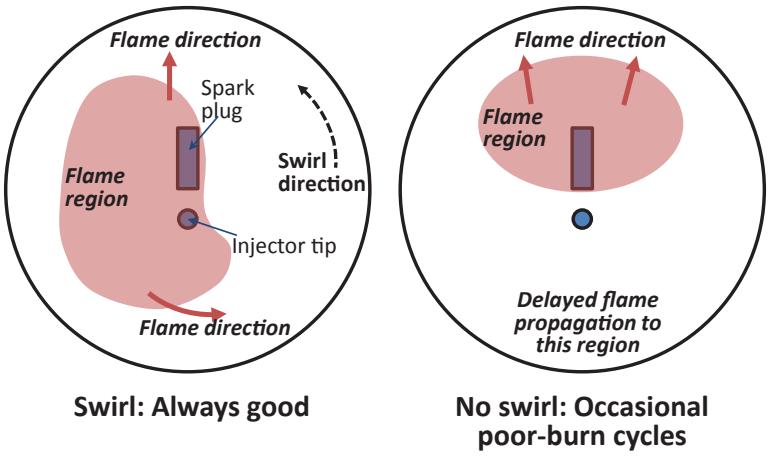


Figure 3. Description of flame spread for stratified-charge operation with and without intake-generated swirl.

To speed up the dilute combustion process, end-gas autoignition can be utilized. However, the regular spark system does not provide sufficient control authority to accomplish stable dilute mixed-mode combustion. Therefore, the more powerful MP ignition system [2] was used for both E30 and gasoline. Figure 6b shows that gasoline and E30 exhibit nearly identical AHRR profiles when CA50 is advanced to near top dead center, with a distinct second peak around 10°CA and a crisp end of combustion. Furthermore, Figure 6a indicates that the autoignition temperatures are practically identical for the two fuels at this operating condition. This is remarkable,

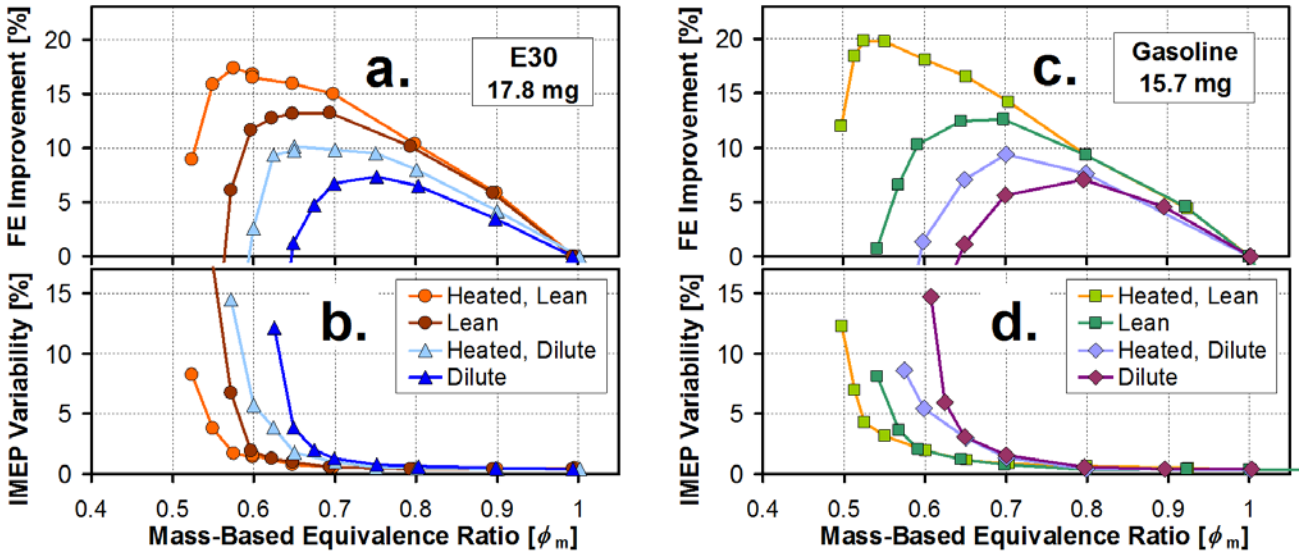
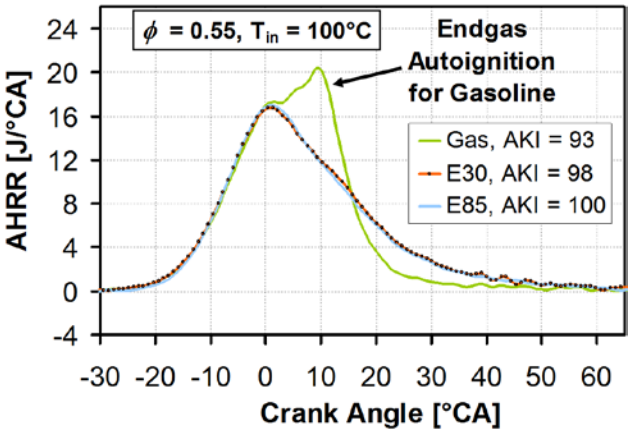
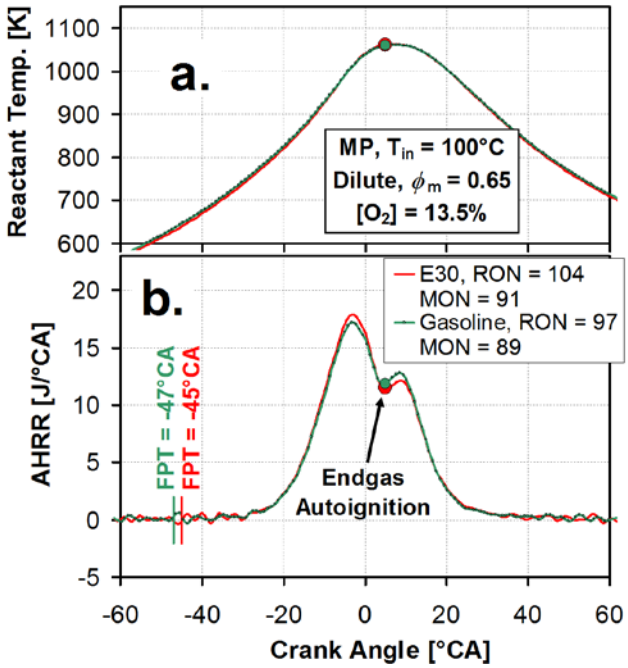


Figure 4. Comparison of E30 and gasoline for well-mixed lean or dilute operation at 1,000 rpm. a and c show improvement of fuel economy relative ϕ = 1 operation. b and d show $IMEP_n$ variability.



AKI – Anti-Knock Index; T_{in} – intake temperature

Figure 5. Comparison of heat release rate for heated lean operation with gasoline, E30, and E85.



FPT – first pulse timing

Figure 6. The use of MP ignition to induce stable stoichiometric dilute mixed-mode combustion for both E30 and gasoline. a) estimated $T_{end\text{-}gas}$, b) AHRR.

given that the legend of Figure 6a indicates that RON is 7 units higher for E30, and MON is 2 units higher. At the operating conditions of Figure 6, the effective octane index [3] must be identical for the two fuels. This implies that this particular operating point is "beyond MON." These and other results motivate future work to assess the relevance of RON and MON for advanced combustion modes.

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 SI engines.
- Conceptual models and descriptions of stratified SI combustion have been developed that explain the mechanisms whereby intake-generated swirl acts to stabilize combustion.
- E30 and gasoline show very similar combustion behavior for stratified operation, suggesting that

stratified-charge combustion systems can be made fully compatible with mid-level ethanol blends.

- For well-mixed operation, a comparison of E30, E85, and gasoline reveals that lean operation with intake-air preheating provides higher fuel economy gains than stoichiometric dilute operation. The inferior performance of dilute operation is partly caused by slower combustion caused by an exhaust gas recirculation-induced reduction of the reactant [O_2].
- For stoichiometric dilute operation with intake heating, a multi-pulse ignition system can be used to induce mixed-mode combustion, providing faster combustion and higher efficiency. For such operation, differences in RON and MON become irrelevant, with E30 and gasoline showing identical autoignition temperatures and AHRR profiles.

References

1. M. Sjöberg and W. Zeng, "Combined Effects of Fuel and Dilution Type on Efficiency Gains of Lean Well-Mixed DISI Engine Operation with Enhanced Ignition and Intake Heating for Enabling Mixed-Mode Combustion," accepted for SAE Congress 2016.
2. 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.
3. Kalghatgi, G., "Fuel Anti-Knock Quality - Part I. Engine Studies," SAE Technical Paper 2001-01-3584, 2001.

FY 2015 Publications/Presentations

1. W. Zeng, M. Sjöberg, D.L. Reuss and Z. Hu, "The Roles of Spray and Flow for Spray-Guided Stratified-Charge DISI Combustion," 17th Annual Conference of ILASS-Asia, October 2014.
2. 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," presented at 2014 SAE International Powertrain, Fuels and Lubricants Meeting, and published in SAE Int. J. Engines 7(4):1781–1801, 2014.
3. W. Zeng, M. Sjöberg, and D.L. Reuss, "Combined Effects of Flow/Spray Interactions and EGR on Combustion Variability for a Stratified DISI Engine," published in Proceedings of the Combustion Institute, 35(3):2907–2914, 2015.
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," published in International Journal of Engine Research, 16(3):306–322, 2015.
5. M. Sjöberg, W. Zeng and Z. Hu, "Efficiency Gains for Various Combinations of Enhanced Ignition, Intake Heating and Fuel Type for Lean or Dilute DISI Engine Operation," presented at Advanced Engine Combustion Review Meeting, February 2015.
6. W. Zeng, M. Sjöberg and Z. Hu, "Utilizing Intake Boost and Double Injections for Enhanced Stratified-Charge DISI Operation," presented at Advanced Engine Combustion Review Meeting, February 2015.
7. M. Sjöberg, "Efficiency Benefits of Lean or Dilute Well-mixed DISI Engine Operation with Advanced Ignition, Intake Heating and Various Fuel Types," presented at SAE 2015 High-Efficiency IC Engine Symposium.
8. W. Zeng, M. Sjöberg, D.L. Reuss and Z. Hu, "The Role of Spray-Enhanced Swirl Flow for Combustion Stabilization in a Stratified-Charge DISI Engine," presented at SAE Congress, April 2015.
9. M. Sjöberg, "Advanced Lean-Burn DI Spark Ignition Fuels Research," presented at the 2015 Annual Merit Review and Peer Evaluation Meeting, June 2015.
10. Y. Yang, J.E. Dec, M. Sjöberg, and C. Ji, "Understanding fuel anti-knock performances in modern SI engines using fundamental HCCI experiments," published in Combustion and Flame, 162(10):4008–4015, 2015.
11. M. Sjöberg, W. Zeng, Z. Hu, and M. Mehl, "Examination of Gasoline, E30 and E85 for Well-mixed Lean or Dilute DISI Engine Operation," presented at AEC Program Review Meeting, August 2015.
12. W. Zeng and M. Sjöberg, "Comparing Single- and Double-Injection Strategies for Spray-Guided Stratified-Charge DISI Combustion," presented at AEC Program Review Meeting, August 2015.

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II.3 Gasoline Engine and Fuels Offering Reduced Fuel Consumption and Emissions (GEFORCE)

Overall Objectives

- Establish key engine technologies and fuel characteristics that enable very high fuel efficiency with very low emissions in future vehicles

Fiscal Year (FY) 2015 Objectives

- Execute Cooperative Research and Development Agreement (CRADA) and non-disclosure agreement (NDA) to establish legal framework for the collaboration between ORNL, Coordinating Research Council (CRC), and GM
- Establish baseline engine platform in a test cell at ORNL
- Begin development of advanced research engine to support the project
- Establish relationship with a fuel manufacturer and begin production of the matrix of fuels planned for the project

FY 2015 Accomplishments

- A CRADA with CRC and an NDA with GM were fully executed, allowing the project to proceed.
- GM shipped the baseline engine, a 2.0 L LTG engine, to ORNL to begin test cell preparations for the advanced research engine, and began development of the advanced research engine.
- CRC selected Gage Products as a fuel supplier, putting in place a purchase order and releasing Gage Products to begin production of the entire matrix of fuels.

Future Directions

- Work with the baseline engine to help guide calibration of the advanced engine for each fuel in the matrix
- Install and commission advanced research engine
- Begin calibration and mapping of the advanced engine for each fuel in the experimental matrix
- Utilize engine maps for each fuel to produce estimates of vehicle fuel economy and emissions to identify promising combinations of engine technology and fuel formulation that enable significant improvements in fuel economy and emissions performance ■

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Introduction

The current state of the art in gasoline engine architecture is the gasoline turbocharged, direct injection engine. Such engines are presently in production, but are prevented from achieving even greater efficiency because of the onset of knock, which can irreversibly damage the engine. Techniques for avoiding knock include delaying the ignition timing relative to the piston position, which reduces peak temperatures and pressures in the cylinder and thus removes the knocking condition. Under some conditions where changing ignition timing is insufficient to remove knock, additional fuel is added to cause the combustion conditions to be fuel-rich, which can further cool the in-cylinder conditions. However, the displacement of ignition timing from the thermodynamic optimum location and the use of fuel rich combustion both degrade the fuel efficiency of the engine.

Historically, the onset of knock is most often associated with very high power driving events that occurred infrequently and did not have a significant impact on fuel efficiency. However, the current trend of reducing engine displacement while improving specific power ratings (downsizing) and reducing the engine speeds experienced during most driving modes (downspeeding) are increasing the importance of knock avoidance during a larger portion of typical driving conditions (both on certification cycles and those typical of consumer use). Thus, knock avoidance is rapidly becoming one of the most important limitations to increasing vehicle fuel efficiency.

Ever-tightening emissions regulations have challenged engine designs for many years, and continue to do so. Recent emissions regulations have continued to apply more pressure to reduce emissions, particularly of non-methane organic gas and oxides of nitrogen (NO_x). Particulate matter (PM) emissions have historically not been problematic for gasoline engines; however, tightening regulatory limits require that direct injection gasoline engines be designed with more attention to their PM emissions than had been the case with previous gasoline engine architectures, perhaps requiring the use of gasoline particulate filters. Fuel formulation could also play a strong role in PM emissions reductions, since in-cylinder charge motion and fuel injection strategies could benefit from consideration for fuel properties such as the distillation curve, fuel chemistry, density, and viscosity in order to minimize non-methane organic gas, NO_x, and PM formation during the combustion process. Hence, there is also a strong opportunity to reduce emissions by taking advantage of potential future fuel formulations.

Approach

The project goal is to establish key engine technologies and fuel characteristics that enable very high fuel efficiency with very low emissions in future vehicles. The goal will be achieved through a combination of engine research to develop performance data followed by system-level vehicle modeling to determine vehicle fuel economy benefits.

The base engine will be a state-of-the art GM LTG 2.0 L gasoline, turbocharged, direct injection engine. The engine will be equipped with additional hardware that is representative of anticipated mainstream technologies for the 10–20 year future timeframe. The engine will be paired with a matrix of fuels that has been designed to investigate potential future gasoline formulation directions. The matrix includes fuels that will allow independent investigation of the impacts of ethanol content, octane rating, and particulate formation tendency.

The combination of the research engine and designed fuel matrix will enable this study to develop key insights into linkages between fuel formulation directions and the resulting critical engine technologies that are needed to meet future fuel efficiency and emissions constraints in the United States. The close involvement of CRC and its member companies in the program provides a unique opportunity to influence the product planning of multiple large automotive and energy companies simultaneously.

Results

A key first step in launching the project was to complete the necessary legal arrangements with the project partners. A considerable amount of time and effort was put forth this year to accomplish this step. A CRADA was developed with the CRC to formally establish a working relationship to support this project. GM, as the supplier of the research engine for the project and a member company of CRC, was also involved in the CRADA negotiations. Resolutions to the concerns of all parties were identified, resulting in a CRADA that all parties were able to approve. The final version of the CRADA was signed in August 2015. Additionally, GM and ORNL anticipated the need for GM to supply ORNL with details associated with the engine design and engine controller functionality that are proprietary. These details were deemed critical to the success of the project. Hence, an NDA between GM and ORNL was needed to protect GM's proprietary information from disclosure to outside parties, including other members of CRC. Completion of the NDA was undertaken in parallel with the development of the CRADA with CRC. After considerable effort, an NDA that was acceptable to both GM and ORNL was signed in July 2015.

Simultaneously, plans for the engines to support the project were put into motion at GM. The production version of the 2.0 L LTG engine uses a square geometry, meaning that the bore diameter is the same as the length of the stroke. To increase the compression ratio while retaining acceptable combustion performance, lengthening the stroke was required. The research engine for the GEFORCE project will utilize the block, head, and other components from a 2.0 L LTG engine. A larger crank from a production GM engine will be fitted, as well as custom shorter length connecting rods to accommodate the larger throw crank. These changes, in combination with the production pistons from the LTG, will result in an engine of approximately 2.4 L displacement and increased compression ratio to enable capture of efficiency benefits offered with the fuels in the matrix with increased Research Octane Number. A second set of custom pistons will allow the engine to be returned to a compression ratio similar to the production LTG engine, allowing optimization for use with the regular grade fuels in the matrix. An advanced turbocharger manufactured by Mitsubishi Heavy Industries is also being fitted to the research engine to provide improved turbocharging capabilities compared with the production engine. Finally, an exhaust gas recirculation system for the engine was selected based on other work ongoing at GM. These components are currently being integrated to produce

the research engine, which is expected to be delivered to ORNL in the fall of 2015.

Meanwhile, a production LTG engine was shipped to ORNL to aid in developing and verifying the test cell infrastructure needed for the project. Data from this engine will also be used to develop fuel efficiency and emissions targets that will help guide calibration of the research engine with the matrix of fuels for the project. Delivery of the first LTG engine to ORNL satisfies milestone MS 1.1 (see Table 1). The baseline engine has not yet demonstrated operability (milestone MS 1.2) because of delays resulting from the need to complete the CRADA and NDA before the engine and controller could be shipped to ORNL, but is on track for demonstration of operability in the first quarter of FY 2016. The investigators feel that with all the required preparatory work complete the project can make good progress and will complete on time.

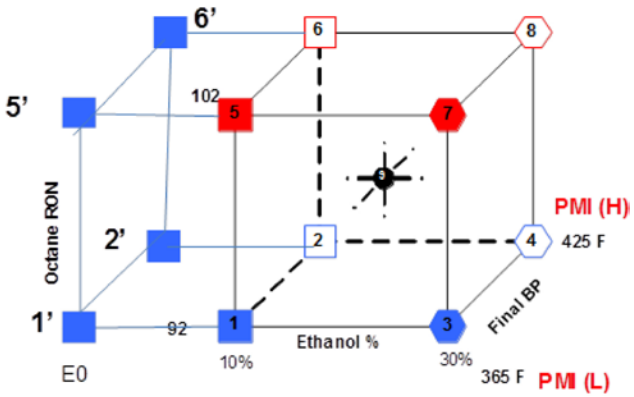
Acquisition of the fuels needed for the project was also be a goal for the year. The CRC project committee circulated a list of desired fuel blends and constraints on blending to three fuel providers and solicited expressions of interest and cost estimates to provide the fuels (see Figure 1). The committee selected Gage Products of Ferndale, Michigan, to manufacture the fuels. CRC issued a purchase order to Gage Products and authorized Gage to begin production in August 2015. All of the fuels will be produced in one batch to minimize undesirable batch-to-batch differences in fuel blends. As about 90 drums of fuel are being produced, Bay Logistics, an offsite storage facility for the fuels relatively near the fuel provider, has been identified and contracted to receive the fuels, store them, and ship them to ORNL as needed to support engine operations as the project progresses. The project scope and milestones originally anticipated fuels being produced and shipped directly to ORNL one at a time as they were needed. Producing all of the fuels at once has advantages in terms

Table 1. GEFORCE Project Milestone Table

Milestone Summary Table
Recipient Name: Oak Ridge National Laboratory
Project Title: Gasoline Engine and Fuels Optimized for Reduction of Fuel Consumption and Emissions (GEFORCE)

Task Title	Milestone Type	Milestone Number	Milestone Description	Anticipated Date (Months from Start)	Milestone Status
Establish Engine	Milestone	MS 1.1	Deliver Engine to ORNL	6	**Complete**
Establish Engine	Milestone	MS 1.2	Demonstrate engine operability	9	Anticipated completion in FY 2016 Q1
Procure Fuels	Milestone	MS 2.1	Establish contract with fuel manufacturer	3	**Complete**
Procure Fuels	Milestone	MS 2.2	Deliver first fuel to ORNL	9	**Complete**
Procure Fuels	Go/No-go	MS 2.3	Go/No-go based on project progress	12	**Complete - GO**
Procure Fuels	Milestone	MS 2.4	Complete delivery of fuels to ORNL	27	Ahead of schedule
Optimize and map engine	Milestone	MS 3.1	Complete first fuel optimization	15	
Optimize and map engine	Milestone	MS 3.2	Complete sixth fuel optimization	21	
Optimize and map engine	Go/No-go	MS 3.3	Go/No-go based on project progress	24	
Optimize and map engine	Milestone	MS 3.4	Complete final fuel optimization	30	
Vehicle System Modeling	Milestone	MS 4.1	Establish baseline vehicle fuel economy and emissions levels	18	
Vehicle System Modeling	Milestone	MS 4.2	Complete vehicle models for all fuels	33	
Reporting	Milestone	MS 5.1	Submit annual report for Project Year 1	12	**Complete (This Report)**
Reporting	Milestone	MS 5.2	Submit annual report for Project Year 2	24	
Reporting	Milestone	MS 5.2	Submit annual report for Project Year 3	36	

Q1 – first quarter



BP – boiling point; PMI – particulate matter index; RON - Research Octane Number

Figure 1. GEFORCE project target fuel matrix

of consistency between fuel blends and reduces risk associated with the fuel acquisition task of the project. The progress on this task equivalently satisfies milestones MS 2.1, MS 2.2, and MS 2.3, which were respectively to establish a contract with a fuel manufacturer, deliver the first fuel, and to make a go/no-go decision for the project based on successful acquisition of fuels. Milestone MS 2.4 is on-track for early completion in the first half of FY 2016 based on the new strategy of producing all of the fuels at once.

Conclusions

Drafting and execution of the CRADA and NDA required more time and effort than had been previously anticipated. Nevertheless, this objective was key to moving the project forward and was achieved this year. While these negotiations were occurring, simultaneous progress was made on readying the test cell with the baseline engine at ORNL and on development of the advanced research engine at GM. Progress on the acquisition and delivery of the fuel matrix has also been achieved, with plans now focusing on production of all of the fuels for the project in one batch at the beginning of the project. These accomplishments have placed the project on a firm foundation as it moves forward into FY 2016 to begin studies with the advanced research engine.

II.4 Fuel and Lubricant Effects on Emissions Control Technologies

Overall Objectives

- Ensure that new fuels and lubricants do not negatively impact emissions and emissions control systems
- Identify or alleviate concerns associated with changes in fuels and new lubricants
  - Including renewable fuels (alcohols and biodiesel are current primary focus)
- Investigate unique characteristics of fuels that enable increased efficiency
  - For example, high octane biofuel blends
- Efforts in this task are completed through five subtasks:
  - Emissions control opportunities when using biofuels and biofuel–gasoline blends
  - Fuel and lubricant formulation impacts on gasoline direct injection (GDI) particulate emissions
  - Techniques for identifying lubricant and fuel species in emissions control devices
  - Compatibility of ionic liquid (IL) lubricant additives with three-way catalysts (TWCs)
  - Compatibility of biodiesel with diesel emissions control devices

Fiscal Year (FY) 2015 Objectives

- Investigate potential of isobutanol in Ag-based catalyst for selective catalytic reduction (SCR) control of NO_x emissions
- Complete sample collection for particle chemistry and morphology studies from a relevant GDI engine platform running at least two different fuels
- Using a suite of novel laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate–orthophosphate interactions with catalytic emissions control
- Through collaboration with the National Renewable Energy Laboratory (NREL), Manufactures of Emission Controls Association, National Biodiesel Board, and Cummins, evaluate impact of long-term exposure of biodiesel-based metals on heavy-duty truck emission control systems
  - Finalize and present conclusive results on the impact of long-term exposure of biodiesel-based metals on heavy-duty truck emission control

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FY 2015 Accomplishments

- Emissions control opportunities when using biofuels and biofuel–gasoline blends
  - Lean gasoline engine experiments confirm potential for lean NO_x control with ethanol blends
  - Demonstrated isobutanol (iBuOH) has similar lean NO_x reduction performance to ethanol
- Fuel and lubricant formulation impacts on GDI particulate emissions
  - Determined start-stop does not have a major impact on particulate matter (PM) formation on E0 (gasoline) or E30 (blend of 30% ethanol, 70% gasoline); however, when using iBu24 (blend of 24% isobutanol, 76% gasoline), PM increases overall and during start-stop

- Fuel blend chemistry shown to have significant effect on PM chemistry; GDI very different than diesel

- Techniques for identifying lubricant and fuel species in emissions control devices
  - Used a suite of laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate–orthophosphate interactions with catalysts
- Compatibility of IL lubricant additives with TWCs
  - Identified P-form on TWC is different when using IL additive compared to zinc dialkyl dithiophosphate (ZDDP); aluminum phosphate formation preferred with IL and cerium phosphate with ZDDP
- Compatibility of biodiesel with diesel emissions control devices
  - Through collaboration with NREL, Cummins, Manufactures of Emission Controls Association, and the National Biodiesel Board, completed long-term exposure of heavy-duty truck emissions control system with full-useful life exposure of Na at ASTM-specified level

Future Directions

- Emissions control opportunities when using biofuels and biofuel–gasoline blends
  - Sulfur and thermal exposure; identify membranes of interest and evaluate separation potential with biofuel blends
- Fuel and lubricant formulation impacts on GDI particulate emissions
  - Complete PM kinetic study with E30 and iBu24; translate findings to reaction parameters
- Techniques for identifying lubricant and fuel species in emissions control devices
  - Complete extraction analysis on the components; compare to engine samples
- Compatibility of IL lubricant additives with TWCs
  - Gasoline and diesel durability studies with new ILs and stable engine platforms
- Compatibility of biodiesel with diesel emissions control devices
  - Confirm findings on emissions and emission control devices and report to stakeholders ■

Introduction

This task is a wide reaching collection of research projects that investigate the potential benefits, impacts, and overall compatibility of new and emerging fuels and lubricants. Efforts are focused on identifying unique properties of the new constituents that can either aid emissions control technologies or interfere with them. This includes measuring new constituents in the gaseous emissions and developing the techniques to properly identify them. The efforts specifically address barriers that have been identified in the Vehicle Technologies Program's Multi-Year Plan:

- Inadequate data for fuel effects on emissions and emission control systems, and
- Inadequate data on long-term impacts of fuel and lubricants on emission control systems.

Additionally, the research aims to elucidate potential effects of increasing renewable fuels to meet the renewable fuel standard.

Approach

This research brings together targeted, engine-based and flow-reactor studies with in-depth characterization of PM, hydrocarbons (HCs), and other emissions to better understand fuel and lubricant effects and interactions with emissions control devices. Efforts in this task are completed through five subtasks:

- Emissions control opportunities when using biofuels and biofuel–gasoline blends
- Fuel and lubricant formulation impacts on GDI particulate emissions
- Techniques for identifying lubricant and fuel species in emissions control devices
- Compatibility of IL lubricant additives with TWCs
- Compatibility of biodiesel with diesel emissions control devices

The results will be discussed independently for each of these subtasks.

Results

Emissions control opportunities when using biofuels and biofuel–gasoline blends

This investigation highlights the synergy between biofuels and lean gasoline emissions control with the focus being on the potential of alcohols as the reductant in the SCR of NO_x over a relatively inexpensive catalyst, 2 wt% Ag/Al_2O_3. A series of experiments was performed on a lean gasoline engine platform and the results confirm the potential for NO_x control with ethanol–gasoline blends. High NO_x conversion was achieved with the gasoline blends, as shown in Figure 1. NO_x conversion using E85 (blend of 85% ethanol, 15% gasoline) as the reductant was similar to E100 and overall fuel penalties were less than 5% for both. E50 (blend of 50% ethanol, 50% gasoline) was able to achieve >90% NO_x conversion, but at a much higher C_1/N and fuel penalty. A key finding was that higher ethanol content in the fuel/reductant significantly reduced HC slip. Additionally, it was observed that under lean conditions, up to 35% of the incoming NO_x could be reduced to NH_3, which would allow the opportunity for a dual SCR approach [1–4].

In other related flow reactor experiments, iBuOH was evaluated as the reductant and it showed similar NO_x reduction activity to ethanol over the same silver catalyst. Over 90% NO_x conversion was achieved between 300°C and 400°C using pure iBuOH (Figure 2), including a 40% peak selectivity towards NH_3 that could be utilized in a dual HC/NH_3 SCR configuration. The iBuOH–gasoline blends are only able to achieve greater than 90% NO_x conversion when operated at a gas hourly space velocity of 10,000 h^{-1} and employing a C_1/N ratio of 12. Isobutyraldehyde and NO_2 appear to function as intermediates in the iBuOH–SCR mechanism, which mirrors the mechanism observed for ethanol–SCR. In general, the performance of iBuOH in the SCR of NO_x over a Ag/Al_2O_3 catalyst is comparable with that of ethanol, although ethanol–gasoline blends display higher NO_x reduction than iBuOH–gasoline blends. The key parameter in employing alcohols in SCR appears to be the C-OH:N ratio rather than the C_1/N ratio.

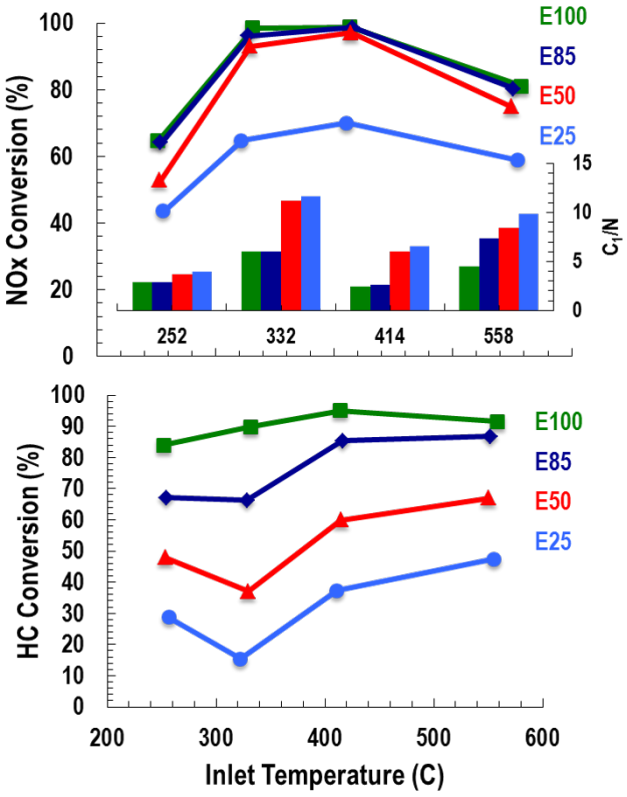

Figure 1. NO_x conversion (top) and HC conversion (bottom) during the lean-burn GDI engine-based evaluation of ethanol–gasoline blends using a 2% Ag/Al_2O_3 silver catalyst. The inset of the top graph refers to the C_1/N ratio used to evaluate each of the blends (the temperature is the value across the bottom of the inset).

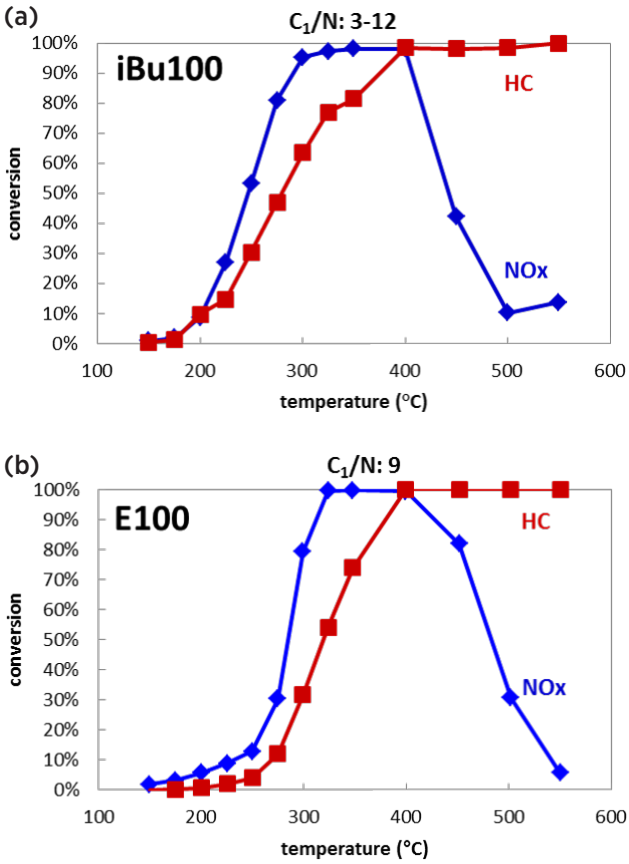

Figure 2. NO_x and HC conversion for the flow reactor based evaluation of (a) 100% isobutanol (iBu100) and (b) 100% ethanol (E100).

Fuel and lubricant formulation impacts on GDI particulate emissions

Particulate emissions efforts were focused on identifying the impact of biofuels during start-stop operation. In previous vehicle tests, the highest PM emissions were observed during the cold start of the Federal Test Procedure (FTP) test cycle, so there was reason to be concerned this would continue for each start sequence. Research was conducted on a 2014 Chevrolet Malibu e-Assist vehicle with 2.5 L GDI engine. The three fuels evaluated, E0, E30, and iBu24, were focused on the evaluation of the fuel oxygen effect on PM mass and size. The results in Figure 3 illustrate that E30 has lowest measured PM and it is unaffected by start-stop operation. In fact, the only fuel that demonstrated any effect on particulate mass from start-stop was the iBu24. It was also determined that the start-stop soot emissions decrease with successive hot starts. Compared to gasoline (E0) real-time soot particulate mass is higher with iBu24, but E30 is equivalent to E0 under non-start-stop conditions.

Further studies were conducted to determine the reactivity of the particulate generated for a range of fuels: E0, E30, iBu24, and iBu48 (blend of 48% isobutanol, 52% gasoline). The latter blend was chosen since it has the same oxygen content as E30, and thus could be another basis of comparison. These reactivity measurements were conducted under the well-controlled conditions provided by a flow reactor system with miniature particulate filter cores. Figure 4a shows the temperatures of 50% and 90% conversion ($T_{50\%}$ and $T_{90\%}$, respectively). It is clear that the particulate generated with E30 is significantly more reactive than E0, which in turn is more reactive than both of the iBuOH–gasoline blends. Interestingly both iBu24 and iBu48 have the same reactivity even though their fuel compositions and oxygen content are significantly different. An additional pulsed oxidation evaluation has been started to identify the fuel impact on the intrinsic kinetic nature of the particulate [5]. Figure 4b shows that the GDI-based particulate is significantly different than diesel-based particulate, as the activation energy for the E0 GDI particulate increases during its oxidation process, i.e., as C/C_0 goes from 100% to 0%. This implies that more energy will be required to fully regenerate

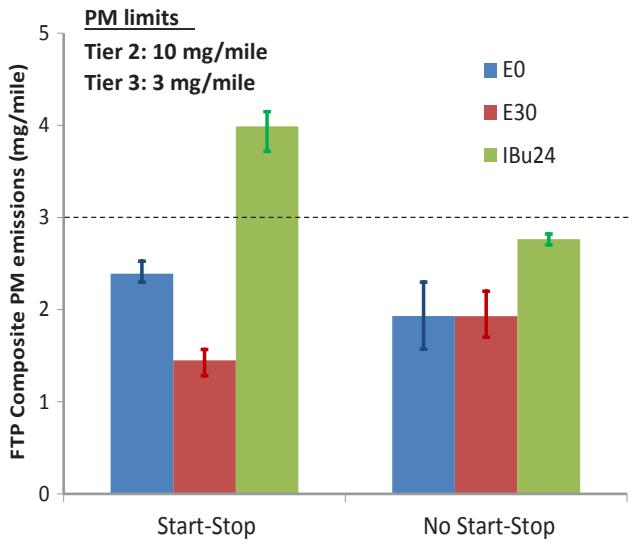

Figure 3. FTP composite PM emissions for E0, E30, and iBu24 under start-stop operation and conventional mode (no start-stop).

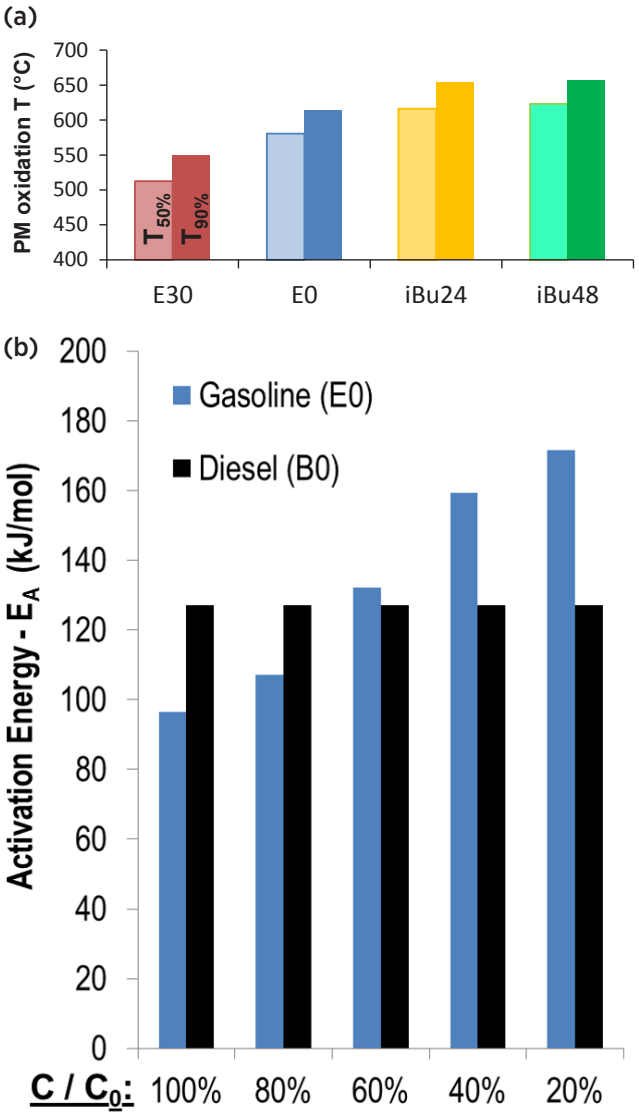

Figure 4. (a) Temperature of 50% and 90% conversion of the PM captured using E30, E0, iBu24, and iBu48. (b) Comparison of the activation energy as a function of fractional remaining PM for gasoline and diesel PM. Results indicate significant change with gasoline PM whereas diesel stays constant.

the particulate filter when used in conjunction with GDI systems.

Techniques for identifying lubricant and fuel species in emissions control devices

Efforts this year focused on developing a method to introduce different forms of phosphorous onto catalysts to examine effects of the initial form. It was developed as a lab-based approach to introduce representative phosphorous compounds that may be present in the exhaust, but which may vary based on the initial form of P in the lubricant. The technique utilizes a heated nebulizer system to introduce the phosphorous compounds as a mist. A commercial (Ford F-250) diesel oxidation catalyst (DOC) was exposed during the test, but only the front section was evaluated for effects. The results shown in Figure 5 illustrate that significant deactivation is observed as the P exposure delayed CO and C_3H_6 conversion significantly and the overall NO to NO_2 reactivity was significantly muted; however, there are minimal differences between the mono- and di-phosphate species.

Compatibility of IL lubricant additives with TWCs

As alternative lubricant antiwear additives are sought that reduce friction and improve overall fuel economy it is important that these additives are also compatible with current emissions control catalysts. The Fuels & Lubricant Technologies subrogram has supported the development of IL lubricant additives that have successfully demonstrated a >2% improvement in fuel economy. In the present work, an oil-miscible phosphorous-containing IL, trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P66614][DEHP]), is evaluated for compatibility with TWCs and compared to the industry standard ZDDP. The TWCs were received from General Motors and were thermally aged to their full useful life (FUL) equivalent. They were not however exposed to a lifetime level of lubricant, which was the focus of this study. The FUL-TWCs were further are aged under different scenarios: neat gasoline (no-additive or FUL_NA), gasoline + ZDDP (FUL_ZDDP), and gasoline + IL (FUL_IL). The aged samples, along with the as-received TWC (FUL_AR), are characterized through

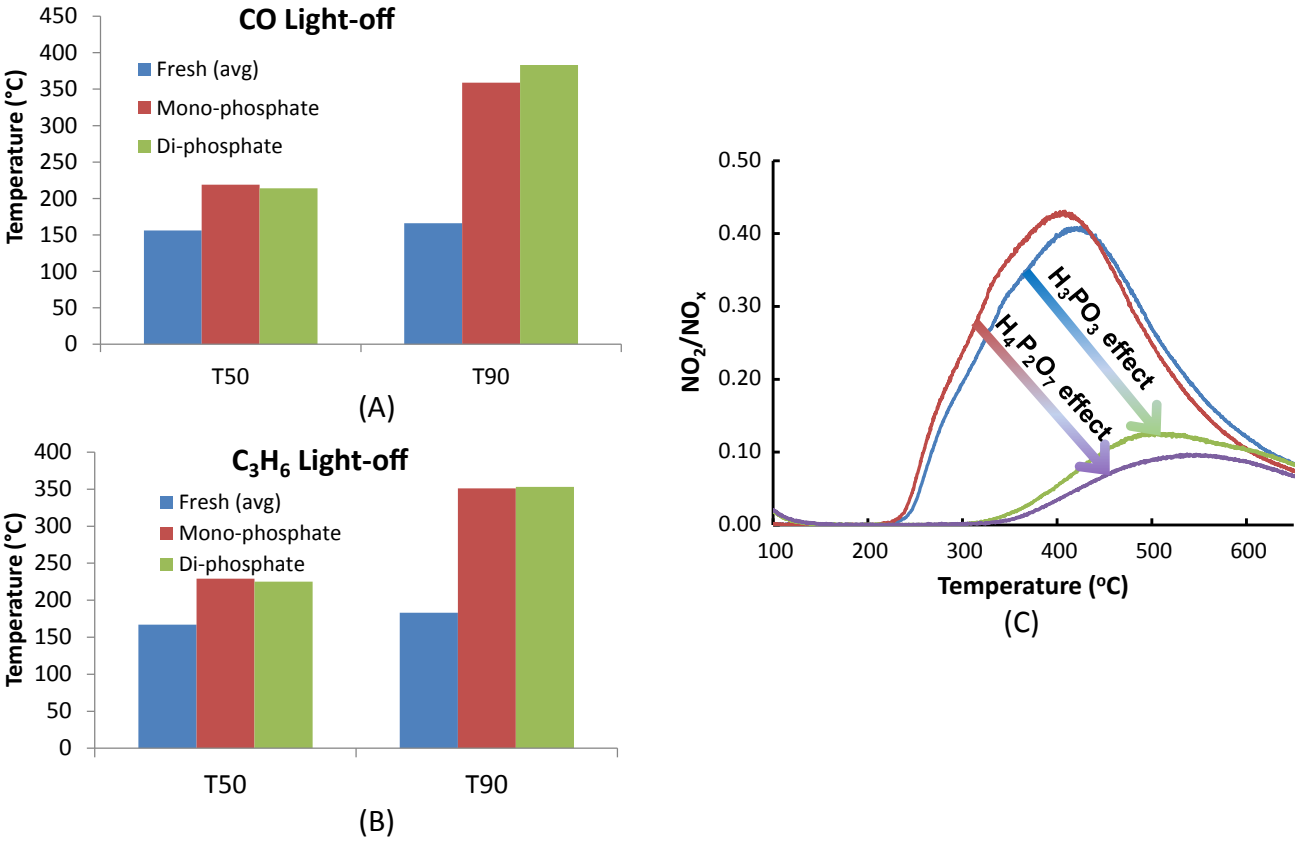

Figure 5. (a) CO and (b) C_3H_6 light off temperatures of the fresh and P-aged DOCs. (c) NO to NO_2 oxidation profiles of the same DOC. All three measurements were performed simultaneously.

various analytical techniques including catalyst reactivity evaluation in a bench-flow reactor. The results show that $T5_{0\%}$ for the ZDDP-aged TWCs increase by 30, 24, and 25°C for NO, CO, and C_3H_6, respectively, compared to the no-additive case. Although the IL-aged TWC also sees an increase in $T_{50\%}$ for CO and C_3H_6, 7°C and 9°C, respectively, it is notably less than ZDDP. Additionally, the IL-aged samples have higher water–gas shift reactivity and oxygen storage capacity than the ZDDP-aged TWC. Characterization of the inlet portion of the aged samples indicate that there is marginally more P in the washcoat when using ZDDP (Figure 6a), the predominant presence of $CePO_4$ in the ZDDP-aged TWC aged by ZDDP (Figure 6b), while its formation was retarded in the case of IL where higher levels of $AlPO_4$ is observed (Figure 6c). Thus the results in this work indicate that the evaluated IL additive has less impact on the TWC than the industry standard, ZDDP.

Compatibility of biodiesel with diesel emissions control devices

In collaboration with NREL and Cummins, impacts of biodiesel impurities on a heavy-duty truck emission control system were studied. An accelerated aging protocol was utilized to simulate the 435,000-mile full useful lifetime required for heavy-duty truck emission compliance. A full production exhaust system (DOC-diesel particulate filter [DPF]-SCR, from a Cummins ISL) was aged on a Caterpillar C9 test stand in 1,001 h using B20 (blend of 20% biodiesel, 80% gasoline) doped with 14 ppm Na which is 14 times the allowable ASTM limit. A three-mode cycle, consisting of 25 min at 260°C (DOC outlet, DPF inlet), 25 min at 380°C and 15 min at 550°C, simulated 22,000 h of thermal aging in 230 h. Emissions evaluations were conducted at ~250 h intervals using a Cummins ISL engine. Micro-cores were extracted at 0, 280, 553, 756, and 1,001 h from the front face of both the DOC and the SCR for further characterization using Brunauer–Emmett–Teller surface area analysis, energy dispersive X-ray spectroscopy, electron probe microanalysis, X-ray diffraction, and bench flow reactor studies.

Although elevated NO_x emissions were observed during the FTP evaluation of the system, all observed deactivation can be attributed to other effects such as P deactivation in the DOC decreasing NO to NO_2 oxidation, and mild Pt contamination in the SCR leading to direct NH_3 oxidation. The primary impact of the Na in the measured system was the increased ash in the DPF. The DPF contained 857 g (50 g/L) of ash following aging of which only 210 g could be attributed to the lube oil. Based on this study, we predict that Na in biodiesel will contribute to a 20% increase in the overall ash emissions

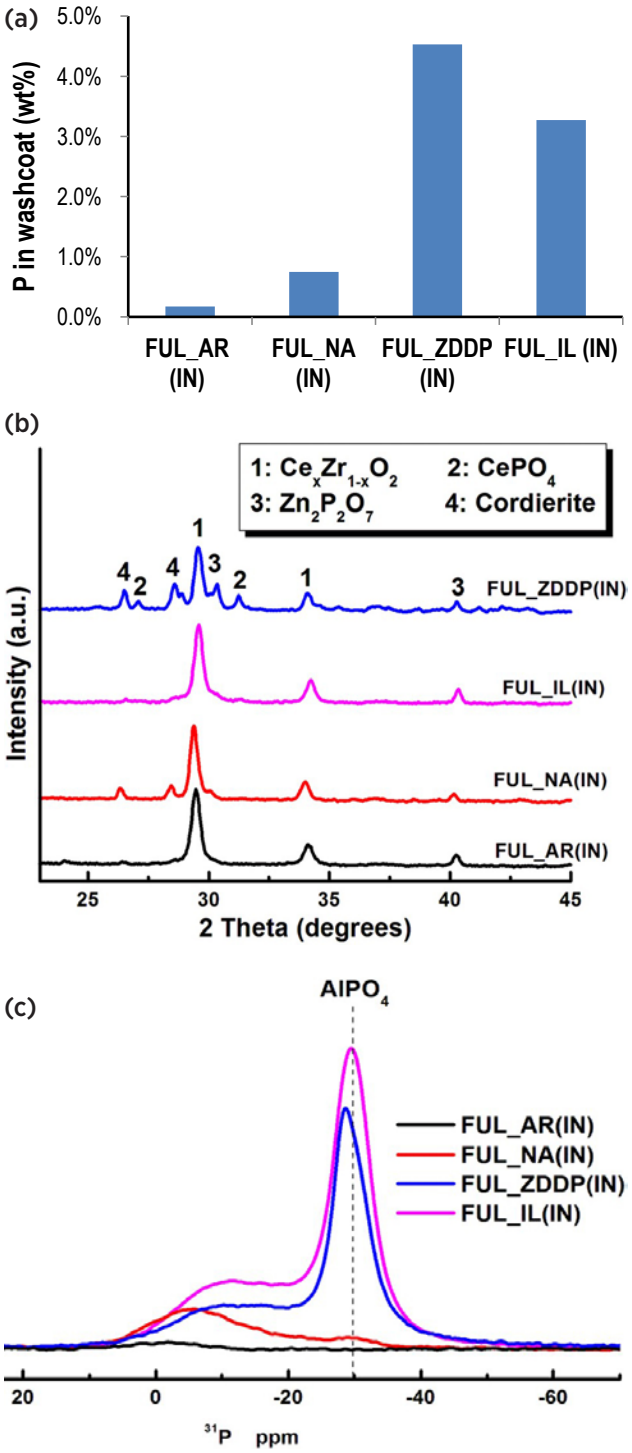

Figure 6. (a) Inductively coupled plasma mass spectrometry result of total P found in washcoats of each TWC. (b) X-ray diffraction patterns and (c) ^{31}P nuclear magnetic resonance spectra of the inlet parts of FUL_AR, FUL_NA, FUL_ZDDP, and FUL_IL.

if the current 5 ppm Na + K specification is maintained. Information from this study is relevant for setting fuel standards for biodiesel.

Conclusions

- Lean gasoline engine experiments confirm the potential for lean NO_x control with ethanol blends
- Demonstrated iBuOH has similar NO_x reduction performance to ethanol
- Determined start-stop does not have a major impact on PM formation on E0 or E30
- Fuel chemistry shown to have significant effect on GDI PM chemistry; GDI PM has different reactivity than diesel PM
- Used a suite of laboratory-based approaches to assess lubricant phosphorus speciation and report on preferential polyphosphate–orthophosphate interactions with catalysts
- Established durable engine platform for well-controlled and repeatable TWC exposure to fuels and lubricant additives; being employed with second generation IL-additive
- In a collaboration with NREL and Cummins, investigating the impact of 1 ppm Na in B20 on heavy-duty truck emission control, it was determined that the primary impact will be an ~20% increase in ash content
  - System NO_x increase does not appear to be directly attributable to Na, but instead P poisoning of the DOC and Pt contamination of the SCR

References

1. C. DiMaggio, G. Fisher., K. Rahmoeller and M. Sellnau, SAE J. Fuels Lubr. 2 (2009) 66, also listed as SAE 2009-01-2077.
2. G. Fisher, C. DiMaggio, D. Trytko, K. Rahmoeller and M. Sellnau, SAE Int. J. Juels Lubr. 2 (2010) 313, also listed as SAE 2009-01-2818.
3. US patent 7,431,905.
4. US patent 7,399,729.
5. Pihl. J.A.; Lewis, J.A.; Toops, T.J.; Adelman, B.J.; Derybowski, E.M. (2013) Top. Catal. 56:499–503.

FY 2015 Publications/Presentations

1. Vitaly Y. Prikhodko, Josh A. Pihl, Todd J. Toops, John Thomas, James E. Parks II, Brian West, "Selective Catalytic Reduction of Oxides of Nitrogen with Ethanol/Gasoline Blends over a Silver/Alumina Catalyst on Lean Gasoline Engine," SAE Technical Paper Series 2015-01-1008 (2015) 1.
2. D. William Brookshear, Jeong-Gil Nam, Ke Nguyen, Todd J. Toops, Andrew Binder, "NOx Performance of Cu-Chabazite SCR Catalysts Under Severe Sulfur Poisoning from Marine Diesel Engine's Fuels," Catalysis Today 258 (2015) 359–366.
3. 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," International Journal of Engine Research, published online December 26, 2014.
4. Todd J. Toops, Chao Xie, William Brookshear, Samuel A. Lewis, Ed Hagaman, Michael J. Lance, "Compatibility of Emerging Fuels and Lubricants on Emissions Control Devices using Accelerated Aging Techniques," DOE 2014 Annual Progress Report.
5. Storey, John Morse, et al. "Investigation of the potential impact of lubricant contribution to the formation of particulate matter with reactivity controlled compression ignition on light-duty diesel engines." Emission Control Science and Technology 1, no. 1, 64, (2014).
6. (INVITED) Michael Lance and Todd J. Toops, "Impact of Metal Impurities on Catalyst Durability," 2014 Biodiesel Technical Workshop, Kansas City, MO, October 28–29, 2014.
7. Vitaly Y. Prikhodko, Josh A. Pihl, Todd J. Toops, John Thomas, James E. Parks II, Brian West, "Selective Catalytic Reduction of Oxides of Nitrogen with Ethanol/Gasoline Blends over a Silver/Alumina Catalyst on Lean Gasoline Engine," SAE World Congress, Detroit, MI, April 21–23, 2015.
8. Storey, John Morse. "Challenges of decreasing particulate emissions in LDVs and passenger cars." 2015. Presented at Chonnam University, Gwangju, Korea. March 9, 2015.
9. Storey, John Morse, et al. "Challenges of decreasing particulate emissions in LDVs and passenger cars," 7th Integer Emissions Summit & DEF Forum USA 2014, Itasca, Illinois, USA, October 28–30, 2014.
10. Zelenyuk, Alla N., et al. "Detailed Characterization of Particulates Emitted by Lean-Burn Gasoline Direct Injection Engine," 2014 DOE Crosscut Workshop on Lean Emissions Reduction Simulation, Dearborn, Michigan, April 29, 2014.

III. Lubricants for High Engine and Vehicle Fuel Efficiency

The Vehicle Technologies Office (VTO) supports research and development of advanced lubricants to enable higher engine and vehicle efficiency. Lubricants face increasing demands including viscosity reduction, wear protection, and compatibility with exhaust emissions control devices. Although friction reduction and lower viscosity oils offer a small improvement in fuel economy, it should be noted that a 1% increase in fuel economy across the U.S. light duty fleet equates to a savings of over a billion gallons of gasoline. VTO often leverages the national laboratories' unique capabilities and facilities to conduct this research. To enable further developments in these areas, VTO also supports research at universities and additive companies into novel additives and other approaches.

III.1 Lab-Engine Correlation and In Situ Validation of Fuel-Efficient Engine Lubricant Technologies

Overall Objectives

- Develop accurate and reliable correlations between friction data and wear mechanisms from a select set of benchtop and engine tests of fuel economy, durability, and reliability
- Utilize the protocols, techniques, and knowledge established to work with industry to evaluate candidate solutions under a common set of conditions
- Identify a range of conditions (temperature, speed, load, and reciprocating length) that are relevant and critical to a fired engine power cylinder at top dead center (TDC)
- Use test protocols and methods that can simulate component conditions to develop and evaluate technologies in a rapid, cost-effective, and repeatable manner
- Test components from actual engines
- Distinguish between benefits that can be realized by implementing different technologies (finishing processes, types of coatings, materials, and lubricants)
- Simulate experimental results from a reciprocating test rig using numerical models

Fiscal Year (FY) 2015 Objectives

- Modify the reciprocating tribometer to include angle adjustability
- Initiate scuffing test methodology

FY 2015 Accomplishments

- Broadened network of industrial collaborators
- Procured system able to deliver nanoliter quantities of lubricating oil to simulate starved conditions
- Acquired engine components for evaluation
- Initiated the development of test methodology to simulate scuffing, a major failure mechanism of concern to industrial collaborators
- Developed a new data acquisition program that can be used to perform a computer-controlled scuffing routine, during which the load is increased in a step-wise fashion, but also to record friction and automatically stop the test when a specified high friction is reached

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Future Directions

- Improve existing friction test protocols to examine the effect of contact pressure, metallurgy, temperature, speed, and oil degradation
- Develop test protocols to create scuffing reliably and compare to scuffing failures observed in engine surfaces
- Design a wear test to accurately enable the screening of new-technology ring coatings and fully formulated oils
- Investigate the durability and reliability of journal bearings ■

Introduction

There is a growing need to develop advanced tribological systems for engines, drivetrains, and auxiliary systems to address the demand for improved vehicle efficiency, utilization of alternative fuels, and implementation of new emissions strategies. The design of new and improved systems often involves a progression of increasingly more complex and costly research and development 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 and actual

engine components may then follow to demonstrate that the technology will function on real-world materials. The rig tests are followed by single-cylinder tests using fired engines, multi-cylinder engines, and eventually, vehicle and fleet studies. As the technology progresses from one stage of test complexity to the next, the results are perceived to be more and more representative of real-world conditions; however, the costs of the tests increase dramatically (upwards of $100,000 for a sequence V test).

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 utilize protocols that are representative of vehicle conditions, such that they can accurately be used to screen technologies in the early stage of development and thus avoid expensive and time-consuming builds that will fail in the full-scale tests. Laboratory tests utilizing reciprocating rigs are rapid, cost-effective, and repeatable. They can provide information on the behavior of a system operating under certain conditions. Using prototypical components, the relevance of benchtop tests to the real world must be determined.

Results

During this project a range of conditions (temperature, speed, load, and reciprocating length) that are relevant and critical to a fired engine at TDC was identified, and test methods were developed to evaluate candidate solutions under a common set of conditions. Through this work different technologies (finishing processes, types of coatings, materials, and lubricants) were characterized [1,2]. However, it has not been possible to quantify the benefits that can be realized by such modifications in the real world. Implementation of a new technology would require ensuring that there are long-term benefits in terms of durability. Discussions with academia and industry have made it clear that scuffing, a catastrophic phenomenon, is of great importance and must be better understood for different surface technologies. Scuffing as it relates to contact between the piston ring and cylinder liner has to be avoided while wear has to remain low for a combustion engine to function properly.

Therefore, the determination of a scuffing load is of great interest. Scuffing load is a function of temperature, speed, surface roughness, other topographical parameters, and the amount of oil present at the contact. The latter depends on the test configuration, i.e., does the oil need to be replenished, does it form a pool, or is it allowed to drain. Therefore, one needs to be concerned with the initial amount of oil, the oil supply rate, and the method by which it is delivered and distributed over the area of contact.

The amount of oil delivered to the contact is important to simulate engine conditions at TDC. Experiments performed using a small amount of oil (1 μL) showed that the friction waveforms changed from waveforms with a cusp denoting mixed lubrication regime to square form denoting boundary regime friction during the test when oil was allowed to form a small pool by placing individual drops that spread throughout the contact. Similar experiments at temperatures up to 170°C, a rotational speed of 300 rpm, and a stepped load up to 2,700 N load caused a tribochemical film to form, but showed that scuffing did not occur. The coefficient of friction was monitored for any sudden increase during the test because such increase could indicate that a scuffing event might have occurred. These experiments indicated that oil delivery to the contact was not very well controlled with this oil delivery method, and even 1 μL of oil provided sufficient lubrication that prevented scuffing under the conditions investigated.

Therefore, during this year Argonne's Tribology group explored alternative ways to supply oil consistently. Additionally, the group's reciprocating tribometer was modified to include the extra capability of angle adjustment. This modification was the result of discussions with industrial partners and the Massachusetts Institute of Technology Consortium. The angle will also determine oil delivery and might allow for the replication of scuffing in the laboratory via precise oil delivery to the tribological contact to replicate the severe starved condition encountered in an engine at TDC.

To modify the existing reciprocating tribometer, a computer-assisted design software was used to create models of the parts that needed to be machined to make the changes required to allow for tilting of the assembly. The base that held the assembly together was measured, and a new plate was made based on the dimensions. A housing and a shaft reducer were also designed and built to install a new right-angle gear motor and allow the tribometer's bearing to be coupled with the motor's hollow shaft bearing.

The modified reciprocating tribometer was built by a unistrut construction and is referred to as the adjustable-angle reciprocating tribometer (AART). A photograph is shown in Figure 1.

The amount of oil in the tribological contact at TDC is not very well known, but oil film thickness of cylinder liners with different honing characteristics was shown to be in

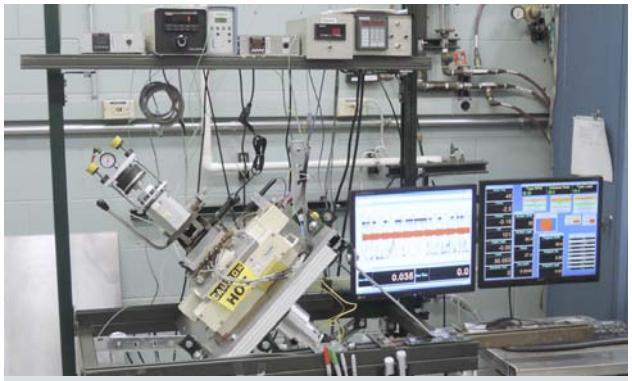


Figure 1. AART inclined at 45°

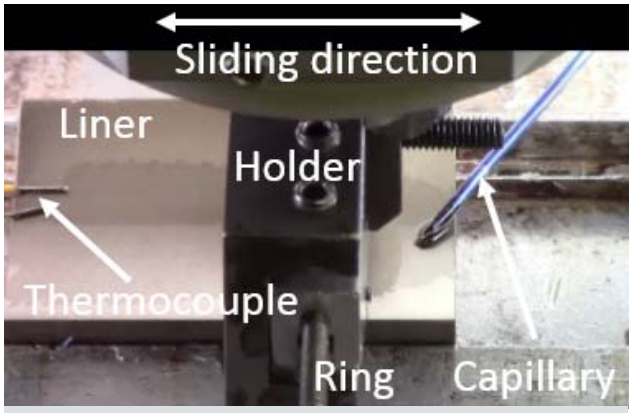


Figure 2. Test specimens installed in AART showing ring and liner and capillary

the range of 0.2 µm to 3 µm depending on the load and cylinder liner [3]. Petra et al. also shed some light into the oil amount and temperature necessary to simulate engine conditions at TDC [4]. In this work they tested the oil supply range from 0 µl/min to 1.0 µl/min. They stated that even though there is no specific information how much oil has to be delivered in the contact, the oil supply rate can be estimated based on oil consumption rates. For an 83-mm bore diameter, an oil supply rate of 1.0 µL/min corresponds to an oil consumption of 1.3 g/h per cylinder, which is the same magnitude as oil consumption measurements of engines [5,6], but the oil supply might be less than 1.0 µL/min because oil transport into the combustion chamber is not only through the ring liner contact, but also through ring grooves [7,8].

To deliver precise amounts of oil into the contact, a high-pressure liquid chromatography pump capable of low oil supply rates (0.1 µL/min) was procured. Oil was delivered onto the liner surface contact with a capillary tube. A thermocouple was welded onto the liner segment to monitor temperature. The ring-on-liner test setup is shown in Figure 2.

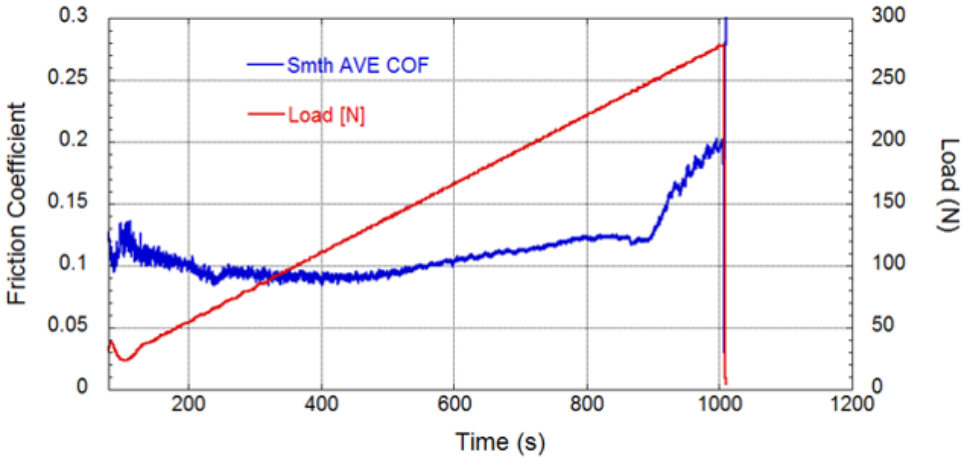
A unique feature that has been implemented in the test setup is the use of a camera that records the test so that general morphological changes on the liner with the time they occurred can be connected. Video images are obtained at 30 Hz, so that at 10x speed, images are obtained at 3 Hz.

When the AART carriage is reciprocated at 3 Hz, the carriage will be at the same position for each frame and will appear to be stationary, even though it is in reciprocating mode. Alternatively, if the AART is in reciprocating mode at a slightly lower frequency, e.g., 2.98 Hz, then the position will appear to slowly move back and forth. The ability to record images that show the surface condition throughout the test greatly increases our understanding of changes in how surface topography, friction, and wear are correlated.

Attributes related to the onset of scuffing were identified. An important feature commonly associated with scuffing of metallic engine parts is a relatively sudden increase in friction. Scuffing tests commonly use stepped loading to determine a critical load limit. It should not be expected that the same result will be obtained if the load is held constant for the same time, because at each step there could be subsurface damage accumulation not produced by a constant load. Petra et al. used a constant load until they observed failure, indicated by the coefficient of friction exceeding 0.3 for more than 30 s within a 6 h test [4]. While this method addresses the time-dependent progression of damage on the contact surface, it requires long test durations and forces the tribosystem to operate at high contact pressures for long periods without control of how the surfaces are changing during the long duration test. It is speculated that the changes that most likely cause scuffing to occur are topographical changes of the liner surface.

The testing performed during this period seeks to understand the mechanism that causes failure by monotonically increasing the load while minimizing the time required per test. The criterion for scuffing using the AART was a coefficient of friction momentarily reaching 0.2. In experiments where the coefficient of friction reached values above 0.2, unwanted wear was generated. This wear is very different from the phenomenon of scuffing. A typical test where the load was increased according to a linearly increasing mathematical function is shown in Figure 3.

Different mathematical functions were used to study the effect that loading rate has on scuffing load. The loading



COF – coefficient of friction

Figure 3. Tribological test results where the load was increased linearly and where scuffing occurred

rates studied were 1,000 N per 10 min, 40 min, and 60 min. Due to the complexity in setting up the radius of curvature precisely for every test, the scuffing load was normalized with respect to the track width for each test. Microscopy was employed to precisely measure the contact width under horizontal and vertical illumination. A sample is shown in Figure 4. Under the two types of illumination, distinct features were produced due to scuffing.

Depending on the way the test track width is defined, the scuffing load value will vary. Currently, more statistical data are needed in order to assess what illumination will produce accurate, repeatable, and significant results.

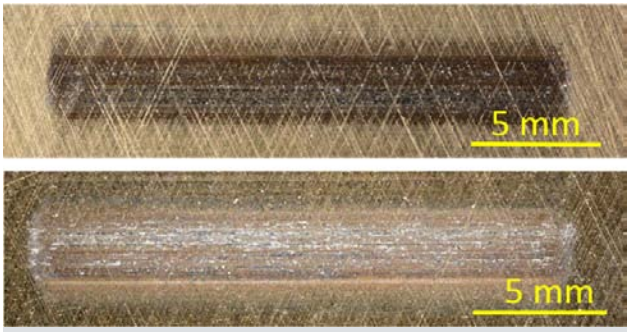


Figure 4. Horizontal (top) and vertical illumination (bottom) of the same test track

Conclusions

- The development of a test methodology to simulate scuffing, a major failure mechanism of concern to industrial collaborators, has been initiated.
- Scuffing is a difficult phenomenon to understand but a coefficient of friction of 0.2 was found to be a useful threshold that enabled scuffing to be reliably detected while avoiding unwanted wear.
- Several original equipment manufacturers have shown interest in the creation of a test method that causes scuffing reliably and allows the development of the comparison between scuffing load limits measured in the laboratory using the same components and engines.

References

1. Demas, N.G., Ajayi, O.O., Erck, R.A., and Fenske, G.R., Tribological studies of coated pistons against cylinder liners in laboratory test conditions, Lubrication Science, 24:5, 216–227, 2012.

2. Demas, N.G., Timofeeva, E., Routbort, J.L., and Fenske, G.R., Tribological effects of BN and MoS_2 nanoparticles added to polyalphaolefin oil in piston skirt/cylinder liner tests, Tribology Letters, 47:1, 91–102, 2012.

3. Spencer, A., Avan, E.Y., Almqvist, A., Dwyer-Joyce, R.S., Larsson, R., An experimental and numerical investigation of frictional losses and film thickness for four cylinder liner variants for a heavy duty diesel engine, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, 227, 1319–1333, 2013.

4. Petra, O., Müller, T., Füßer, H.-J., Bartel, D., The influence of oil supply and cylinder liner temperature on friction, wear and scuffing behavior of piston ring cylinder liner contacts – A new model test, Tribology International, 94, 306–314, 2016.

5. Ito, A., Shirakawa, H., Nakamura, M., and Yoshida, K., A study on the mechanism of lubricating oil consumption of diesel engines, SAE Technical Paper 2005-01-2169, 2005.

6. Herbst, H.M., and Priebsch, H.H., Simulation of piston ring dynamics and their effect on oil consumption, SAE Technical Paper 2000-01-0919, 2000.

7. Usui, M., Murayama, K., Oogake, K., and Yoshida, H., Study of oil flow surrounding piston rings and visualization observation, SAE Technical Paper 2008-01-0795, 2008.

8. Thirouard, B., Characterization and modeling of the fundamental aspects of oil transport in the piston ring pack of internal combustion engines, Ph.D. Thesis, Massachusetts Institute of Technology (MIT), Dept. of Mechanical Engineering, 2001.

FY 2015 Publications/Presentations

1. Demas, N. G., Adjustable angle reciprocating tribometer development, MIT Consortium Meeting, March 10–12, 2015.

2. Demas, N. G., Scuffing methodology development, MIT Consortium Meeting, November 17–19, 2015.

III.2 Integrated Friction Reduction Technology to Improve Fuel Economy without Sacrificing Durability

Overall Objectives

- Develop a GF-6A (backward compatible) 0W-20 fuel efficient lubricant with at least 2% fuel economy improvement over a 5W-30 2014 GF-5 commercial oil (baseline oil) using the most up to date GF-6 specification engine test sequence available at the time (milestone due date)
- Develop a 0W-16 GF-6B fuel efficient lubricant that exceeds 2% fuel economy improvement over the baseline oil
- Develop test protocols to measure engine durability using the developed 0W-16 oil, and evaluate the effectiveness of surface texture, diamond-like-carbon, and encapsulated additives in maintaining and/or enhancing durability in using GF-6B oils

Fiscal Year (FY) 2015 Objectives

- Obtain additive components and base oils from partners and suppliers
- Evaluate friction modifiers (FMs) and antiwear additives using industrial standard test methods and in-house test procedures and select the best combination
- Conduct surface texture and microencapsulation research to be evaluated for their impact on durability in the third year to enhance fuel economy and durability
- Formulate a fuel efficient 0W-20 GF-6A and conduct ASTM Engine Sequence VIE (latest test procedure available at the time) and measure fuel economy improvement over the baseline oil (2014 5W-30 GF-5 commercial oil)

FY 2015 Accomplishments

- Lubricant tested in ASTM Engine Sequence VIE tests and showed 2.3% fuel economy improvement over the 2014 5W-30 GF-5 commercial oil
- Evaluated various FMs in industrial standard bench tests and in-house tests
- Evaluated various antiwear additives under low viscosity formulations and high temperatures
- Successfully formulated a GF-6A lubricant based on these evaluations

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- [3]General Motors Company, Detroit, MI

Additive Company Partners:

- R.T. Vanderbilt, Norwalk, CT
- Afton Chemicals, Richmond, VA

Future Directions

- Formulate GF-6B 0W-16 ultra-low viscosity lubricants
- Conduct engine tests to measure fuel economy of this oil
- Prepare surface texture and microcapsules for durability testing in the third year ■

Introduction

The combustion of fossil fuels such as gasoline and diesel to transport people and goods is the second largest source of CO_2 emissions, accounting for about 31% of the total Unites States CO_2 emissions and 26% of the total Unites States greenhouse gas emissions in 2013 [1]. The United States imports about 9 million barrels of petroleum per day. Improving the fuel economy of cars, therefore will reduce the Unites States' dependence on foreign oils and reduce carbon emission. The new 2012 Corporate Average Fuel Economy standard raised fuel economy from 27.5 mpg in 2012 to 54.5 mpg by 2015. This project supports this national goal.

In 2012, the Japanese Automotive Manufacturers Association petitioned SAE J300 to establish a new ultralow viscosity grade of lubricants for enhanced fuel economy. SAE approved the new 0W-16 classification in 2014 (2.3 mPa·s at 150ºC). The concern is that such low viscosity oils may cause wear. This project aims to: (1) develop a prototype GF-6A 0W-20 formulation that has 2% fuel economy improvement for the legacy fleet; (2) develop a prototype GF-6B 0W-16 formulation and measure its fuel economy; and (3) develop durability test protocols to evaluate engine durability using such oils.

Approach

Ultra-low viscosity lubricants need lower molecular weight oxidative stable base oils. Careful selection of base oils with good solvency is needed. While low viscosity reduces hydrodynamic drag and pumping energy, it still needs good FMs, robust antiwear (AW) additives, and good high temperature viscosity index improvers to create robust fuel efficient lubricants.

To formulate a robust low viscosity lubricant, the industrial partners and other additive suppliers were solicited to provide individual additive component and base oils samples for the project. A large number of base oils and additive components were collected.

Results

Evaluation of FMs

Miller [2] and Ushioda [3] studied the effect of low viscosity oils on fuel economy using motored engine torque tests and ASTM Engine Sequence VID engine dynamometer tests to evaluate various low viscosity oils. They found that by just lowering the viscosity of the oil and holding the formulation constant, lower viscosity oils can have the same Sequence VID test results without improvement. They reasoned that a lower viscosity would shift the lubrication regime to more boundary lubrication, thereby increasing friction. This was balanced by the reduced drag under hydrodynamic lubrication conditions. So to increase fuel economy, one must find ways to reduce the boundary friction. The motored engine torque test verified this hypothesis. From their test results, they concluded that low viscosity oils will need to reduce boundary and elasto-hydrodynamic lubrication friction in order to gain the fuel economy improvements.

Based on their findings, many FMs were tested using the Mini Traction Machine (MTM) and Plint ring-on-liner tests. The tests were designed to evaluate the effectiveness of various FM additives across the boundary, mixed, and hydrodynamic lubrication regimes.

Figure 1 shows typical MTM results comparing five FMs in boundary, mixed, and hydrodynamic lubrication regimes. FM “e” shows lower boundary friction but higher mixed and hydrodynamic friction. Both organic and inorganic FMs were evaluated.

Evaluation of AWs

Since AW additives have the potential to interact with FMs, the test protocols call for screening AWs in a formulation with a fixed FM. The best AW additive selected from the screening then go through another round of screening where the AW additive is fixed and various FMs are inserted. This way, the best AW–FM combination can be selected.

As shown in Figure 2, three AW additive combinations have the least amount of wear as measured by the Plint ring and liner wear test which uses production ring and liners from the engine. The wear test duration is longer than usual in order to obtain measureable wear mass loss from the tests. The test precision is about 10%.

Formulation and Engine Testing

With the optimum base oils blend selected, and the best combination of FMs and AWs selected, a series of 0W-20 formulations were designed and tested in an array of bench and rig tests to select the best formulation for the Engine Sequence VIE tests. The candidate oil was then tested in engine tests to compare to the baseline oil of a 2014 commercial oil to show 2% fuel economy improvement. The VIE test has not been finalized by

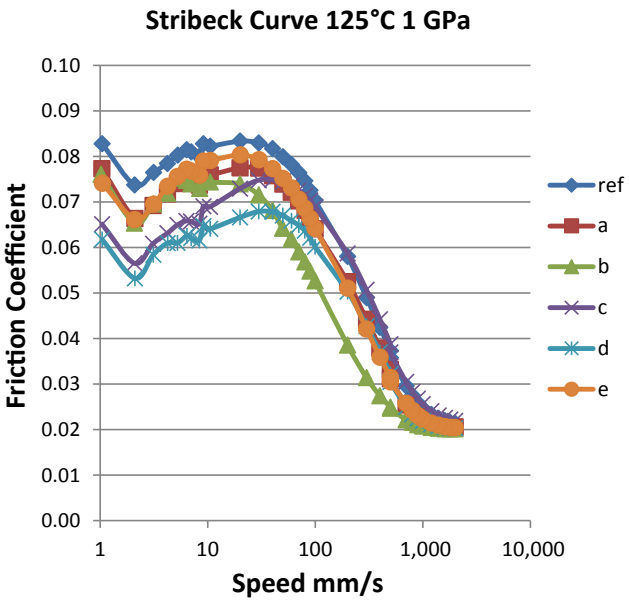

Figure 1. FM evaluation using the MTM at 125°C, 50% roll-slide ratio, 1 GPa load, and increasing speeds.

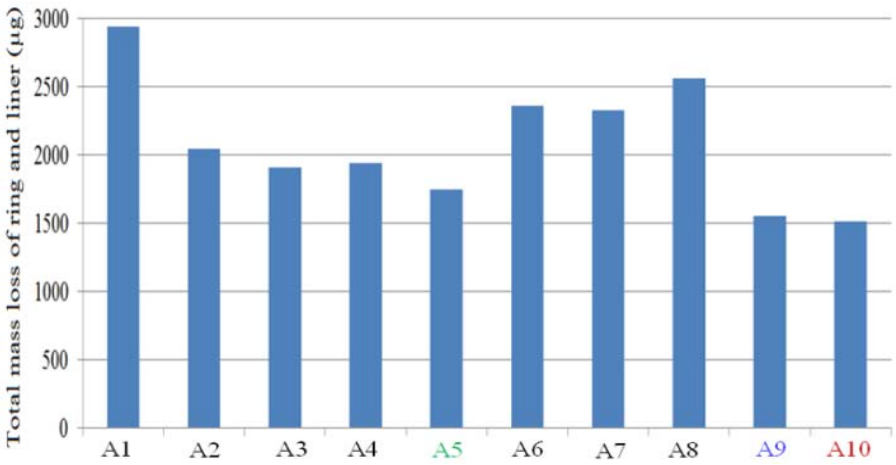

Figure 2. Wear mass loss of various antiwear additive combinations using the Plint ring and liner test at 100°C, 6 Hz, 240 N, 15 h test duration

ASTM which is in the process of developing GF-6 specification test limits. Since there is no industry wide engine test statistics available at this time, it was decided to run the tests using a single engine on the same test stand and back-to-back testing with repeat tests. This is the most precise comparison testing of two oils.

Table 1 shows the newly developed oil exhibiting ~2.4% fuel economy improvement over the baseline oil.

Conclusions

The project goal of developing a GF-6A oil that exceeds the 2% fuel economy improvement target was met successfully. This oil is backward compatible, i.e., it can be used by the legacy fleet, and fulfills the programmatic goal called for in the solicitation.

Table 1. Fuel economy improvement of new GF-6A oil vs 2014 commercial baseline

	New Candidate	New Candidate Repeat	2014 Commercial Baseline Oil	2014 Commercial Baseline Oil Repeat	Improvement for Candidate (0W-20) Over Benchmark (5W-30)
Run no.	6-3-34-3	6-6-34-6	6-4-34-4	6-5-34-5	
EOT date	8/28/2015	10/28/2015	9/18/2015	10/13/2015	
Test stand	Number 6	Number 6	Number 6	Number 6	
Engine number	34	34	34	34	
Oil viscosity grade	0W-20	0W-20	5W-30	5W-30	
FEI-1 (new broken-in)	1.84%	2.13%	1.19%	1.01%	0.89%
FEI-2 (aged)	2.37%	2.28%	0.72%	0.92%	1.51%
FEI-SUM	4.21%	4.41%	1.91%	1.93%	2.39%

EOT – end of test; FEI – fuel economy improvement

References

1. EPA website: http://www3.epa.gov/climatechange/ghgemissions/gases/co2.html

2. Miller, W.T., Van Dam, W., Parsons, G., "Recent development in GF-6, the new North American gasoline engine oil performance category: Part 1: the new J3000 viscosity grade; implications and formulation tradeoffs," SAE paper 2012-01-1707, 2012.

3. Ushioda, N., Miller, T.W., Sims, C.B., Parsons, G., Sztenderowicz, M., "Effect of low viscosity passenger car motor oils on fuel economy engine tests," SAE 2013-01-2606, 2013.

FY 2015 Publications/Presentations

1. F. Zhao, S. Hsu, "Microencapsulation of additives," STLE Annual Conference, Dallas Texas, May 17–21, 2015.

2. S. Hsu, F. Zhao, "New generation of low viscosity fuel efficient lubricants: key technical issues," Tribology in Industry and Research Symposium, Wiener Neustadt, Austria, November 25, 2015.

III.3 ORNL–Shell: Ionic Liquids as Multi-Functional Lubricant Additives to Enhance Engine Efficiency

Overall Objectives

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

Fiscal Year (FY) 2015 Objectives

- Investigate compatibility of the top candidate IL with other engine oil additives
- Finalize the formulation for a prototype low-viscosity engine oil using a top candidate IL as an anti-wear (AW) additive
- Demonstrate fuel economy improvement (FEI) for the prototype IL-additized fully formulated engine oil using standard multi-cylinder engine dynamometer tests

FY 2015 Accomplishments

- Two media reports highlighting the newly discovered synergism between IL and zinc dialkyldithiophosphate (ZDDP)
- Three journal papers including one in *Advanced Materials* (impact factor: 17.49)
- Two invention disclosures
- Three conference presentations including one invited talk
- Three-dimensional visualization of the tribofilm composition structure using atom probe
- Compatibility of the top candidate IL with other engine oil additives, particularly detergents and dispersants, was determined
- Prototype fully formulated SAE 0W-16 engine oil containing a combination of IL and ZDDP as anti-wear additives was produced

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- Evaluated IL+ZDDP additized prototype engine oil using Sequence VIE engine dynamometer test; results demonstrated FEI of 2.12% over the standard reference oil and 0.25% over a similar prototype engine oil in the same viscosity grade but using ZDDP only as the AW additive

Future Directions

- Complete investigation of the effects of an IL + ZDDP combination on three-way catalyst using an accelerated small engine test
- Funding Opportunity Announcement/Cooperative Research and Development Agreement joint project between ORNL and Shell ends on December 31, 2015 ■

Introduction

For an internal combustion engine, ~10–15% of the energy generated is lost to friction. Developing effective additive packages in combination with 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 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; and (7) multi-cylinder fired engine fuel efficiency dynamometer tests (ASTM D 7589 Sequence VIE).

Results

We had previously reported an interesting synergism between phosphonium–organophosphate ILs and ZDDP. Further characterization of the tribofilm formed by IL + ZDDP was conducted to gain a deeper understanding of the wear protection mechanism. In FY 2015, we were able to generate three-dimensional visualization of the tribofilm composition structure using an atom probe. Tribofilms are believed to be composites of ceramic, metallic, and organic compounds as a result of tribochemical interactions among metal surface, wear debris, oxygen, and lubricant AW additives, however, their exact composition structures are little known. Taking advantage of ORNL's atom probe tomography expertise and facility, we currently are applying this technique to reveal the composition structures of selected tribofilms. For example, Figure 1 shows the side view and a sliced top view of the elemental maps of a tribofilm formed by IL + ZDDP. An interesting network of metal phosphates and oxides is clearly shown in the sliced top view, implying cross-linking among phosphate compounds.

A combination of tetraoctylphosphonium bis(2-ethylhexyl) phosphate ($[P_{8888}][DEHP]$) and ZDDP was formulated into a prototype low-viscosity (SAE 0W-16) engine oil based on the results of the compatibility study between the IL and other lubricant additives, particularly detergents and dispersants. The molecular structure of the IL and ZDDP are shown in Figure 2. The two lubricants were formulated with almost identical compositions except for the AW content. One contained only ZDDP (800 ppm phosphorous), and the other contained ZDDP + $[P_{8888}][DEHP]$ (400 ppm phosphorous contribution from each). Table 1 shows the mass percentage composition of each experimental formulation (EF) including detergent (DT), dispersant (DP), viscosity modifier (VM), antioxidant (AO), friction modifier (FM), pour

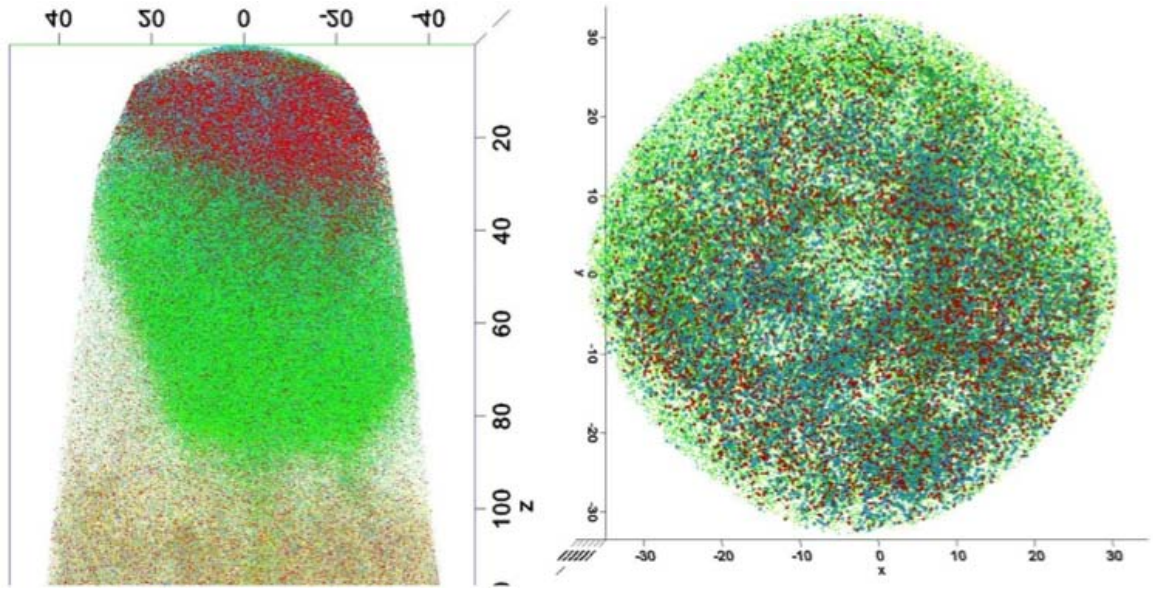


Figure 1. Atom probe revealing the three-dimensional composition structure of the tribofilm formed by IL + ZDDP: a network of metal phosphates and oxides. Color scheme: P: red, Zn: light blue, O and FeO_x: green, and Fe: yellow.

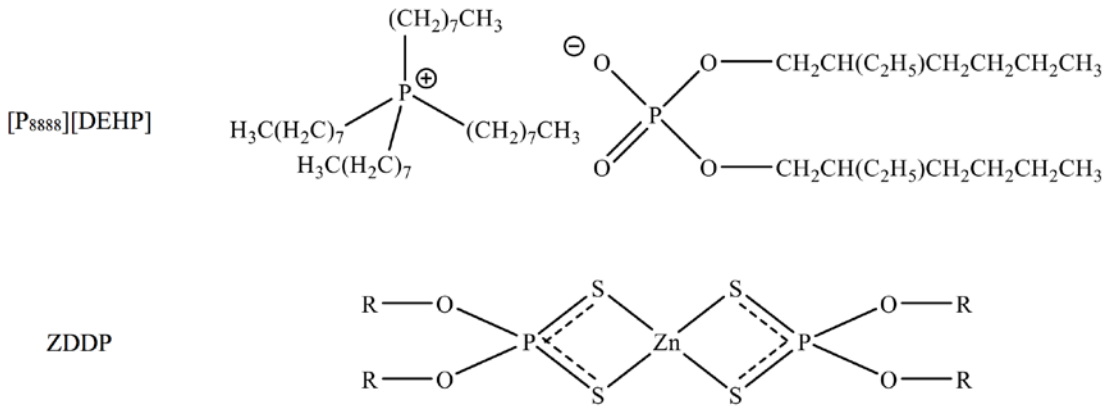


Figure 2. Structures of tetraoctylphosphonium bis(2-ethylhexyl) phosphate ([P_{8888}][DEHP]) and zinc dialkyldithiophosphate.

Table 1. Experimental formulation additive composition

Engine oil	DT	DP	VM	AO	FM	PPD	AF	AW	
								ZDDP	IL
EF w/o AW	3%	2%	2.4%	1%	0.8%	0.3%	0.03%	0%	0%
EF + ZDDP	3%	2%	2.4%	1%	0.8%	0.3%	0.03%	0.8%	0%
EF + IL + ZDDP	3%	2%	2.4%	1%	0.8%	0.3%	0.03%	0.4%	0.52%

w/o - without

point depressant (PPD), antifoaming (AF) agent and AW additive.

The lubricants' friction and wear performance were first evaluated using tribological bench tests. Boundary lubrication tests were conducted using ball-on-flat reciprocating sliding at 100°C. As shown in Figure 3, EF + 0.52% [P_{8888}][DEHP] + 0.4% ZDDP produced the lowest wear, a roughly 90% reduction over EF without AW. Stribeck curves were built for these two EF lubricants using ball-on-disc rolling/sliding and results were benchmarked against an SAE 20W-30 reference oil. Twenty scans for each lubricant were completed to determine how friction behavior changes as a tribofilm forms on each surface. Figure 4 shows the results of these Stribeck scans. The reference oil and EF + 0.8% ZDDP each exhibit a pattern of increasing friction as the number of scans increases. The IL-containing lubricant shows the opposite trend although over a narrower band of friction. As a result, the steady-state friction curve, an average of the last three of 20 scans, for EF + 0.52% IL + 0.4% ZDDP is substantially lower than the other two lubricants as shown in the summary chart (Figure 4). EF + 0.52% IL + 0.4% ZDDP exhibits the highest advantage over EF + 0.8% ZDDP in the mixed regime, but as elastohydrodynamic regime is approached, the friction curves tend to converge as expected for lubricants of the same viscosity grade. Surface roughness measurements were taken after the Stribeck scans revealed a correlation of surface roughness with the friction behavior as the IL-containing lubricant produced a smoother surface.

With very encouraging results for the IL-additized formulated oil in the previous boundary wear and friction tests and in both mini-traction machine Stribeck scan experiments, we moved forward with full-scale, multi-cylinder, fired engine fuel economy evaluation. Standard Sequence VIE engine dynamometer tests were conducted at Intertek Automotive Research (San Antonio, Texas). The Sequence VIE engine test measures fuel economy over six stages of engine operation varying parameters such as torque, speed, and oil temperature. The engine test-determined FEIs are shown in Table 2. In agreement with bench test friction measurements, EF + 0.52% IL + 0.4% ZDDP demonstrated improved fuel economy in all six stages compared with the reference oil by 2.12% and EF + 0.8% ZDDP by 0.25%, respectively. Stages 4–6, which constitute 35.7% of the final weighted score, subject the test engine to increased levels of boundary lubrication (BL) and mixed lubrication (ML) regimes;

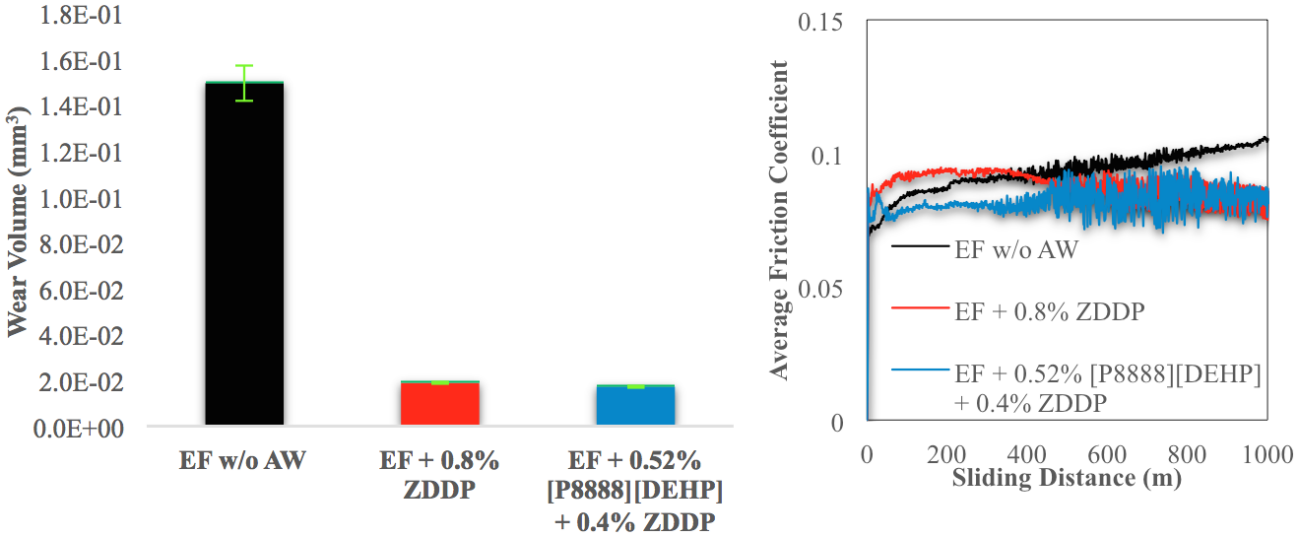
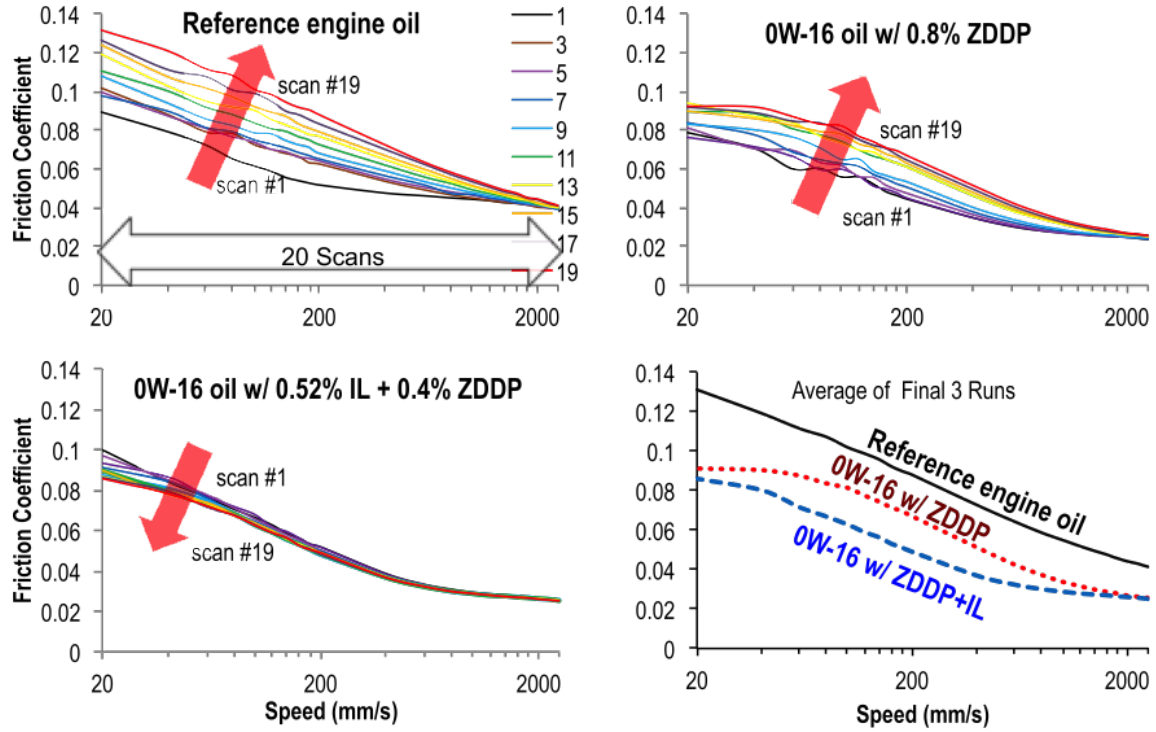


Figure 3. Wear (left) and friction (right) results for reciprocating sliding bench tests. Ball wear volumes (in green on top of each bar) and error bars are included but are very small for the second and third entries. Averaged friction results for two repetitions per lubricant.



w/ – with

Figure 4. Stribeck curves. Twenty scans were completed with the steady-state friction curve representing the average of the final three scans for each lubricant.

under these conditions there is more pronounced benefit as a result of adding the IL (0.76%, 0.48%, and 0.79% for Stages 4–6, respectively) compared to ZDDP only. On the other hand, Stages 1–3 show smaller IL-induced improvements because elastrohydrodynamic lubrication (EHL) and hydrodynamic lubrication (HL) are the dominant lubrication regimes. These test results indicate that an IL, such as $[P_{8888}][DEHP]$, can function in tandem with ZDDP in an AW context improving fuel economy across a spectrum of engine operating conditions.

Table 2. FEIs determined by Sequence VIE engine dynamometer tests (FEI 1)

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Weighted FEI
Lubrication Regime	EHL/HL Dominant			More BL/ML	Some BL/ML	More BL/ML	
EF w/ 0.8% ZDDP	2.36%	2.84%	1.66%	3.72%	5.98%	3.03%	1.87%
EF w/ 0.4% ZDDP + 0.52% IL	2.54%	2.91%	1.77%	4.48%	6.46%	3.81%	**2.12%**
IL-induced FEI	0.17%	0.07%	0.11%	0.76%	0.48%	0.79%	**0.25%**

Further improvements in performance may be allowed by formulation optimization. The latest work on ILs' compatibility with detergents and dispersants at ORNL indicates that two-way compatibility between IL and detergent or dispersant may not be able to be easily translated into three-way compatibility among IL, detergent, and dispersant. Detailed results of the three-way compatibility and associated formulation have been filed as a joint invention disclosure between ORNL and Shell. The encouraging results presented here provide a glimpse into what future advantages this new class of ionic additives may provide.

Impacts of IL and IL + ZDDP on exhaust emission catalysts are being investigated using an accelerated small engine test. Each additive was mixed with fuel and combusted in a test engine with exhaust treated with a three-way catalyst. Engine load was varied throughout the test in order to maintain a constant catalyst temperature. Results will be reported in the Cooperative Research and Development Agreement final report.

Conclusions

In FY 2015, the ORNL–Shell team further investigated the IL + ZDDP lubricating mechanisms and developed a prototype low-viscosity (SAE 0W-16) engine oil using IL + ZDDP as anti-wear additives. Through bench tests, we have shown that the combination of the IL and ZDDP in formulated oil is more effective in wear protection than using ZDDP only. Stribeck curve measurements showed marked IL-induced friction reduction in the mixed and boundary regimes. The full-scale engine fuel economy dynamometer experiments provided direct evidence of fuel economy improvement as a result of adding IL in formulated oil in a Sequence VIE engine test with weighted FEI of 2.12% and 0.25% over the reference oil and ZDDP-only formulation, respectively. The strong correlation between the bench and engine test results suggests promising potential for the IL additive technology.

FY 2015 Publications/Presentations

1. J. Qu, W.C. Barnhill, H. Luo, H.M. Meyer, D.N. Leonard, A.K. Landauer, B. Kheireddin, H. Gao, B.L. Papke, S. Dai, "Synergistic effects between phosphonium-alkylphosphate ionic liquids and ZDDP as lubricant additives," *Advanced Materials* 27 (2015) 4767–4774.

2. W.C. Barnhill, H. Gao, B. Kheireddin, B.L. Papke, H. Luo, B.H. West, J. Qu, "Tribological bench and engine dynamometer tests of a low viscosity SAE 0W-16 engine oil using a combination of ionic liquid and ZDDP as anti-wear additives," *Frontiers in Mechanical Engineering* 1 (2015) 12, DOI: 10.3389/fmech.2015.00012.

3. W.C. Barnhill, J. Qu, H. Luo, H.M. Meyer III, C. Ma, M. Chi, B.L. Papke, "Phosphonium-organophosphate ionic liquids as lubricant additives: effects of cation structure on physicochemical and tribological characteristics," *ACS Applied Materials & Interfaces* 6 (2014) 22585–22593.

4. J. Qu, "Low-Viscosity Lubricants Using Ionic Liquids as Base Stocks or Additives," Symposium on Molecular Chemistry and Lubricant Rheology, *STLE 70th Annual Meeting,* Dallas, May 17–21, 2015. (Invited)

5. W.C. Barnhill, J. Qu, H. Luo, B.H. West, B.L. Papke, H. Gao, B. Kheireddin. "Compatibility of a Phosphonium-Organophosphate Ionic Liquid with Common Engine Oil Additives with Tribological Bench and Engine Tests." *70th Annual Society of Tribologists and Lubrication Engineers Meeting*. Dallas, TX, May 17–21, 2015.

6. J. Qu, W.C. Barnhill, H. Luo, H.M. Meyer, D.N. Leonard, A.K. Landauer, B. Kheireddin, H. Gao, B.L. Papke, S. Dai, "A Synergistic Hybrid Anti-Wear Additive by Combining a Phosphonium-Alkylphosphate Ionic Liquid and a ZDDP," *2015 STLE Tribology Frontiers Conference, Denver*, October 25–27, 2015.

Special Recognitions & Awards/ Patents Issued

1. "ORNL, Shell develop a less friction/wear hybrid lubricant additive," *World Industrial Reporter*, September 2, 2015.

2. "Reduce wear with synergistic lubricant pair," *Materials Views*, July 28, 2015.

3. J. Qu, W.C. Barnhill, H. Luo, B. Kheireddin, H. Gao, B.L. Papke, "Lubricant Formulations Containing Phosphonium-Organophosphate Ionic Liquids," ORNL Invention Disclosure #201503587, August 24, 2015.

4. J. Qu, H. Luo, "Ionic Liquids Containing Protic or Symmetric Aprotic Ammonium Cations and Phosphinate Anions as Lubricant Additives," ORNL Invention Disclosure #201503529, May 14, 2015.

III.4 Improving Fuel Economy through Formulation Design and Modeling

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 J1321) without adverse impacts on vehicle performance or durability. This will be accomplished through engine, transmission and axle lubricant formulation design, modeling, and testing.

A target level of performance:

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

Fiscal Year (FY) 2015 Objectives

- Run National Renewable Energy Laboratory (NREL) Cummins ISL 8.9 L engine fuel efficiency verification tests at on the two heavy-duty engine oil candidates and the baseline; the tests will be run under two cycles: Federal Test Procedure (FTP) and the Supplemental Emissions Test (SET), approxiamtely 2% fuel efficiency improvement is expected
- Run axle efficiency tests on axle oil candidates and the baseline; approximately 0.5% fuel efficiency improvement is expected
- Perform SAE #2 tests on transmission fluids to pick a candidate which has equivalent or higher maximum torque but lower delta torque than the baseline
- Perform J1321 test on above oils on Class 6 trucks at the Transportation Research Center; overall, a fuel efficiency improvement of 2% is expected

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FY 2015 Accomplishments

Engine Oil:

- Candidate 1: NREL Cummins ISL 8.9 L fuel efficiency testing results: FTP cycle 1% improvement, SET cycle 1.7% improvement
- Candidate 2: NREL Cummins ISL 8.9 L fuel efficiency testing results: FTP cycle 1.5% improvement, SET cycle 1.1% improvement
- Note: The target was not met. Reformulation and retesting are underway. A six-month, no-cost extension of the second budget period was applied for and granted.

Axle Oil:

- Axle rig efficiency test showed that both candidates performed better than the baseline in all test conditions

where temperature reduction was up to 16.4°C, and efficiency improvement was between 0.63% to 1.36% under demanding conditions.

- Note: A milestone was booked on March 27, 2015.

Transmission Fluid:

- Conducted nine SAE #2 friction tests. One formula is able to meet the performance target: equivalent or higher Max Torque but lower Delta Torque than the baseline.
- Note: A milestone was logged on June 25, 2015.

Future Directions

- Reformulate the two engine oil candidates per the learning from NREL Cummins ISL 8.9 L engine fuel efficiency verification tests
- Rerun the NREL Cummins ISL 8.9 L fuel efficiency engine test on the above two engine oil candidates; improvement of around 2% against the baseline is anticipated
- Conduct SAE J 1321 test on the three types of lubricants at Transportation Research Center Inc. in East Liberty, Ohio; greater than 2% total fuel efficiency is expected ■

Introduction

Improving automotive fuel efficiency can help preserve energy resources and reduce greenhouse gas emissions [1]. 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 efficient 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 an antiwear agent, antioxidant, viscosity index improver, corrosion inhibitor, and friction modifier. With advanced technology of lubricant additives, low viscosity lubricants have been developed by adding special antiwear agents and friction modifiers. Special base oils and viscosity modifiers can also contribute to the performance of low viscosity lubricants with higher fuel efficiency.

Approach

Valvoline has ability in formulating automotive lubricants from individual ingredients and conducting bench top, engine dynamometer, 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 [2-4]. 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, dynamometer, track, and fleet testing to reach the target.

Results

Engine Oil

Engine fuel efficiency tests were performed by the Renewable Fuels and Lubricants testing laboratory at NREL in Golden, Colorado. Testing was performed on a 2012 Cummins ISL 8.9 L diesel engine. The engine is rated at 345 hp at 1,900 rpm and is certified to 0.33 g/bhp-hr for NO_x emissions. The engine was connected to a low inertia electric alternating current dynamometer with a rated loading capability of 600 hp. The fuel consumption of the engine was measured during testing using a high precision scale that sends instantaneous weight signals to the data acquisition system. Two engine test cycles were used for testing of the lubricant, the FTP transient drive cycle, and the 2010 SET ramped modal cycle. The FTP is 1,200 s long and consists of multiple sections of transient operation of engine load and speed [5]. The SET cycle consists of 14 steady-state points and was modified to 4,151 s long [6]. The results along with oil properties were summarized in Table 1.

Oil 1 and Oil 2 had a different performance trend under the two testing modes. In the FTP cycle, Oil 2 has a higher fuel efficency than Oil 1 while in SET cycles Oil 1 performed better. Since the FTP cycle is more relative

Table 1. Property of Engine Oil Candidates and Their Baseline

	Oil 1	Oil 2	Baseline
	5W-30	5W-20	PB15W-40
KV @ 100°C (cSt)	10.2	8.4	15.42
Viscosity Index	172	167	134
BOV	4.39	5.03	6.09
HTHS @150°C (cP)	3.01	2.85	4.16
FE modeling (%)	2.05	2.05	baseline
Rheology	better		
Tribology		better	
FTP cycle FE (%)	1	1.5	baseline
SET cycle FE (%)	1.7	1.1	baseline

KV – kinematic viscosity; BOV – base oil viscosity ; FE – fuel efficiency; HTHS – high temperature high shear

to urban driving and the SET cycle freeway driving, the results still make sense in corresponding to different characters of the two oils. In the SET cycle, every steady-state point has various data. Figure 1 indicates that the most improvement is seen at higher engine speeds and lighter engine loads.

Axle Oil

The Axle Rig Efficiency Test was a modified nine-hour test based on SAE J1266 method with three speeds and three torques. The temperature was not controlled but monitored so that it can be used to differentiate the performance based on friction, churning, and heat transfer. The axle oil candidates performed better than the baseline in all test conditions where the most temperature reduction was up to 16.37°C. The efficiency improvement was between 0.63% to 1.36% under demanding conditions. Figure 2 shows the details.

Transmission Fluid

SAE #2 tests conducted were based on the Allison TES 295 Graphite Clutch Friction Test. Steel and graphite clutch plates were used. In a typical cycle when the engagement speed reached 3,600 rpm, a constant pressure of around 827 kPa was applied and the torque was then monitored. The results can be reviewed in Figure 3. ATF 2 meets the performance target; it has equivalent maiximum

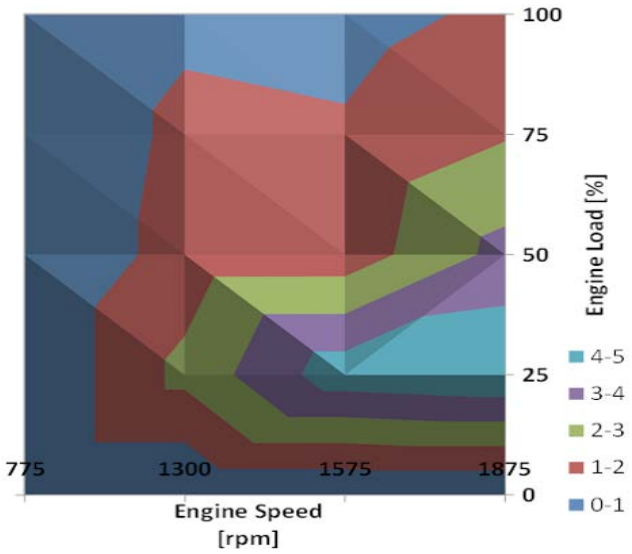


Figure 1. Map plot of fuel economy improvement from Engine Oil 1 over the Reference Oil. Contours are percent improvement in fuel efficency.

torque but lower delta torque. The tests on Ref and ATF 2 were also repeated once and the results show good repeatability. ATF 2-LV is the lower viscosity version and doesn't meet the performance target. ATF 2 is chosen as the transmission fluid candidate for the J1321 test.

Conclusions

- Two engine oil candidates showed opposite trends in two testing cycles for the fuel efficiency engine dynamometer test. While the results fell short to achieve 2% improvement in fuel efficency, it sheds light on the fact that friction control is also important for low viscosity heavy-duty engine oils. The learning will be utilized in the reformulation.
- Two axle oil candidates have efficiency improvement of more than 0.5%.
- The transmission fluid candidate has equivalent maximum torque but lower delta torque than the reference.

References

1. EPA website: http://www3.epa.gov/climatechange/ghgemissions/gases/co2.html
2. V.L. Kersey, A.E. Sworsiki, T.L. Caudill, J.F. Frederick, T. Bidwell, F.E. Lockwood, "Method of Testing and Proving Fuel Efficiency Improvements," U.S. Patent Application 20120109579 A1.

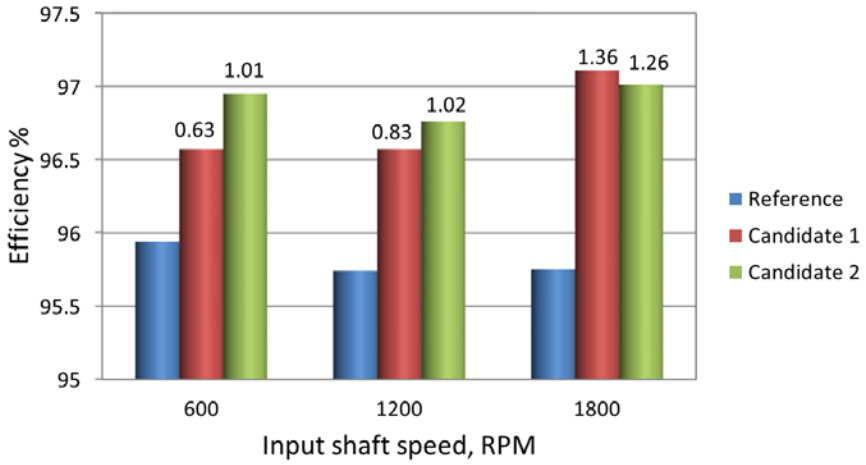
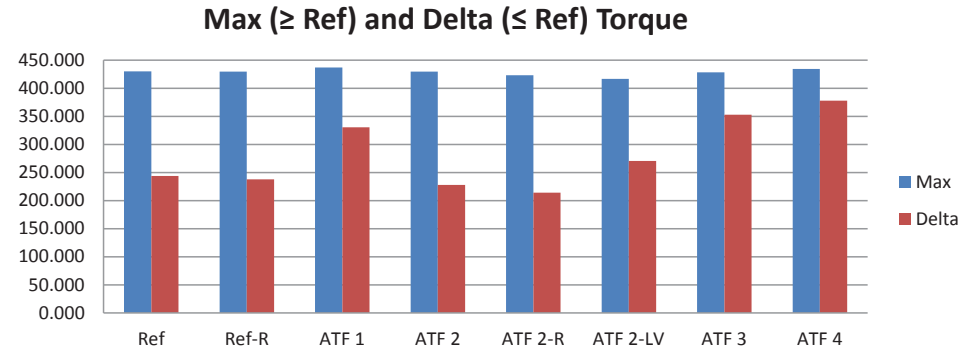


Figure 2. Axle efficiency plot for gear oils



Max – maximum; ATF – automatic transmission fluid; Ref – reference

Figure 3. SAE #2 test results for transmission fluids (delta torque is magnified by 10).

3. 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.

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

5. FTP cycle: http://www.dieselnet.com/standards/cycles/ftp_trans.php

6. SET cycle: http://www.dieselnet.com/standards/cycles/set.php

Publication/Presentation

1. A.S. Kolekar, A.V. Olver, A.E. Sworski, F.E. Lockwood, G. Wu, X. Cheng, 'Gear and Engine Oils with reduced Surface Tension," publication number 20150148272.

2. G. Wu, A. Kolekar, K.Duho, D. Dotson, F.E. Lockwood, "Improve Fuel Economy Through Formulation Design and Modeling," Presentation, U.S. Department of Energy 2015 Annual Merit Review Meeting, June 11, 2015, Washington, D.C.

III.5 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 Funding Opportunity Announcement 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) 2015 Objectives

- Attain one new synthetic base oil feedstock by applying simple chemistries in maximum two steps
- 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
- Evaluate various polymeric architectures conformational changes as they pertain to viscosity changes, via computations/modeling.
- Continue dynamic light scattering (DLS) studies and conduct small-angle neutron scattering (SANS) experiments of synthesized viscosity modifier analogs

FY 2015 Accomplishments

- Initial base oil synthetic strategies led to several candidates
- Synthesized several novel base oils that have built-in polarity for friction control and have an added advantage of being miscible with existing mineral oil base stocks for a drop-in oil package formulation
- Determined pour point of the above base oils and four materials met industrial requirements
- Completed simulations of a series of four model compounds that have structural similarities to the compounds subjected to DLS studies
- Established collaboration with a researcher at the National Institute of Standards and Technology's Small-Angle Neutron Scattering facility and co-authored a proposal for beam time at the National Institute of Standards and Technology user facility
- Completed SANS experiments which are in agreement with DLS measurements
- Demonstrated temperature-induced conformational and size changes using simulations, DLS and SANS

Future Directions

- Evaluate at least three synthesized base oils for viscosity, wear, and friction against unadditized commercial base oils
- Continue to investigate the potential of tribopolymers as a renewable in situ additive and expand beyond caprolactams and caprolactones
- We will conduct these investigations at the Southwest Research Institute (SwRI) who are set up with the proper rig for testing tribopolymers. Despite our efforts in optimizing testing conditions, we were unable to

obtain meaningful data of known materials with our unidirectional tribometer

- Evaluate friction and wear of generated materials at SwRI
- Demonstrate the value of modeling in predicting viscosity changes with temperature of viscosity modifiers
- Investigate shear thinning simulations to build a predictive model spanning various architectures and topologies ■

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, and SANS (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 very few published fundamental studies that provide insight into the changes in molecular conformation that are thought to occur as viscosity modifiers reduce the decrease in viscosity with increasing temperature, though there are many reasonable claims based on empirical data. One of the shortcomings of the existing studies is that they do not encompass a wide variety of structures and architectures. Though it is a challenging task to glimpse into temperature-induced changes at the molecular level, DLS, SANS, 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 originally proposed was the modification of vegetable oils or other easily accessible synthetic oils to obtain synthetic polyesters. Synthetic polyesters, with few exceptions, have been oversubscribed in the published literature, so instead, this year our research focused on the synthesis of amide or amine-containing analogs. Nitrogen containing additives have enhanced interactions with surfaces, and could offer an added advantage to polyesters.

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 proposed 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 into 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). Data that clearly suggests a change in size indicative of thermoresponsive behavior is considered a positive result.

Results

Task 1

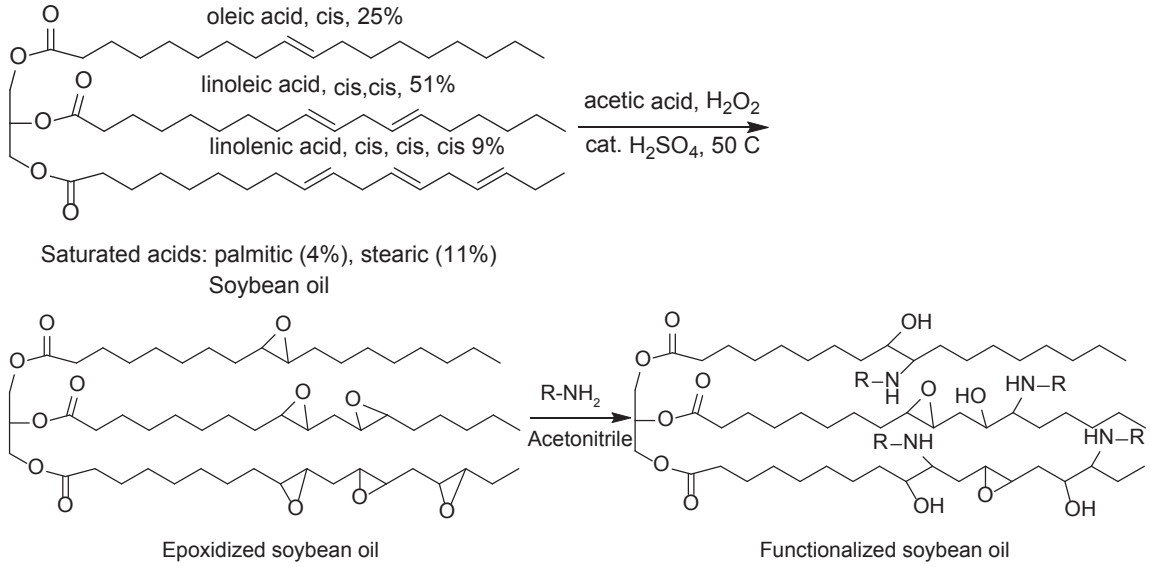
In order for any synthetic oil to be implemented, it has to have to have a cheap, commercially available source of starting materials to be able to stay competitive with any other petroleum-based oils. One of the strategies explored was the use soybean oil, which was epoxidized and subsequently reacted with an amine or an alcohol. Although the transformation was successful, the material had a high viscosity, where it had the appearance of grease rather than fluidic oil. This transformation is illustrated in Scheme 1. Partial epoxidation followed by reaction with amine or alcohol resulted in an oil at room temperature, as opposed to a thick resin-like product. These types of products tend to be a mixture of compounds, much like the starting material.

In addition, novel low molecular weight compounds suitable for base stock applications were prepared in one step from available starting materials. Compounds which appeared fluidic at room temperature were evaluated via kinematic viscosity (KV) measurements (KV40, KV100), their viscosity indexes (VIs) were calculated, and their pour points determined. This data is captured in Table 1.

Several analogs look very promising as base oils themselves based on the VI and pour point values, and they would deserve further tribological investigations. Other analogs, such as 61828-30A, might provide friction reduction benefits as an additive.

Task 2

In order to test our set up and testing protocol, we followed Kadjas' work as a benchmark who reported caprolactam as an effective additive that underwent tribopolymerization at room temperature in hexadecane [1]. The tribometer is a pin-on-disk, hard steel ball on steel disk (16-20 Rockwell), the pin is fixed, while the disk undergoes a circular motion (unidirectional tribometer). The wear trenches (concentric circles) were then evaluated using a profilometer to determine the profile of the groove, and finally, PeakFit data software was used to generate area values of the wear trenches. The load applied was varied from low to high (5 N, 10 N, 15 N, 20 N, and 30 N) to probe for an effect. After numerous trials which included heating the oil to speed up the chemical reaction, increasing the load, and increasing the length of time, the experiment was run up to 8 h hardening the disk from an 18 to a 63 on the Rockwell hardness scale, literature results could still not be reproduced. Our conclusion was that the unidirectional tribometer is not the proper testing platform for tribopolymerization additives, due to the excessive loss of heat from one revolution to the next, which prevents heat-induced polymerization at surfaces. However, an interesting observation was that caprolactam, as well as other additives produced an increased wear regardless of the oil matrix used, which is contrary to literature reports. The path forward is to conduct wear testing at SwRI who have the proper reciprocal rig for testing wear, as a purchased service.



Scheme 1. Illustrative chemical transformation of soybean oil to attain a multi-functional base oil

Table 1. Viscosity properties and pour point of selected analogs (all compounds were tested as neat materials with the exception of * which was tested as a 10% solution in Exxon Mobil Group I oil

Sample ID	KV40 (cP)	KV100 (cP)	VI	Pour Point (°C)
61828-31*	30.75	5.166	113	9
61828-20R	39.3	8.7	215	-48
61828-39R	21.9	5.4	214	-12
61828-28	155.6	19.2	139	-30
61828-29	60.7	7.7	94	-15
61828-30A	110.6	12	100	-3
61828-44	tbd	tbd	tbd	-12

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 been sparsely conducted before [4], and it is not without challenges. Factors such as polymer aggregation, fluctuations in diffusion and density with temperature, and deviations from the spherical model particularly for polymers, make the data interpretation challenging at the very least. The test subjects for this task were two commercial polymers and two PNNL polymers developed under a different Vehicle Technologies Office project which are shown to be effective as viscosity modifiers, with VIs increasing in the order: Bench 2 > 61888-15 > Bench 1 ≥ 61753-159. If the polymers were thermoresponsive in the same way, meaning the mechanism which leads to viscosity increase was based on similar molecular deformations with temperature, we would expect the size expansions from low to high temperature to follow the same trend as VI. DLS data depicted in Table 2 and Figure 1 (a, b, c, d) suggests a more complex mechanism than a simple uncoiling of the polymer with temperature.

The data was quite surprising, in that only one analog, shows an increase in size with temperature, contrary to general belief of how viscosity modifiers work. Bench 2 although has the highest VI of all analogs has a very modest increase in size up to 95°C, while the other benchmark, Bench 1 has a severe decrease in size with temperature. This study suggests that viscosity is affected by mechanisms other than increasing molecular size with temperature.

In the first stage of the project, fully atomistic simulations are being used to model representative VI improvers, including linear, branched, star, and hyperbranched structures. The simulations are run at a range of temperatures to investigate how increased temperature affects the structure of the molecules. Structural changes are characterized in terms of features that may increase viscosity, including aspect ratio and radius of gyration.

Initial model compounds were polyisobutylene polymers of different architectures with 100 repeating units and 9-octylheptadecane as the base oil mimic. Distribution histograms to visualize the frequency of specific conformations were plotted. A Gaussian function was then fitted to the histogram to quantify the distribution. Figure 2 shows the distribution of the radius of gyration for linear, comb, hyperbranched and starbranched polyisobutylene structures. The size of the linear structure increases with temperature, implying that the polymer is uncoiling with temperature. This observation is supported by an increase in the mean and maximum value of the radius of gyration. The radius of gyration does increase with temperature for the linear analog, and less pronounced for the comb analog, however remains about the same in the case of hyperbranched structure and in fact decreases for the star structure. This predictive behavior suggests different thermoresponsive mechanisms.

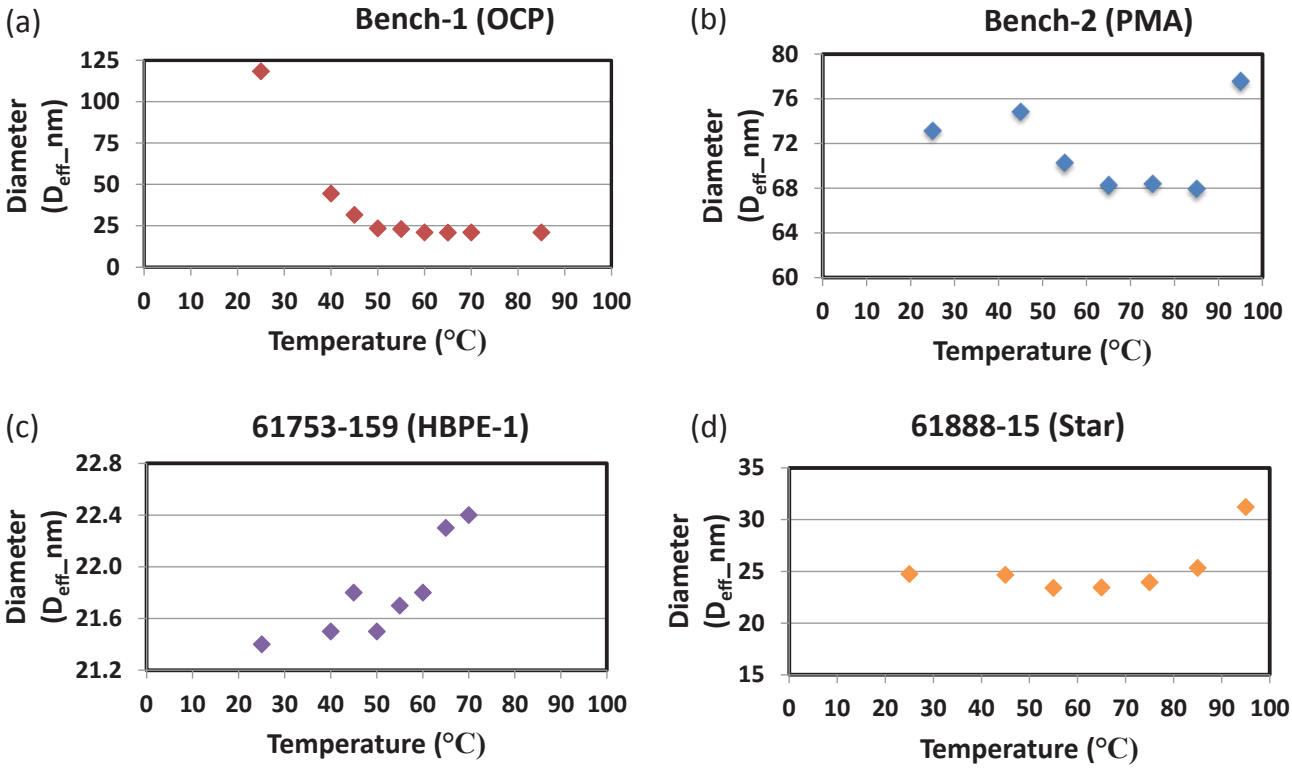


Figure 1. (1a, 1b, 1c, 1d). DLS plots of various polymeric analogs at a concentration of 0.5% in hexadecane at low and high temperatures.

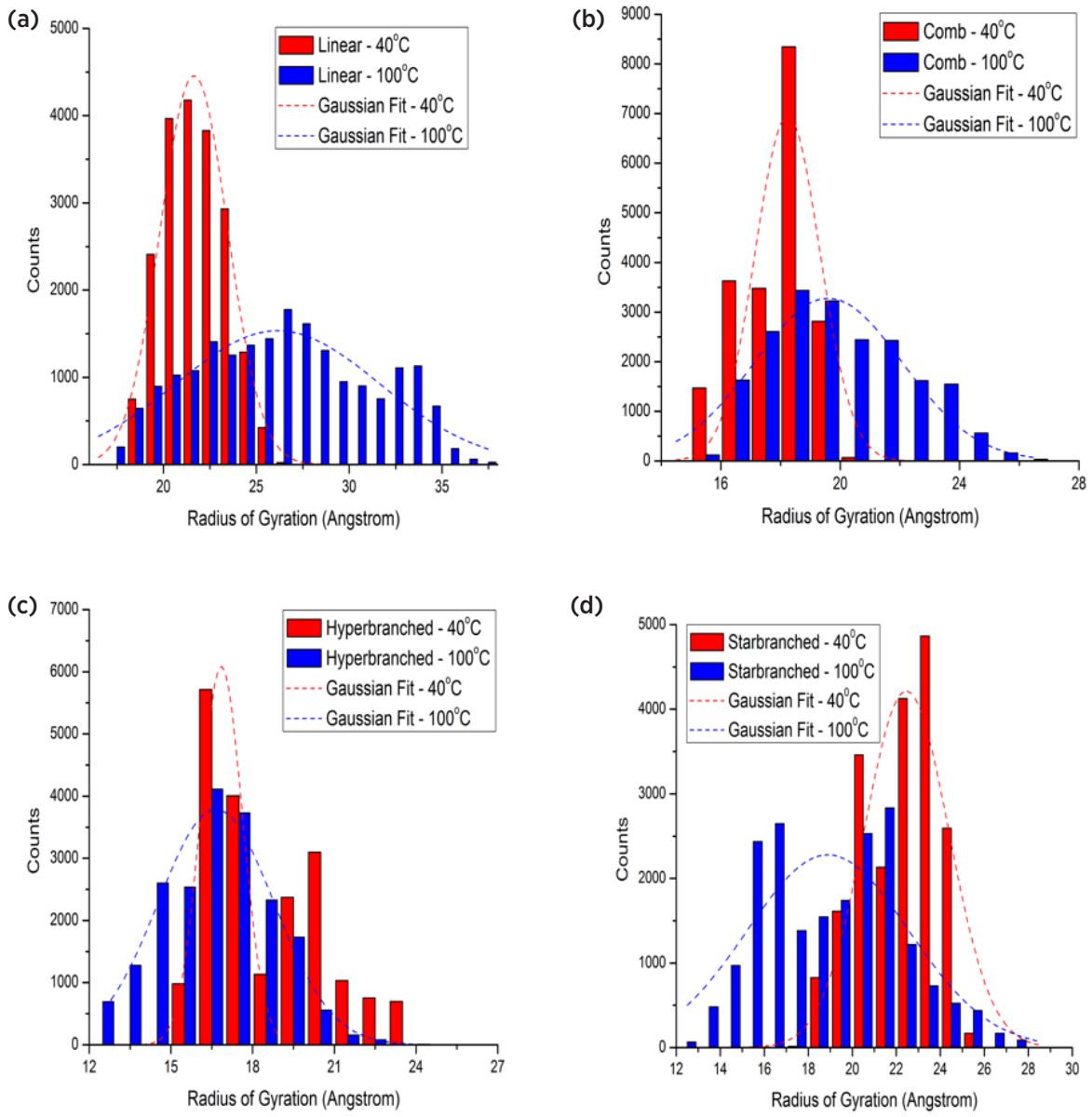
Table 2. Diameter of selected polymers detected by DLS at room and high temperature (T). A negative percent change indicates a decrease in size with temperature.

Sample	Diameter low T (nm)	Diameter high T (nm)	% change
Bench 1 (OCP)	118.37 (25°C)	21.0 (85°C) 21.0 (70°C)	-82.2% -82.2%
Bench 2 (PMA)	73.2 (25°C)	77.6 (95°C) 68.4 (70°C)	6.3% -6.5%
61753-159 (HBPE)	21.4 (25°C)	22.4 (70°C)	4.6%
61888-15 (Star)	24.7 (25°C)	31.2 (95°C) 23.9 (70°C)	26.2% 3.27%

OCP – olefin co-polymer; PMA – polymethacrylate; HBPE – hyperbranched polyethelene

Conclusions

- A series of polyamides and polyesters were synthesized in an effort to achieve a multi-functional base oil. The KV, VI, and pour point of six of the compounds which were fluidic at room temperature, were evaluated.
- From a molecular design perspective, several empirical guidelines have taken shape: unsaturation, lack of symmetry, and moderately long alkyl chains are important features in designing a fluid base oil.
- Despite our efforts in optimizing our testing protocols of tribopolymerization additives, we were unsuccessful



OCP – olefin co-polymer; PMA – polymethacrylate; HBPE – hyperbranched polyethelene

Figure 2 (a, b, c, d). Distributions of the radius of gyration of the linear, comb, hyperbranched and star poly-isobutylene polymer structure with 100 repeating units, at 40°C and 100°C.

at achieving wear reduction using the unidirectional pin-on-disk capability at PNNL. These experiments will be conducted either at Oak Ridge National Laboratory or at SwRI.

- DLS measurements suggest a promising tool at detecting molecular size changes with temperature for lubricant applications, and subsequently provide an insight in the viscosity increase mechanism.
- Simulations 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. Ideally, the data from SANS, molecular dynamics simulations and DLS will give an insight in the mechanism by which viscosity modifiers really work.

References

1. New condensation-type monomer combinations, as ashless antiwear compositions; C. Kajdas; M.J. Furey; R. Kempinski; J. Valentino; Wear, 2001, v 249, 235–239.

2. A critical assessment of tribopolymers as antiwear mechanism; M.J. Furey; C. Kajdas; G.J. Molina, World Tribology Conference 2005; WTC2005-63308 (p. 621–622).

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;

4. Michael J. Covitch1, Kieran J. Trickett; How Polymers Behave as Viscosity Index Improvers in Lubricating Oils; Advances in Chemical Engineering and Science, 2015, 5, 134–151.

FY 2015 Publications/Presentations

1. Ramasamy, Uma Shantini; Cosimbescu, Lelia; Martini, Ashlie. Temperature-Dependent Conformations of Model Viscosity Index Improvers. Tribology & Lubrication Technology 71.5 (May 2015): 30–31.

2. Uma Shantini Ramasamy, Lelia Cosimbescu, Ashlie Martini; Characterization of Model Viscosity Index (VI) Improvers; Tribology Frontiers Conference, Denver 2015.

III.6 A Novel Lubricant Formulation Scheme for 2% Fuel Efficiency Improvement

Overall Objectives

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

Fiscal Year (FY) 2015 Objectives

- Synthesis and characterization of sulfur (S)-and-phosphorus (P)-free heterocyclic friction modifiers (FMs) for boundary lubrication (BL)
- Design and synthesize a novel di-block copolymer-based viscosity modifier (VM) for low shear at high speeds
- Surface functionalization of solid-state lubricating nanoparticles (NPs) for friction reduction and wear prevention
- Conduct tribological studies and confirm at least 10% BL friction reduction together with significant wear reduction
- Molecular dynamics (MD) modeling of the FMs and VMs, and surface physical/chemical investigations

FY 2015 Accomplishments

- Synthesized and characterized three major families of heterocyclic FMs
- Designed and conducted the synthesis of the first generation of di-block copolymers as VMs
- Identified excellent heterocyclic FMs that were capable of reducing BL friction more than selected commercial products by means of laboratory scale tests
- Functionalized the NPs, demonstrated their good solubility in base oils and plausible friction reduction together with improvements in wear and scuffing resistances of mating surfaces
- Conducted ultra-thin film measurements and verified reinforcement of lubricant film in the BL regime
- Investigated FMs' surface adsorption ability and VMs' shear-thinning transition via MD simulations
- Trained postdoctoral researchers, graduate, and undergraduate students; three graduated, one with a Masters of Science and two (partially involved) with doctorates

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Future Directions

- Finalize synthesis of the di-block copolymer VMs
- Comprehend the tribo-rheological properties of the newly synthesized VM
- Further improve the design of the heterocyclic FMs and functionalized NPs
- Develop a strategy for formulating additive packages (including FMs, VMs, and NPs)
- Conduct an in-depth mechanism investigation for VMs and a physical/chemical surface study for FMs

- Perform further laboratory tests at more severe conditions for oil aeration effects and oxidation stability
- Initiate Ricardo engine simulation and industrial verification tests ■

Introduction

Achieving more than 2% fuel efficiency improvement of light- and medium-duty vehicles requires a 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 FMs are needed as a component to achieve this boundary lubrication goal. The frictional loss due to high viscous shear at high speeds cannot be simply tackled by using an oil of low viscosity because this will raise the friction at low speeds. We need a chemically and mechanically stable VM 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 rates via molecular deformation, not scission. More friction reduction mechanisms should also be included, such as using NPs; hexagonal boron nitride (h-BN or α-BN) and boron oxide (B_2O_3) are two of well-known solid lubricants, which can be excellent material choices for the NPs.

Approach

The fuel efficiency goal has to be accomplished by reducing friction in the entire operation regime. The S- and-P-free heterocyclic FMs and the shear-thinning VMs should be able to significantly lower frictions in boundary (low speed) and hydrodynamic (high speed) lubrication regimes, respectively, and the NPs-based additives will facilitate reducing extra friction and wear. The research tasks include synthesizing "designer" additives, characterizing their properties at conditions comparable to those in real-world applications, modeling the frictional and viscosity behaviors for design optimization, and testing their friction reduction capability. The present research is being conducted collaboratively by a Northwestern University–Argonne National Laboratory team, supported by collaborative industries. All additives were synthesized or prepared at Northwestern University's chemistry laboratory and tested at the tribology laboratories at Northwestern University and Argonne National Laboratory.

Results

Synthesis of thermally stable and S- and P-free heterocyclic FMs

Different hexahydrotriazines were synthesized as the first family of S –and P-free heterocyclic FMs. However, their thermal stability was tested to be low, and two methods were introduced to improve the thermo-stability, spacer enlargement and aromatization, leading to formation of N-heterocycle derivatives and triazine compounds, respectively. Representative results of a N-heterocycle derivative (Additive 1) are shown in Figure 1. Thermogravimetric analysis reveals that Additive 1 decomposes at a fairly high temperature (>300ºC, Figure 1a). Additional continuous heating tests at 90ºC were conducted with periodic nuclear magnetic resonance

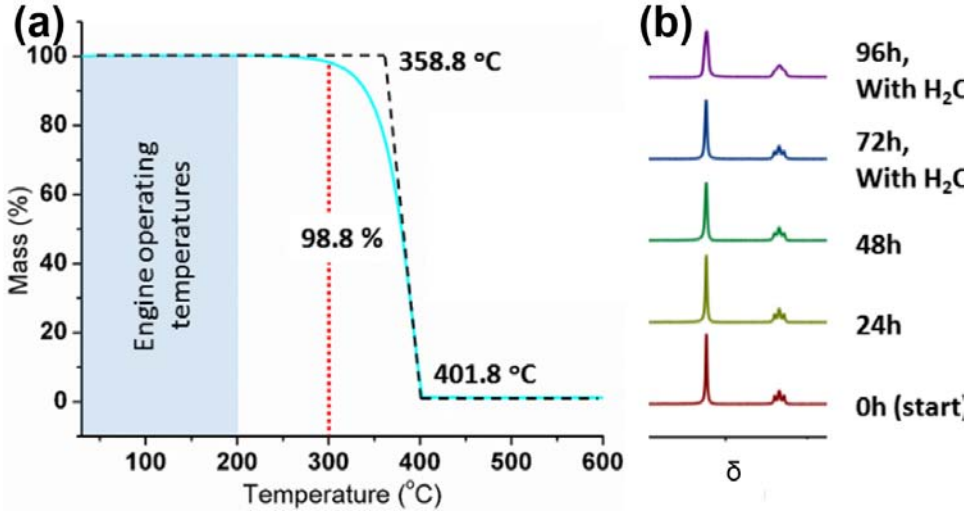

Figure 1. (a) Thermogravimetric analysis curves of Additive 1. (b) ^{1}H NMR spectra (only showing heterocyclic protons) for Additive 1 during extended heating at 90°C.

(NMR) spectroscopy analysis. Additive 1 shows no structural changes throughout (Figure 1b), even after addition of water to mimic the atmospheric moisture. The other N-heterocycle derivatives and triazine compounds demonstrate exceptional thermal stability as well.

Improvement of BL performances: friction reduction and wear elimination.

Pin-on-disk tests were performed from 25ºC to 200ºC to study the high temperature BL properties of the new heterocyclic FMs. Selected results are shown in Figure 2. Additive 1 outperforms selected commercial FMs and reduces friction up to ~49% over a commercially available fully formulated motor oil (5W30 oil) at 100ºC (Figure 2a), close to the average temperature of a passenger car engine at 90ºC. Additive 1 continues to reduce friction in the BL regime as temperature increases and about 70% friction reduction has been obtained over Group III oil at 200ºC.

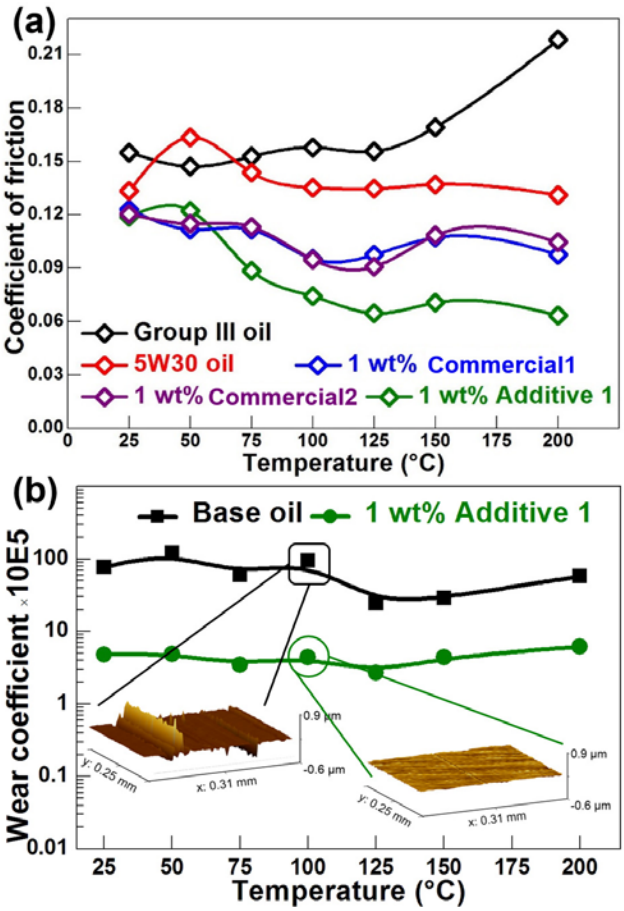

Figure 2. (a) Pin-on-disk BL testing results of Group III oils with and without FMs. (b) Wear coefficients of surfaces lubricated with Group III oil with and without FMs; example wear scars from the pin-on-disk tests at 100°C are inserted.

Analyses of the wear scars from the pin-on-disk tests were conducted with a white light interferometry. Additive 1, which reduces the most friction, is able to decrease the wear coefficient by an order of magnitude (Figure 2b). Specific wear scar examples from the tests at 100°C are also given in the figure as insets. The track groove volumes are smaller, and the volume of the deformed material built up by the wear track decreases, both indicating less wear.

In addition to the boundary friction results shown in Figure 2, more high temperature tests were conducted for the other cyclen derivatives and triazine compounds synthesized. These FMs and their hybrids with different side groups have also demonstrated notably improved BL performances.

BL improvement mechanism: enhanced surface adsorption and BL film reinforcement.

X-ray reflectivity and X-ray photoelectron spectroscopy (XPS) measurements evidence an enhanced surface adsorption process by the heterocyclic FMs. X-ray reflectivity first quantifies a 6.51 nm thick adsorbed layer of Additive 1 on a silicon substrate. XPS spectra in Figure 3a demonstrate that the nitrogen atoms from Additive 1 molecules are adsorbed by the steel surface, while the base oil molecules fail to show a visible adsorption process. Nanoscratch tests and contact angle measurements (results are not shown here) proved similar results for the improved surface adsorption. Moreover, mass centers of the heterocyclic molecules are proven to approach the substrate during an MD simulation process. The interaction energy was found to increase with the approaching. The higher interaction energy of FMs suggests that the increased number of surface active nitrogen atoms enhances the adsorption strength. Simulations at variable temperatures show that Additive 1 maintains consistently higher interaction energy over the entire temperature range modeled (Figure 3b).

Lubricant film in BL regime is evaluated under pure rolling operations using an elastohydrodynamic lubrication measurement system. Figure 3c reveals that Additive 1 enables the base oil to form a thicker BL film at a high temperature (125°C). On the contrary, commercial FMs do not reinforce the BL film. The blue and purple dotted lines in Figure 3c show that their thicknesses drop rapidly with speed and decrease to almost zero at very low speeds, indicating no effective BL film promotion by the commercial FMs.

In the BL regime, FMs play two principal roles, reinforcement of the BL film and enhancement of surface adsorption. Commercial FMs could improve surface

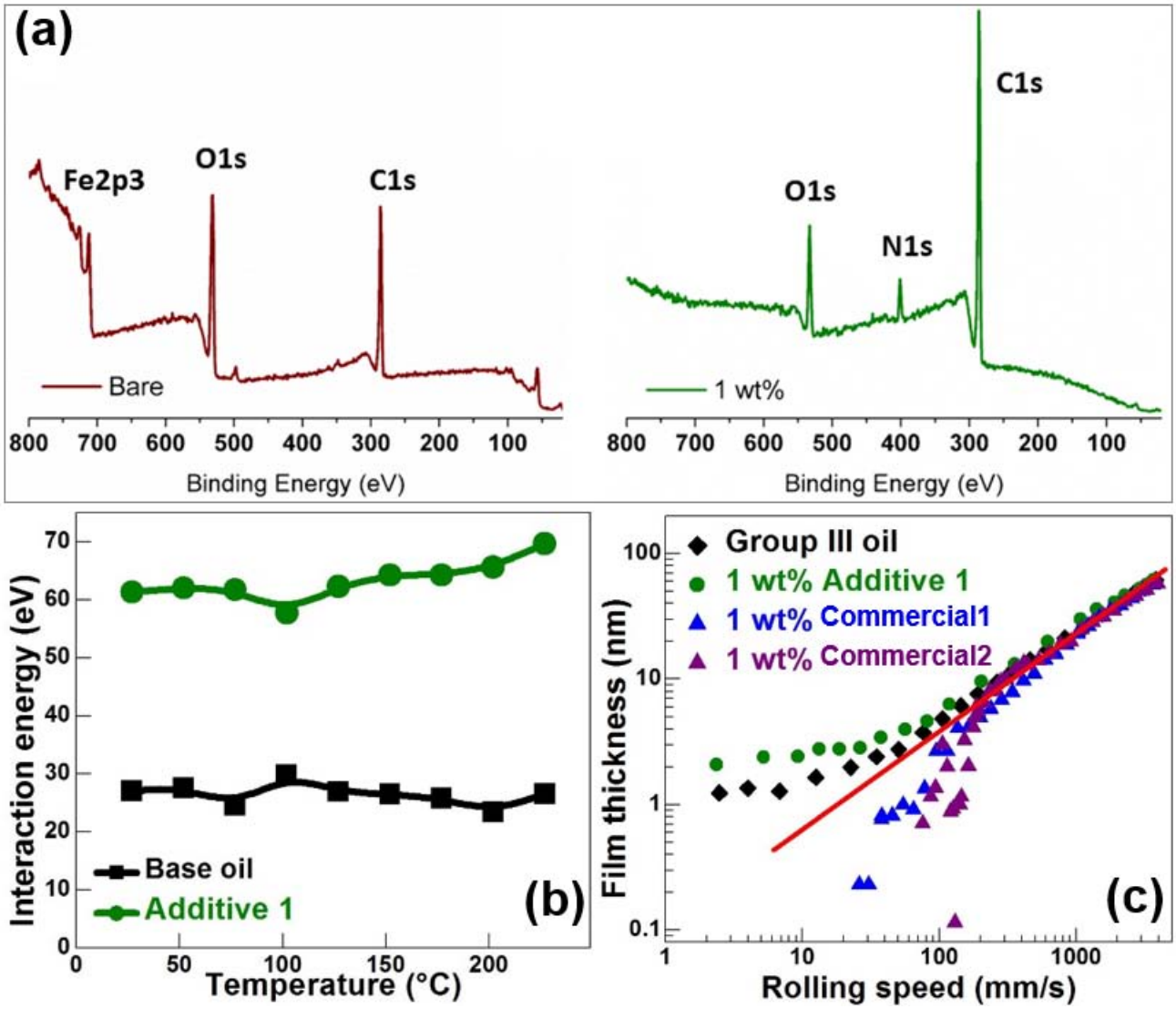

Figure 3. (a) XPS analysis of a steel substrate dip-coated in pure PAO 4 (left) and a 1 wt% loading of Additive 1 in PAO 4 (right). (b) Interaction energy at elevated temperatures obtained from MD simulations. (c) Elastohydrodynamic lubrication tests for different additive mixtures in Group III oil at 125°C.

adsorption only. The novel heterocyclic FMs developed in the current research is capable of enhancing both principal roles, which are believed to account for the significant friction and wear reductions at high temperatures.

Design and synthesis of novel viscosity modifier: a new di-block copolymer.

The challenge in the synthesis of the di-block copolymer stems from the need to combine different polymer blocks produced from different types of polymerization. Our approach to this problem involves synthesizing the branched polymer block first, and then growing the coiled polymer block off of it (Figure 4a). To do this, we developed a method to functionalize the terminus of the branched block with something that can be used as a radical initiator for atom transfer radical polymerization. A primary bromide was prepared and used as the initiator for atom transfer radical polymerization to synthesize the di-block copolymer. Figure 4b shows the carbon NMR spectra of the di-block copolymer together with each type of individual polymers comprising it. Peaks corresponding to branched and coiled polymers are evident in the spectra for the copolymer. The gel permeation chromatography trace for the di-block copolymer was mono-modal, indicating only one type of polymer in the product. We have synthesized a di-block copolymer containing both the branched and coiled blocks.

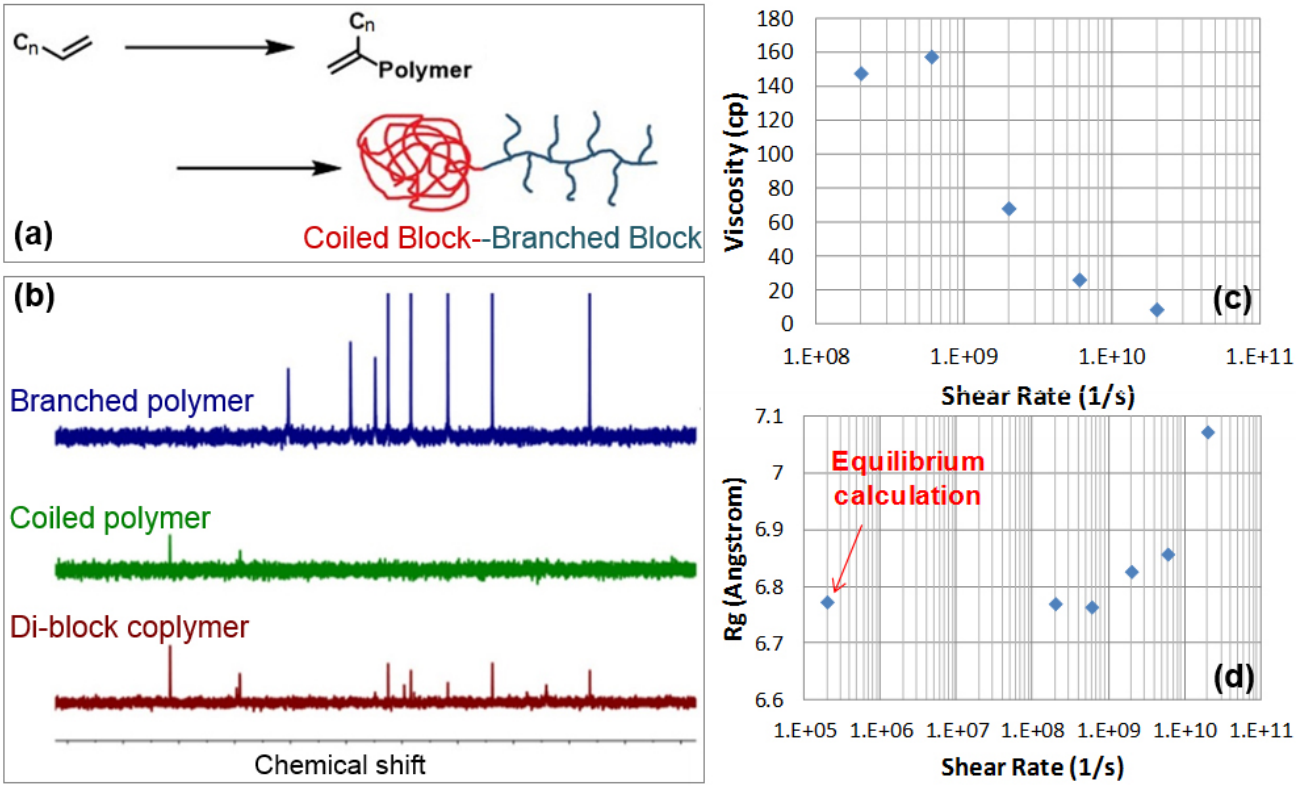

Figure 4. (a) A brief synthetic route for the di-block copolymer. (b) Carbon NMR spectra for the branched polymer, coiled polymer and the di-block copolymer. Calculations of viscosity (c) and R_g (d) under shear for a di-block copolymer molecule using the non-equilibrium MD simulation.

The di-block copolymer was also simulated with a non-equilibrium MD modeling. Figures 4c and 4d show a viscosity decrease correlated with an increase in the molecular radius of gyration (R_g). As R_g increases with shear rate as a result of the temporary shear thinning, a critical shear rate is identified for the occurrence of a shear thinning process for the di-block copolymer molecule, although the copolymer currently modeled has a relatively small molecular weight, Mn = 1,079 Da. Corresponding density (ρ) was calculated to be 0.98 g/cm^3. This value is believed to be reasonable due to comparison of it with other relevant molecules.

Organosilane functionalized NPs as anti-friction and anti-wear additives.

In order to improve B_2O_3 NPs' solubility in base oil, they are functionalized with alkyl chains via a synthetic pathway outlined in Figure 5a. The shrinking of the O-H peak shown by Fourier transform infrared spectroscopies in Figure 5b indicates that the hydroxyl groups on the B_2O_3 surface are bound by silanes to form the Si-O bonds. Organosilanes modify the B_2O_3 surface and lead to formation of capping agent (CA) functionalized NPs (CNP). The friction results measured during the ball-on-flat reciprocating tests are shown in Figure 5c. The one with 0.5 wt% CNPs and 1 wt% FM (Additive 1) performs the best, compared with the results for the other tested oils. Additional four-ball wear tests (Figure 5d) show the most significantly reduced wear by the same combination of CNPs and FM. The combination of these two additives in a single oil shows a synergistic effect for further low friction and wear.

Conclusions

- Novel S- and P-free heterocyclic FMs were synthesized for boundary lubrication improvement, and aromatization and spacers were introduced to improve their thermo-stability.
- The thermally stable FMs help reduce BL friction drastically (maximally by ~70%) in a wide temperature range, which has surpassed the benefits from up-to-date commercial FMs and a fully formulated engine oil.
- The heterocyclic molecules integrate the significant friction reduction capability with a substantially high wear resistance in a single FM.

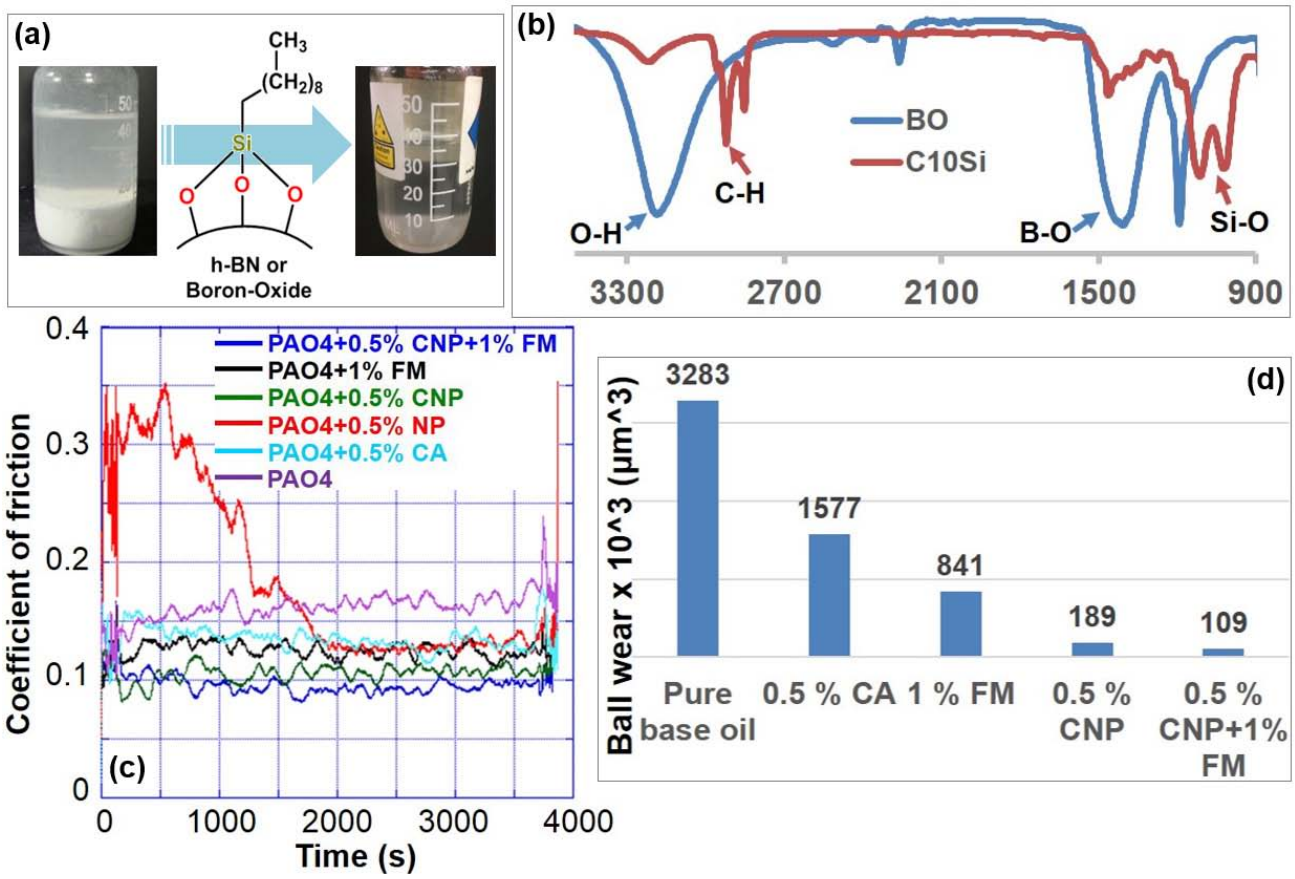

Figure 5. (a) Organosilane functionalization of NPs for suspension in PAO 4 oil. (b) Fourier transform infrared spectroscopies of pristine NPs and CNP with C10Si. Results of reciprocating ball-on-flat friction tests (c) and four-ball wear tests (d) for different NPs-based additives.

- MD simulations and a series of experimental characterizations demonstrate that the enhanced surface adsorption and BL film reinforcement are two major causes for the more superior BL performances of the new FMs.
- Synthesis of the novel di-block copolymer succeeds and the first-generation product is evidenced by NMR and gel permeation chromatography analyses.
- Prediction of the molecular structure–viscosity relationship has been accomplished by means of MD simulations. Temporary shear thinning of the di-block copolymer-based VM is indicated by the change of R_g.
- Different types of organosilanes are used to successfully functionalize the nanoparticle additives.
- Reciprocating ball-on-disk and four-ball wear tests show that the mixture of surface functionalized NPs with a heterocyclic FM improves the overall tribological performance of such partially formulated oil even further.

References

1. Holmberg, K., Andersson, P., and Erdemir, A., "Global energy consumption due to friction in passenger cars," *Tribology International,* **47**, pp. 221–234 (2012).
2. Ehret, P., Dowson, D., and Taylor, C., "On lubricant transport conditions in elastohydrodynamic conjuctions," *Proceedings of the Royal Society of London. Series A: Mathematical, Physical and Engineering Sciences,* **454**, pp. 763–787 (1998).
3. Bronshteyn, L. A. and Kreiner, J. H., "Energy efficiency of industrial oils," *Tribology Transactions,* **42**, pp. 771–776 (1999).
4. Zolper, T., Li, Z., Chen, C., Jungk, M., Marks, T., Chung, Y.-W., and Wang, Q., "Lubrication Properties of Polyalphaolefin and Polysiloxane Lubricants: Molecular Structure–Tribology Relationships," *Tribology Letters,* **48**, pp. 355–365 (2012).
5. Akbarzadeh, S. and Khonsari, M., "Performance of spur gears considering surface roughness and shear thinning lubricant," *Journal of Tribology,* **130**, (2008).

6. Meyer, J. C., Chuvilin, A., Algara-Siller, G., Biskupek, J., and Kaiser, U., "Selective sputtering and atomic resolution imaging of atomically thin boron nitride membranes," *Nano letters,* **9**, pp. 2683–2689 (2009).

7. Berry, G. and T. Fox, *The viscosity of polymers and their concentrated solutions.* Fortschritte der Hochpolymeren-Forschung, 1968: p. 261–357.

FY 2015 Publications/Presentations

1. Liu, P., He, Y., Ren, N., Lockwood, F., Marks, T., Wang, Q., "Viscosity of lubricant mixtures based on molecular dynamics simulations," 70th STLE Annual Meeting, Dallas, TX, May 2015.

2. He, X., Densanker, M., Lu, J., Delferro, M., Chung, Y.W., Marks, T. J., Wang, Q., "Novel boundary-lubrication additives for fuel efficiency improvement," 70th STLE Annual Meeting, Dallas, TX, May 2015.

3. Lu, J., Liu, P., Densanker, M., He, X., Delferro, M., Chung, Y. W., Marks, T. J., Wang, Q., "MD simulation of heterocyclic FMs for boundary lubrication," 2nd STLE Frontier Conference, Denver, CO, October 2015.

4. P. Liu, H. Yu, N. Ren, F.E. Lockwood, Q.J. Wang, Pressure–viscosity coefficient of hydrocarbon base oil through molecular dynamics simulations, Tribol. Lett., 60 (2015) 34.

5. M. Desanker, X. He, J. Lu, P. Liu, Z. Liu, M. Delferro, T.J. Marks, Y.-W. Chung, Q.J. Wang, Alkylsubstutitued-cyclen as a novel sulfur-and-phosphorus-free heterocyclic friction modifier for boundary lubrication, in preparation, 2016.

6. M. Desanker, X. He, B. Johnson, J. Lu, Y. He, M. Delferro, T.J. Marks, Y.-W. Chung, Q.J. Wang, Synthesis of heterocyclic molecules as additives in boundary lubrication regime, in preparation, 2016.

7. J. Lu, X. He, M. Desanker, P. Liu, M. Delferro, T.J. Marks, Y.-W. Chung, Q.J. Wang, Entanglement and self-alignment of heterocyclic friction modifier molecules during surface adsorption: from MD simulation to experiment, in preparation, 2016.

8. M. Desanker, A. Greco, A. Erdemir, M. Delferro, T.J. Marks, Solubilization of boron oxide nanoparticles with organo-silane additives for wear reduction in motor vehicles, in preparation, 2016.

Special Recognitions & Awards/ Patents Issued

1. Wang, Q., International Award, STLE, 2015.

2. Marks, T. J., Luigi Sacconi Medal, Italian Chemical Society, 2015.

3. Marks, T.J., Derek Birchall Award, Royal Society of Chemistry, 2015

4. Delferro, M., Chung, Y.W., Marks, T.J., Wang, Q., Densanker, M., He, X., "Cyclen friction modifiers for boundary lubrication." US Patent (provisional) No. 62/179,564, May 2015.

5. A patent based on triazine compounds is under preparation.

III.7 Development of Modified PAG (Polyalkylene Glycol) High VI High Fuel Efficient Lubricant for LDV Applications

Overall Objectives

- Formulate new modified PAG-based (polyalkylene glycol) 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

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Subcontractors:

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- Dow Chemical Company, Midland, MI

Fiscal Year (FY) 2015 Objectives

- Complete analysis of surface films formed on disks from Mini Traction Machine (MTM) and bucket tappets from motored valvetrain wear tests
- Complete cam and tappet wear measurements using a motored single cam direct acting mechanical bucket valvetrain rig
- Complete evaluation of sludge and vanish protection capability of one PAG oil in ASTM Sequence VG test
- Complete chassis roll dynamometer tests for fuel economy and emission evaluations
- Prepare and submit a final report on the project

Accomplishments

- Friction evaluations were conducted on one PAG base oil and several formulated PAG oils and compared against GF-5 base oil and GF-5 SAE 5W-20 oil at 40°C and 100°C under sliding/rolling conditions using MTM rig
- Completed motored valvetrain wear assessments on two PAG oils (14-2 and 15-1) when fresh and PAG oil 15-1 following 10,000-mile aging on a vehicle; GF-5 SAE 5W-20 oil was also evaluated under the same aging conditions as PAG oil 15-1
- Analyzed bucket tappet surfaces from motored valvetrain tests and MTM disks using Auger spectroscope and time-of-flight secondary ion mass spectroscope to understand the mechanism of friction reduction
- Completed ASTM Sequence VG test on PAG oil 17-1 to understand its sludge and varnish protection capability
- Completed chassis roll dynamometer fuel economy and emission evaluations on PAG oil 15-1 and GF-5 SAE 5W-20 oil following 500-, 5,000-, and 10,000-mile aging on a vehicle with an I-4 engine
- Submitted final report

Future Directions

- Project completed on September 30, 2015 ■

Introduction

The intent of the project "Development of Modified PAG (Polyalkylene Glycol) High VI High Fuel Efficient Lubricant for LDV Applications" is to develop lubricant formulations capable of at least 10% engine friction reduction compared to current GF-5 engine oil technology at the same viscosity grade level most commonly used in the North American market.

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

Approach

The project team consists of technical personnel from Ford Motor Company (Ford), Dow Chemical Company (Dow) and Argonne National Laboratory (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 Evaluations

Figure 1 presents coefficient of friction results obtained from MTM rig for PAG base oil (x97011.00) and various formulated PAG oils and compared against GF-5 SAE 5W-20 oil. In this test a 19-mm diameter polished AISI 52100 steel ball rotated against a rotating polished AISI 52100 steel disk. The tests were conducted at 30 N load (initial contact stress of 0.76 GPa), 150% sliding/rolling ratio, and 100°C oil temperature. The mean sliding speed ranged from 0.002 m/s to 2.8 m/s. A few tests were conducted at 50 N load also for surface analysis. All PAG oils, both base oil without additives and formulated, showed substantially lower coefficients of friction than GF-5 SAE 5W-20 oil. Similar results were observed at 40°C also.

Figure 2 shows time-of-flight secondary ion mass spectra obtained from wear surfaces of PAG base oil XZ97011.00. The PAG base oil spectrum is primarily that of a poly-ether. The structures of two of the fragments that have been identified are shown on the spectrum. Results obtained from another PAG base oil (made from propylene oxide) showed a pattern of peaks that are 58 amu apart which is the mass of a single propylene oxide monomer. In contrast, the spectrum of the 5W-20 base oil (not shown) is significantly different and is dominated by the classic hydrocarbon fragmentation pattern as expected from a mineral-oil-based lubricant. The presence of PAG molecules on the contact surface is believed to be the mechanism for friction reduction.

Motored Valvetrain Wear Evaluations

The wear of the cam lobe and tappet was measured simultaneously using the radiotracer method where the cam lobe and the tappet were activated to Co^{57} and Co^{56}, respectively. A single cam lobe mounted on a shaft rotated against a tappet at 500 rpm, 1,000 rpm, 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

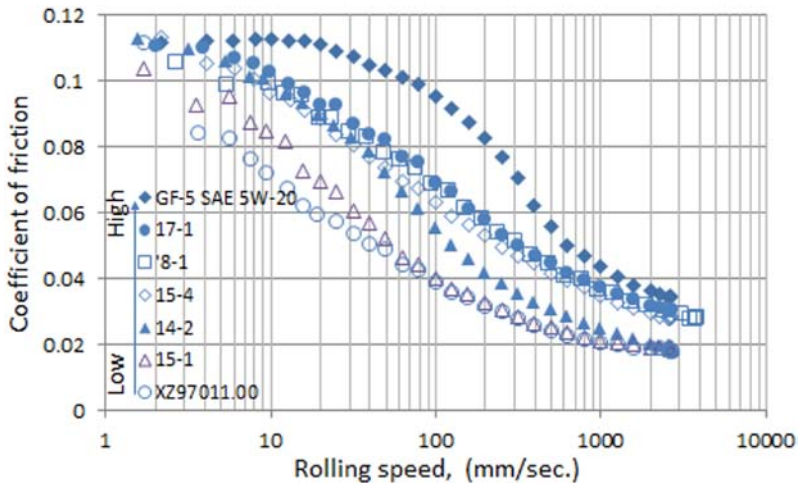

Figure 1. Coefficient of friction at 100°C.

the test. Figure 3 shows cam lobe and tappet wear as a function of test duration for various PAG oil formulations in comparison to GF-5 SAE 5W-20 oil. The repeatability of wear results for GF-5 SAE 5W-20 oil is excellent. There are two wear trends that could be observed. The first indicates the wear for both components increased faster for the first 30–40 hours than in the later portion of the test, which could be due to the breaking-in of surfaces. This is true particularly for the GF-5 5W-20 oil and PAG oils 17-1 and 15-1. The second shows wear increased abruptly during the first few hours and then stayed almost constant for the remaining test duration. This is true for PAG oils 15-4, 14-2, 27-2, and 9-1. "Used 5W-20 oil" and "Used 15-1" PAG oil showed similar wear as the respective fresh oil. "Used" refer to 10,000-mile vehicle aged oil. PAG oils 9-1 and 17-1 primarily differ in antiwear chemistry and friction modifier, and the effectiveness on antiwear chemistry in reducing wear in PAG oil 17-1 is quite evident. The abrupt increase in cam lobe and tappet wear is believed due to the delay in antiwear film formation. PAG oil 15-1 showed the best wear performance and even better than GF-5 SAE 5W-20 oil, while PAG oil 17-1 and 8-1 showed wear performance similar to GF-5 SAE 5W-20 oil.

ASTM Sequence VG Test

ASTM Sequence VG was run to evaluate the capability of PAG oils in controlling deposit formation. This is a 216-hour test designed to simulate moderate temperature taxi and delivery services. The test is run in three stages, with Stage 1 running at 1,200 rpm for 120 min at 68°C oil temperature, Stage 2 running at 2,900 rpm at 100°C oil temperature for 75 min and Stage 3 running at 700 rpm at 45°C oil temperature for 45 min. At the end of test, sludge deposits are rated (on rocker arm covers, cam baffles, timing chain cover, oil pan baffle, oil pan, and valve decks). Also, varnish deposits are rated on piston skirts (thrust) and cam baffles.

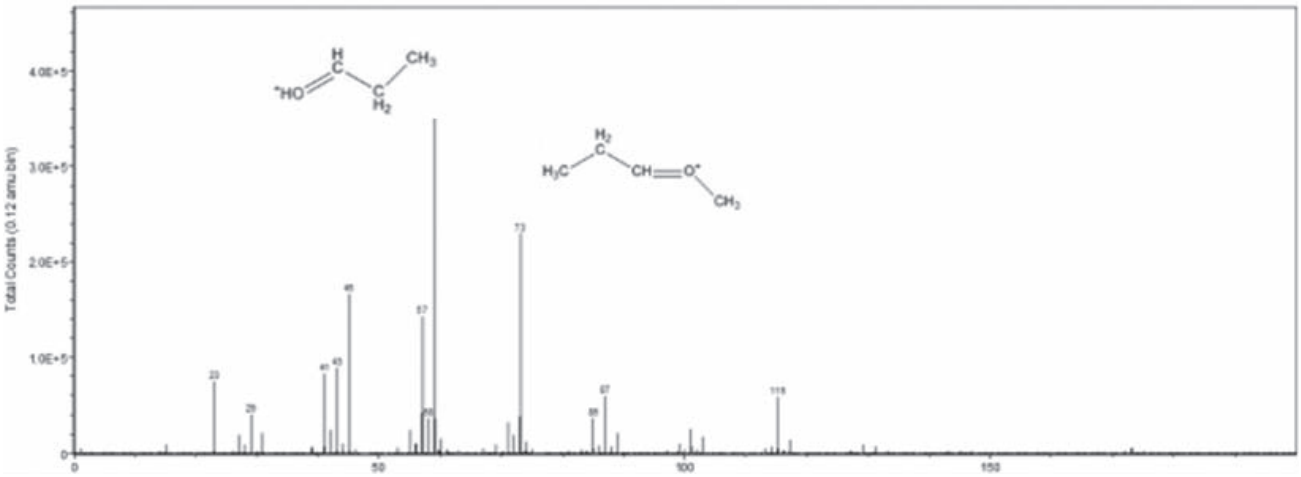

Figure 2. Time-of-flight secondary ion mass spectra data on disk following MTM test with PAG base oil XZ97011.00.

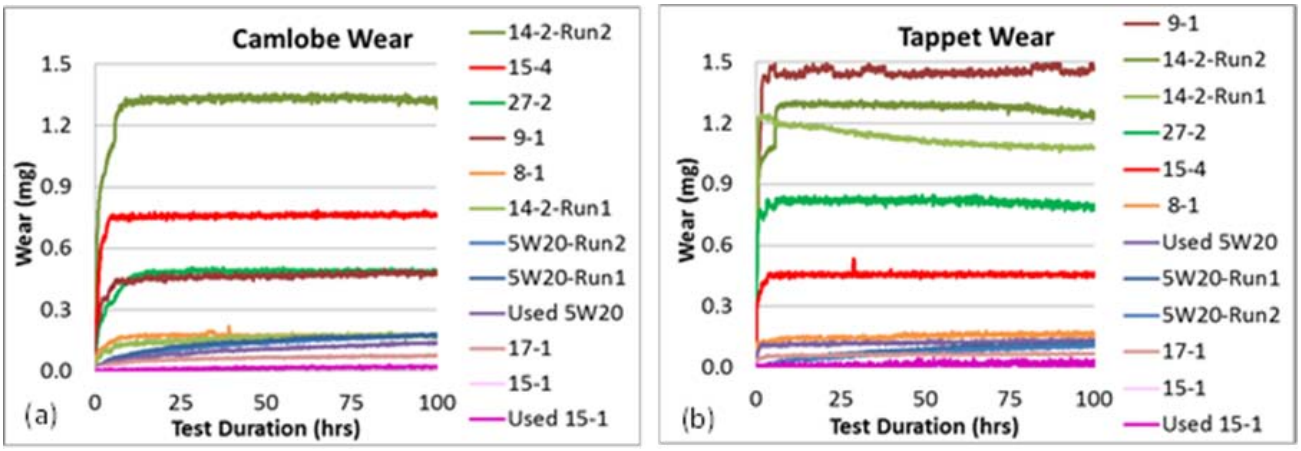

Figure 3. Wear trend observed at 95°C for (a) cam lobe and (b) tappet.

The Sequence VG test was run with PAG oil 17-1. The results are shown in Table 1. PAG oil 17-1 performed well on sludge but not varnish formation.

Table 1. Sequence VG results

Parameters	17-1	GF-5 limits
Average Engine Sludge, Merits	8.76	8.0 minimum
Rocker Cover Sludge, Merits	9.32	8.3 minimum
Average Engine Varnish, Merits	8.19	8.9 minimum
Average Piston Skirt Varnish, Merits	5.17	7.5 minimum
Oil Screen Sludge, % Area	4.96	15 maximum
Number of Hot Stuck Rings	0	None

Chassis Roll Dynamometer Tests

Chassis roll dynamometer fuel economy tests were conducted to evaluate fuel economy improvement capability using Federal Test Procedure metro/highway cycles. The tests were run on a Ford Focus vehicle equipped with an I-4 engine, the same engine used for motored engine tests. The vehicle had 25,000 miles to ensure the engine was broken-in. The existing engine oil was drained, flushed with the candidate oil, and then a charge of fresh oil was added. Two oils were run, GF-5 SAE 5W-20 and PAG oil 15-1. Three to five repeat fuel economy tests were run following 500-, 5,000-, and 10,000-mile accumulation to get an understanding of fuel economy improvement with oil aging. Mileage accumulation was done using R919-Bl-1 cycles. To avoid influence of tire wear and emission system aging on fuel economy a separate set of tires and emission system were used. Oil was added as necessary to maintain recommended fill level. A 50 ml oil sample was collected after each mile accumulation for oil analysis.

Figure 4 shows fuel economy data for the two oils after 500 miles in city cycles within 95% confidence interval. PAG oil 15-1 showed 1% fuel economy benefit in city cycles although no benefits could be observed in highway cycles and the combined (city and highway) cycles over GF-5 SAE 5W-20 oil. The benefit was observed mostly in Phase I possibly due to lower viscosity of PAG oil 15-1 compared to GF-5 SAE 5W-20 oil. No fuel

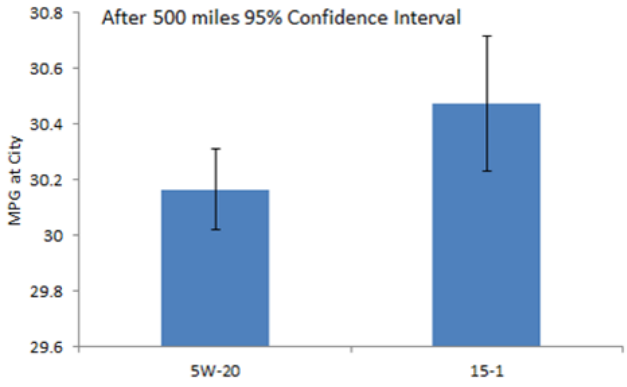

Figure 4. Chassis roll dynamometer fuel economy result on city cycles after 500-mile aging of oil.

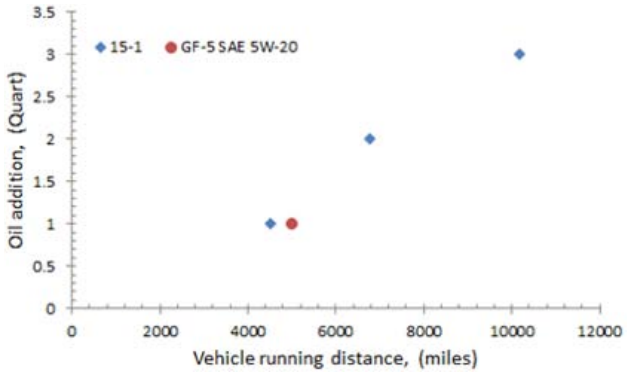

Figure 5. Oil consumption results during mile accumulation.

economy benefit could be observed after 5,000-mile and 10,000-mile accumulation. The emission levels for non-methane hydrocarbon, carbon monoxide, and nitrogen oxide were essentially similar for GF-5 SAE 5W-20 and PAG oil 15-1 and were within the Environmental Protection Agency limits, as expected. The analysis of PAG oil 15-1 samples at 5,000 miles and 10,000 miles indicates that the antioxidant package was substantially consumed by 5,000 miles as evidenced by the total acid number exceeding 1 mg KOH/g. Depletion of the antioxidant package would result in increased oil consumption as shown in Figure 5. Analysis of the used oil specifically for the antioxidants revealed that ~90% were consumed by 5,000 miles and effectively all were consumed by 10,000 miles.

Conclusions

- Under sliding/rolling conditions, PAG base oil and formulated oils showed significantly lower coefficient of friction than GF-5 SAE 5W-20 oil. The presence of PAG molecules on the contact surface is believed to be the mechanism for lower friction.

- Some of the PAG oils showed high initial wear which possibly could be due to delay in antiwear film formation. PAG oil 15-1 showed the best wear performance and even better than GF-5 SAE 5W-20 oil.
- PAG oil 17-1 performed well on sludge but not varnish formation according to ASTM Sequence VG test.
- When PAG oil (15-1) was slightly aged (500 miles), chassis roll dynamometer tests showed fuel economy benefit of about 1% over GF-5 SAE 5W-20 oil in Environmental Protection Agency city cycles and no improvement in highway cycles. The benefit disappeared with oil aging which is believed to be due to severe deterioration of the oil resulting from rapid consumption of the additive package.

III.8 Development of PAG (Polyalkylene Glycol)-Based Lubricant for Light- and Medium-Duty Axle Applications

Objectives

- Formulate new polyalkylene glycol (PAG)-based gear oils that will improve the fuel efficiency of light- and medium-duty applications by 2% over SAE 75W-140 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 antiwear 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

2015 Objectives

- Narrow PAG candidate formulation field to best options
- Measure PAG lubricant friction and wear properties and compare performance to SAE 75W-140 baseline
- Optimize additive package performance
- Demonstrate acceptable wear ratings in system level industry standard lubricant testing

2015 Accomplishments

- System level industry standard load carrying capacity testing (ASTM D6121) was completed for the most promising Generation I (Gen I) PAG formulation and it failed the test due to gear rippling.
- Dow Chemical Company (Dow) and FMC completed hardware and tribofilm analysis and hypothesized prospective deficiencies of the Gen I PAG and additive package.
- Dow and ANL completed various laboratory bench rig tests in oil soluble PAG (OSP) and Generation II (Gen II) PAG formulations.

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Subcontractors:

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- Dow Chemical Company, Midland, MI

- Two OSP formulations and two Gen II formulations were selected as the best candidates, showing wear and friction results comparable to SAE 75W-140.
- The two OSP formulations completed system level load carrying capacity testing and passed the requirements for post-test gear condition.
- Dow completed hardware, tribofilm, and lubricant analysis and confirmed that the adjustments made in OSP formulations and additive package addressed the speculated deficiencies of the Gen I formulation.

Future Directions

- Complete laboratory bench rig tests on OSP and Gen II formulations with hardware test pieces made from FMC hypoid gear steels
- Complete additional industry standard axle system tests, including load carrying capacity, moisture corrosion, oxidative stability, and shock loading testing with OSP and Gen II candidates

- Complete FMC proprietary axle system (efficiency and gear wear) testing with OSP and Gen II candidates
- Define the best candidate formulation
- Complete chassis roll dynamometer tests for fuel economy and emission evaluations when oil is fresh and aged ■

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 75W-140 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 (FMC), Chintan Ved (FMC), Mr. John Cuthbert (Dow), 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

Gen I PAG System Level Testing

Figure 1 shows the rippling gear condition failure that occurred when the Gen I PAG, known as formulation 17-2 [58-1], was tested in the industry standard axle load carrying capacity test (ASTM D6121). This rippling received a rating of 5, where a minimum score of 8 is required to pass. Testing was completed at Intertek and the hypoid gear set was returned to Dow and FMC for analysis.

Gen I PAG Tribofilm Analysis

The failure of the load carrying capacity axle system level test motivated the investigation of the tribofilm and surface chemistry of used test parts. The four-ball wear test was rerun with aged (used) Gen I PAG 17-2 [58-1], and it was discovered that the used lube resulted in a larger wear scar. Tribofilm analysis indicated that the larger wear scar could be attributed to the lack of phosphorous and increased sulfur presence on the surface of the parts that were tested with the used 17-2 [58-1] lube. Figure 2 illustrates how the depleted phosphorous and increased sulfur directly correlates to the increased wear observed in the four-ball wear test.

OSP and Gen II PAG Formulations

These findings lead the direction for the modification of Gen I formulation and additive package into OSP and Gen II options. The OSP options are unique in that their base chemistry permits them to be mineral oil soluble, while the Gen II options are a closer derivative to the base chemistry of the Gen I 17-2 [58-1] formulation. Laboratory rig testing, including four-ball wear testing, Falex EP (extreme pressure) testing, copper corrosion

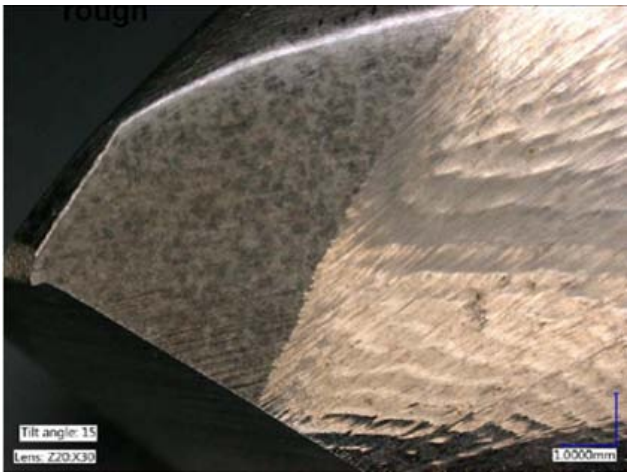

Figure 1. Rippling of wear surface on gear tested with Gen I PAG 17-2

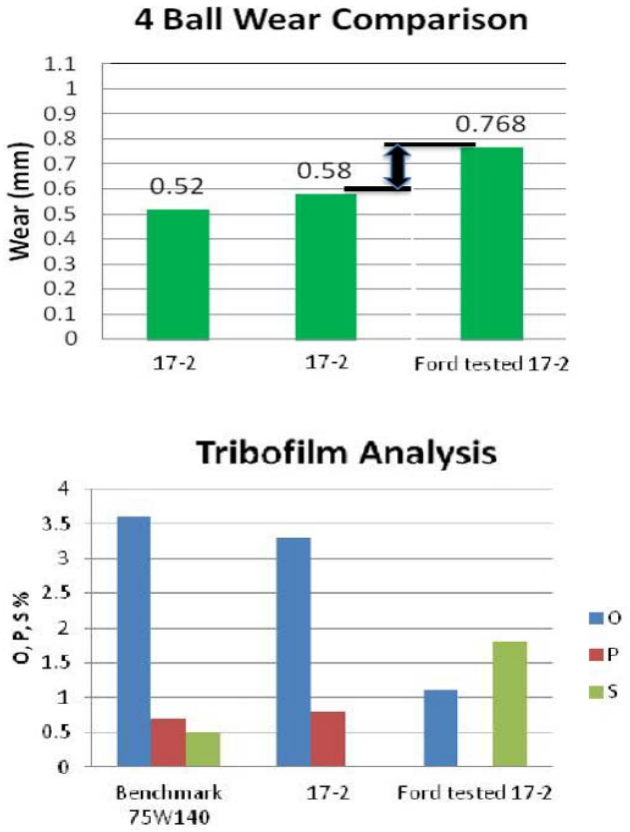

Figure 2. Pre- and post-test wear scar comparison and tribofilm analysis of Gen I PAG 17-2

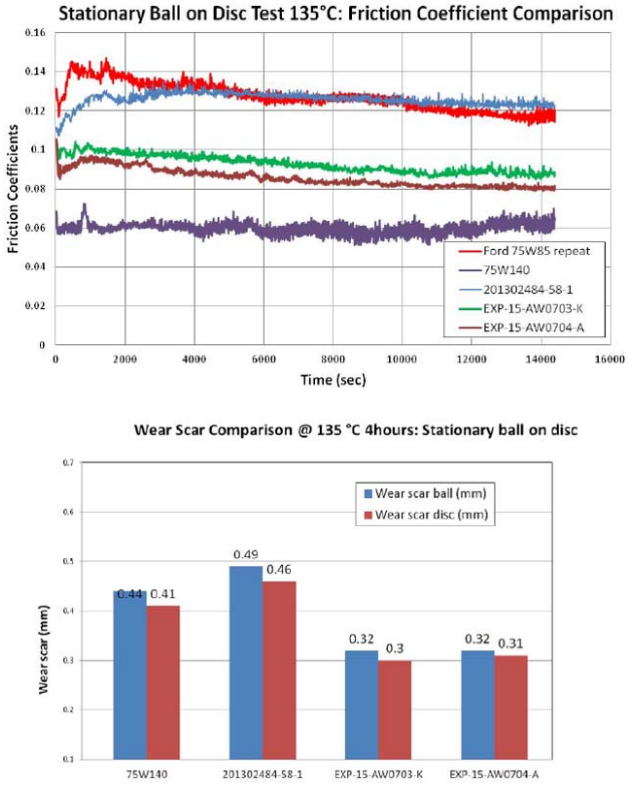

Figure 3. Friction and wear scar data for OSP PAG formulations AW0703-K and AW0704-A compared to baseline gear oils and Gen I 17-2 [58-1]

testing, and oxidation testing of various OSP and Gen II options served to screen and optimize the lube candidates to yield AW0703-K and AW0704-A as the two best OSP candidates, and AW0705-D and AW0705-F as the two best Gen II candidates. OSP candidate AW0703-K and Gen II candidate AW0705-D have similar additive packages, while AW0704-A and AW0705-F also have corresponding additive packages.

Figure 3 depicts friction coefficient and wear scar data for the OSP candidate formulations collected from a stationary ball-on-disc test executed at 135°C for 4 hours. Data is also provided for SAE 75W-140, and Gen I 17-2 [58-1] lubricants for comparison. Although SAE 75W-140 is shown to have the lowest friction coefficient for this test, both OSP formulations show the smallest wear scar width.

Similarly, Figure 4 depicts friction coefficient and wear scar data for the Gen II candidate formulations collected from a stationary ball-on-disc test executed at 135°C for 4 hours. Data again is provided for SAE 75W-140, and Gen I 17-2 [58-1] lubricants for comparison. Although SAE 75W-140 is shown to have the lowest friction coefficient for this test, both Gen II formulations show the smallest wear scar width.

OSP System Level Testing

After the OSP and Gen II formulations showed comparative results in laboratory rig testing to SAE 75W-140, they were tested in the standard load carrying capacity test (ASTM D6121) at Intertek. The results for the two formulations are presented in Table 1. The rippling failure seen with the Gen I PAG did not occur and both formulations met all minimum requirements for the gear conditions.

The post-test pinion gear surface from the axle tested with formulation AW0704-A was analyzed and compared to the pinion surface of the Gen I 17-2 [58-1] tested gears via scanning electron microscopy with energy dispersive X-ray spectroscopy by Dow. The contact area of the gear surface that completed testing with AW0704-A was found to have more phosphorous and less sulfur than the contact area of the gear surface that completed testing with 17-2 [58-1], as seen in Table 2. This affirmed the modifications made to increase the presence of

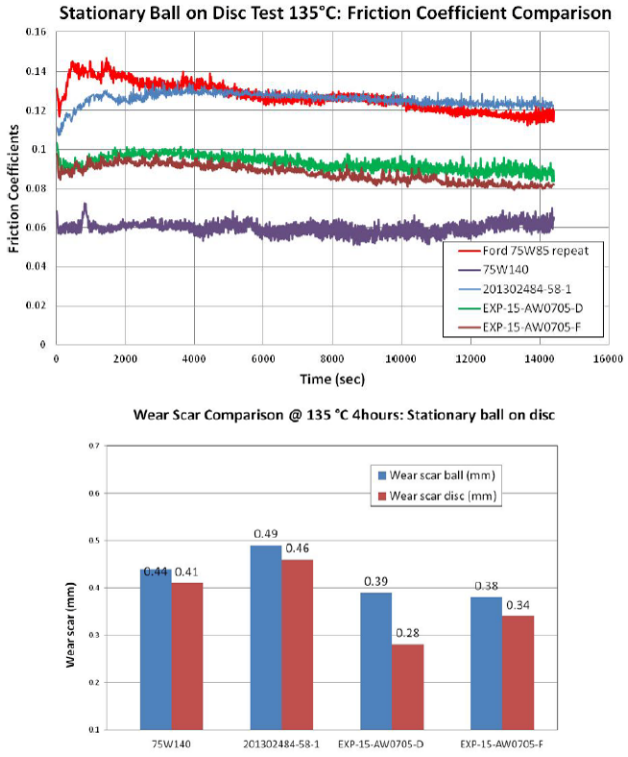

Figure 4. Friction and wear scar data for Gen II PAG formulations AW0705-D and AW0705-F compared to baseline and Gen I 17-2 [58-1]

Table 1. Gear condition ratings for the two OSP formulations for the load carry capacity axle test

OSP PAG AW0703-K			
Gear Condition	Ring Rating	Pinion Rating	Minimum Required
Wear	7	8	5
Ripping	10	8	8
Ridging	8	8	8
Piling/Spaling	9.9	9.9	9.3
Scoring	10	10	10

OSP PAG AW0704-A			
Gear Condition	Ring Rating	Pinion Rating	Minimum Required
Wear	7	7	5
Ripping	10	9	8
Ridging	9	9	8
Piling/Spaling	9.9	9.9	9.3
Scoring	10	10	10

Table 2. Scanning electron microscopy with energy dispersive X-ray spectroscopy surface analysis of phosphorous and sulfur on worn gear surface of Gen I and OSP formulations

PAG Type	Formulation Code	Weight %		
		Oxygen	Phosphorous	Sulphur
Gen I	17-2	14.6	0.5	1.2
OSP	AW0704-A	11.5	3.2	<0.3

phosphorous and reduce the presence of sulfur at the surface from the Gen I PAG to the OSP.

Conclusions

- Gen I PAG formulation failed to meet the rippling requirement in the ASTM D6121 load carrying capacity test. Insight gained from tribo-film analysis on gear surface provided guidance to improved additive package development (Gen II formulations).
- Both OSP and Gen II formulations with improved additive package showed a higher friction coefficient than SAE 75W-140 but comparable wear.
- OSP formulation with improved additive package passed the ASTM D6121 test.

III.9 Modified Thermoresponsive Hyperbranched Polymers for Improved Viscosity and Enhanced Lubricity of Engine Oils

Overall Objectives

- Support DOE's mission in increasing fuel economy by increasing fuel efficiency of gasoline internal combustion engines
- Develop novel polymers with a branched or hyperbranched architecture as viscosity modifiers
- Develop structure–performance relationships and a fundamental understanding of polymer architecture and ability to affect the viscosity of a base oil
- Correlate polarity and friction at boundary surfaces of carefully designed polymers
- 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 tribological results, refine design strategies and synthetic candidates
- Discover one compound which outperforms one of the benchmarks in a side by side viscosity or friction test

Fiscal Year (FY) 2015 Objectives

- Select at least three candidates for ORNL tribology studies from polymers prepared at PNNL
- Identify at least one compound with promising viscosity index (VI ≥ 150) and reduced friction versus benchmarks
- Identify one candidate suitable for engine testing based on viscometric and tribological evaluation
- Obtain complete additive package for final engine oil formulation
- Scale-up best candidate and generate a suitable formulation to be tested in a Sequence 6D test
- Evaluate fuel efficiency performance of the engine while utilizing final formulated oil

FY 2015 Accomplishments

- Many viscosity modifiers (VM) that outperformed at least one of the benchmarks were synthesized

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- Designed multiple polymers with dual performance function in the molecule (viscosity modifier and friction modifier)
- Developed structure–property relationships based on the friction data gathered from ORNL
- Identified three potential VM candidates that meet viscosity and friction requirements
- Selected one candidate for further engine testing, based on performance screening and scalability
- Synthesized ~1.4 kg of selected VM
- Acquired dispersant inhibitor package and Yubase 4 oil for finished formulation
- One patent filed that covers hyperbranched and branched structures

Future Directions

- Explore hybrid structures (comb, branched, and star polymers) as potential next generation additives
- Investigate shear stability of several analogs
- Design novel structures with potential to address several performance metrics, such as viscosity, friction, and wear
- Complete and submit several manuscripts to peer reviewed journals ■

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. PNNL will design hyperbranched, moderately branched, and multi-branched polymers, tailoring them by changing the polarity of the repeat units 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. Furthermore, the polymer structures will reduce friction via metal surface interaction of the polar groups contained therein.

The project has two components: (1) design, synthesis and screening of molecular structures with branched architectures for proof-of-concept experiments, and (2) conduct rigorous friction and viscosity testing of our top candidates, followed by engine tests in a full package formulation. These latter activities will be led by our partners, ORNL and Evonik.

Approach

The use of hyperbranched polymers as lubricant additives is a very novel concept. In the first year of the project we had explored highly polar and aryl polyester hyperbranched structures, and the results were only modest, due to limited oil solubility and low molecular weights. The second year the focus has shifted towards branched and moderately branched architectures which were much more lipophilic and therefore much more soluble in base oils.

In FY 2015 branched poly(ethylene)s (BPEs), with varying topologies and varying polarity were synthesized and investigated as an engine oil viscosity index improver. They provided promising viscosity index improver properties and a substantial decrease in friction. However, due to the unavailability of high-volume pressure vessels necessary for the scale-up of these particular structures, other architectures were explored. Star or radial polymers became the new focus because they provide a great topology control. These polymers are multi-branched and within each arm have smaller pendants (chains), such that they can be viewed as star-PAMA (polyalkyl methacrylates) polymer hybrids. In addition, the introduction of polar groups in the polymer that can reduce friction and achieve a multi-functional lubricant additive, was easily controlled as well. Using this strategy, PNNL prepared homo-polymers (one monomer), co-polymers (two monomers, with random or block topology), and varied the number of arms.

Results

As previously mentioned, the poor viscosity performance results of hyperbranched aryl polyesters prompted a redesign towards BPEs which were soluble in base oils. At only 2% by weight, all materials of this class increased the VI of the base oil above 150, satisfying one of the initial performance parameters. Homo-polymers with varying degrees of branching as well as co-polymers with varying degrees of polarity were prepared for this study [1]. With molar masses greater than 70 kDa, BPEs increased the VI of Yubase 4 (Y4 in Figure 1, Group III, VI = 127; KV100 = 4) to above 150 and was comparable to one of the benchmarks (Figure 1). Although Benchmark 1 and BPEs have similar chemical compositions, their topologies and molar masses differ significantly, which translates into competitive VIs and much lower KV40s (desirable for increased fuel efficiency). Likewise, the normalized friction reduction illustrated in Figure 2, where the base oil's (ExxonMobil Group I) friction contribution was subtracted out, supports further potential fuel economy gains. Friction studies were conducted by PNNL partners at ORNL (Drs. Zhou and Qu) and Figure 2 summarizes a comparison between the friction reduction effect of Benchmark 2 and BPEs (e.g., 53-159, 53-160, and 53-165) at a 2% by weight in ExxonMobil Group I at 25°C and 100°C. As is illustrated, all BPEs out-performed Benchmark 2 at ambient temperatures. At an elevated temperature of 100°C, Benchmark 2 reduced friction to a greater extent, which was competitive with BPE 53-165 but was not as impressive as BPE 53-159/160. It is worth mentioning that due to its elevated KV25, Benchmark 1 could not be used as a baseline in friction tests. For meaningful comparisons near the boundary lubrication speed, analogs need to have similar viscosities at the test temperature to avoid a false positive. Generally a thicker lubricant will have a lower coefficient of friction. BPEs provide a promising route to satisfy viscosity requirements with the added benefit of friction reduction; however they are not amenable to a scale-up protocol at PNNL without a substantial investment. Therefore, PNNL's focus changed towards structures where topology and polarity are easily controlled, while the synthesis is feasible using existing capabilities.

Star-shaped polymers have well-developed synthetic procedures that afford control over chemical composition, molar mass, and topology. In addition, a core-first methodology provides a route towards synthesizing

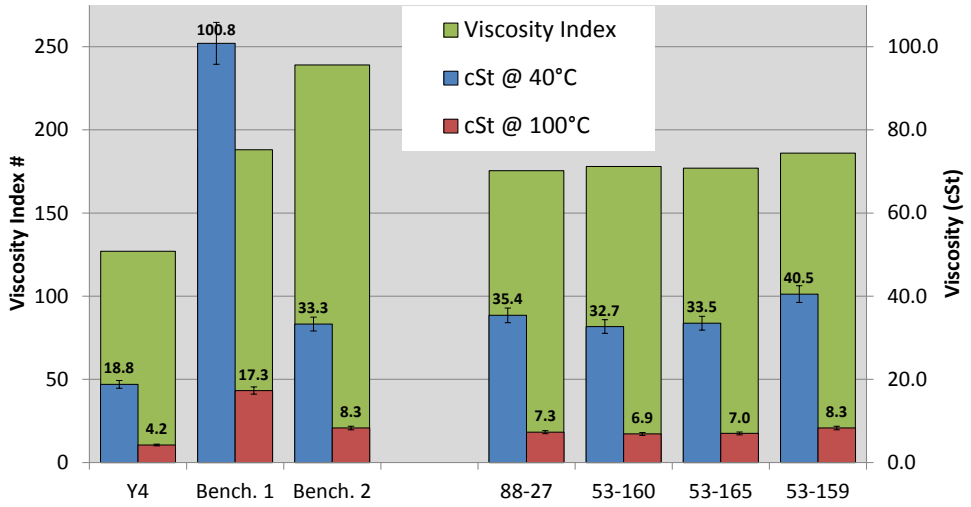

Figure 1. Viscosity and VI performance of the neat oil (Y4) and polymer-oil blend of BPEs at 2% by weight.

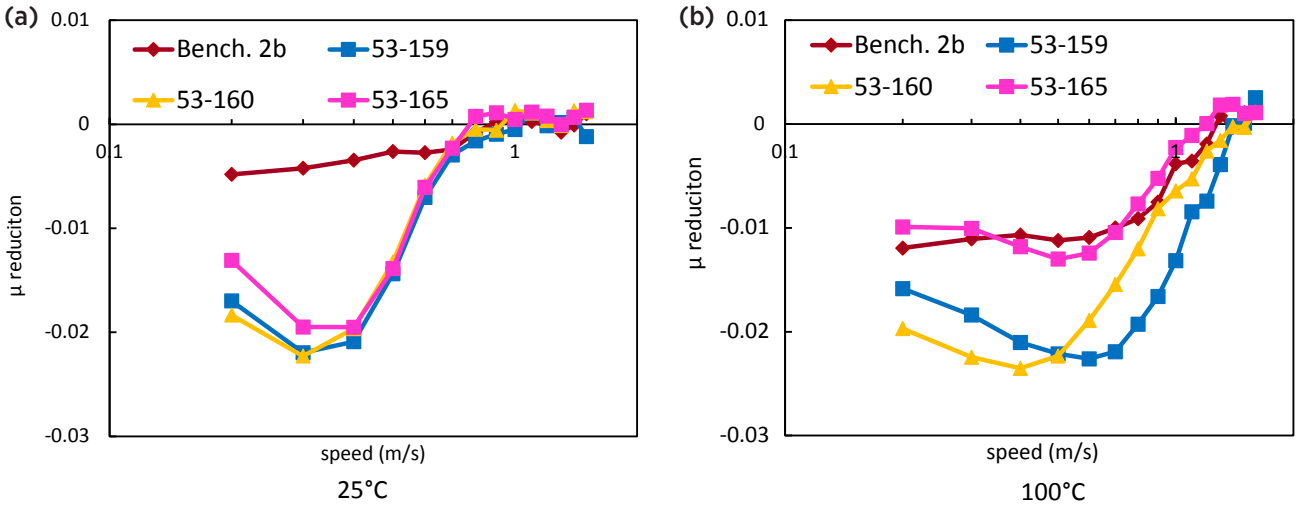

Figure 2. Normalized friction reduction results of Y4 treated with 2% by weight highly-branched homo- and co-poly(ethylene)s at ambient temperature (a) and 100°C (b).

additives with a unique number of arms. In as much, PNNL synthesized two series of star-shaped poly(alkyl methacrylate)s (PAMA; alkyl = C_{12} or C_{18}). The first series investigated the influence of the number of arms (3–16) on viscosity and friction; the second series afforded the study of polar groups influence on lubricant additive performance. Overall, the focus remained on developing a competitive additive that provided a 2% fuel efficiency benefit in an engine test. Homo-[star-shaped]-$PC_{12}MA$ (three-, four-, six-arm) and $PC_{18}MA$ (three-arm; 71-73R) were tested in Y4 at 2% by weight whereupon their viscosities and subsequent VIs were determined. Figure 3 illustrates a clear trend between molar mass and VI, VI increases with increasing molar masses. Generally, a random co-polymer seems to have a higher VI than the respective block co-polymer, and the enhanced polarity in the block depresses the VI. A distinct advantage of polar co-polymers on friction was noticed, in a variable load bearing tester room temperature test versus commercial high viscosity index Benchmark 2. This data, illustrated in Figure 5, shows normalized data for several analogs versus neat base oil at room temperature. The analogs which appear in the negative region will have lower friction than Benchmark 2. The introduction of polar co-monomers appear to have a detrimental effect on VI as compared to the homo-polymers, however the co-polymers still outperform Benchmark 1 (Bench. 1), as demonstrated in Figure 4. A number of monomers were introduced containing various amounts of ethylene glycol or dimethylamine moieties in a block or random topology.

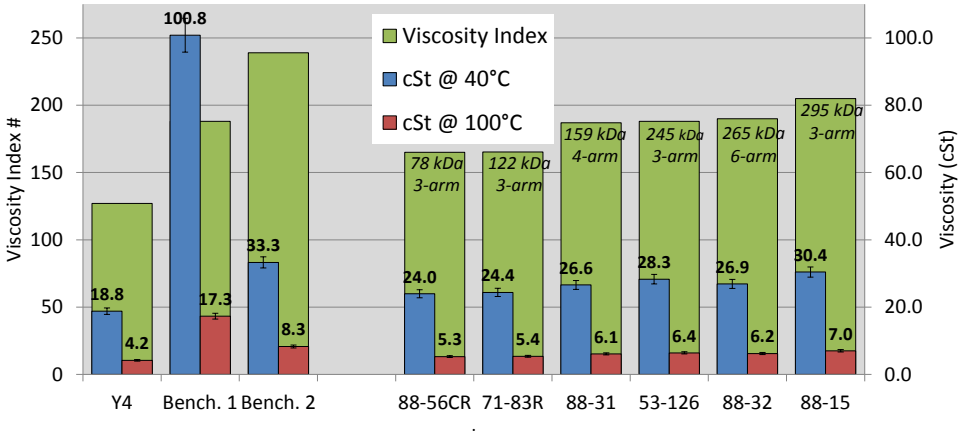

Figure 3. Viscosity and VI performance of Y4 treated with 2% by weight star-shaped homo-PAMAs and their relative performance values to the neat oil and benchmark treated oils.

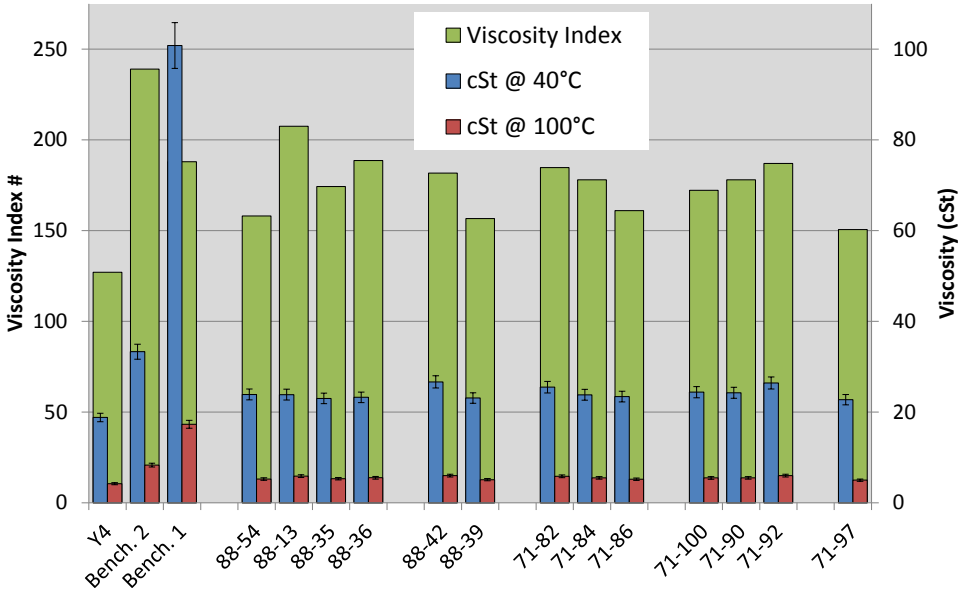

Figure 4. Viscosity and VI performance of Y4 treated with 2% by weight star-shaped co-PAMAs and their relative performance values to the neat oil and benchmark treated oils.

The introduction of polar groups induced an enhanced interaction with metal surfaces as indicated by the room temperature friction data illustrated in Figure 5.

Three of these compounds were selected for further friction and wear evaluation at 100°C to provide a means for narrowing down to one candidate for scale-up. The Plint data illustrated in Figure 6 was generated by our collaborators at ORNL. It appears that all blends, base stock with polymer additive, have a lower coefficient of friction (COF) than Y4. Analog 15 had a COF that increased with time and produced the highest wear results among all analogs. Despite its promising room temperature friction and VI results, the poor wear results made Analog 15 undesirable. After evaluating both performance and minimum time to achieve optimal synthetic scalability of the two remaining candidates, Analog 33 was believed to have the best chance of being produced quickly in kilogram quantities. While Analog 33 demonstrated a modest wear increase compared to Benchmark 2, which is undesirable, the COF of Analog 33 was lower. This may ultimately translate into greater fuel efficiency by reducing points of internal friction.

After several small scale optimization runs, PNNL developed a synthetic methodology which was scalable (500 g), reproducible, and yielded a polymer with 85% conversion. As such, 1.4 kg of polymer was generated, sufficient for two fuel economy engine tests. The next steps included blend studies to determine the polymer

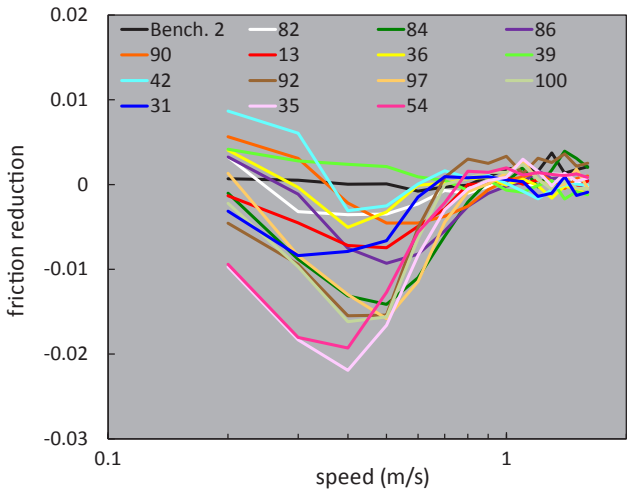

Figure 5. Normalized room temperature friction data using a variable load-speed bearing tester: 50 N load, 8620 steel bar against A2 steel flat, 23°C, 1.6–0.2 m/s speed range.

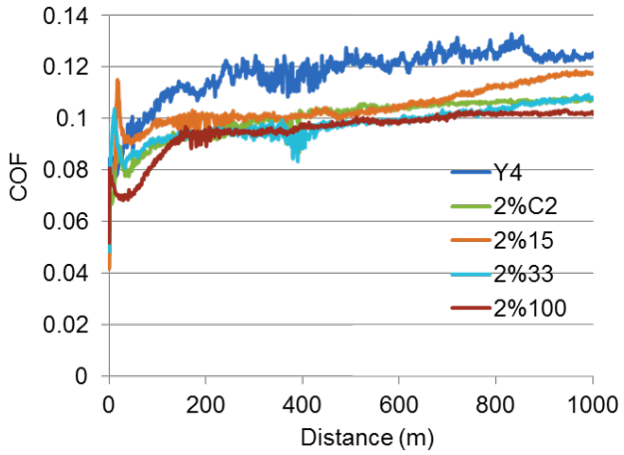

Figure 6. Plint friction data at 100°C, and 100 N of several analogs against Benchmark 2.

concentration required for a full formulation to achieve a 0W-30 finished oil.

Conclusions

- Challenges were overcome by increasing the lipophilicity and the molecular weight of the polymers to achieve high VIs at moderate concentrations.
- Competitive VIs were achieved with several polymers, spanning three classes of compounds.
- Dual functionality was demonstrated in several polymers, which have both VI > 150, and also show reduced COF.
- Several candidates provided superior viscosity and friction performance, and remain potential targets for engine testing.
- One selected candidate was scaled up to 1.4 kg.

References

1. Dong, Z.M.; Ye, Z.B. Hyperbranched polyethylenes by chain walking polymerization: synthesis, properties, functionalization, and applications. Polym Chem-Uk 2012, 3, 286–301.

FY 2015 Publications/Presentations

1. Two-page "Hot Labs" feature running in September's print edition of Mechanical Engineering magazine: "Slick Research."
2. ACS 2015, Denver, Colorado. "Investigations of non-linear polymers as high performance lubricant additives," J. W. Robinson, Y. Zhou, P. Bhattacharya, J. Qu, J.T. Bays, L. Cosimbescu.
3. STLE 2015, Dallas, Texas. "Investigations of Polymer Molecular Design for High Performance Lubricant Additives," Lelia Cosimbescu, Joshua Robinson, Tim Bays, Priyanka Bhattacharya, Jun Qu, Yan Zhou.
4. AICHe Salt Lake City, Utah, 2015. "Exploiting Polymer Architecture and Molecular Composition towards Performance Enhancing Lubricant Additives," Lelia Cosimbescu, Joshua Robinson, Tim Bays, Jun Qu, Yan Zhou.

Special Recognitions and Awards/ Patents Issued

1. Patent filed: Branched Polymers as Viscosity and/or Friction Modifiers For Lubricants; Application No. 14/823,838; Lelia Cosimbescu, Joshua W. Robinson, Priyanka Bhattacharya.

III.10 Lubricant Technology Development

Overall Objectives

- Develop technologies (coatings, additives, and basefluids) that reduce parasitic friction losses in engines and drivetrains and maintain or improve component reliability and durability
  - Develop hybrid basestock fluids as lubricants to minimize viscosity and thus improve fuel economy
  - Design and develop novel colloidal-based lubricant additive system that can provide sustainable friction reduction while ensuring reliability and durability of both new and legacy vehicles
  - Identify and develop non-ferrous coatings that incorporate catalytically active ingredients that form lubricious carbon-based boundary films from long-chain hydrocarbon molecules of lubricating oils

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Fiscal Year (FY) 2015 Objectives

Basefluids:

- Characterize rheological properties and friction and wear of PAO (polyalphaolefin)-polyol ester and other molecular variants of ester fluid mixtures
- Evaluate the effect of antiwear (AW) and friction modifier (FM) additives on the friction and wear performance of PAO-polyol ester fluid mixtures

Additives:

- Establish lubricant system performance benchmark with commercially available state-of-the-art advanced engine and gear lubricants
- Identify, synthesize, and characterize nano-particles suitable (<20 nm size) for colloidal lubricant formulation
- Evaluate the rheological and tribological properties of lubricant formulated with colloidal additives

Coatings:

- Optimize coating microstructure, adhesion, hardness, surface roughness, and chemistry
- Characterize chemical and structural nature of carbon-based boundary films and elucidate lubrication mechanism
- Perform short- and long-duration friction and wear tests to demonstrate superior performance under conditions typical of actual engine components (load, speed, and temperature)

FY 2015 Accomplishments

Basefluids:

- Measured the rheological and traction properties for several PAO-ester hybrid basestock blends. The composite fluids showed superior kinematic viscosity, cold crank viscosity (CCV), high temperature high shear (HTHS) viscosity, and traction behavior compared with current mineral oil basefluids; under severe contact conditions, hybrid fluids showed superior performance, and addition of AW and FM additives was not detrimental to the tribological performance of composite fluids

Additives:

- Established friction benchmark for current advanced lubricant to be 0.08–0.13 under boundary lubrication regime
- Identified, synthesized, and characterized with analytical transmission electron microscopy (TEM), five AW, four FM, and five extreme pressure particulate additives

- Completed measurements of rheological properties and preliminary friction and wear performance of colloidal additives in PAO under reciprocating sliding contact

Coatings:

- Developed and optimized a range of non-ferrous coatings consisting of MoN and VN as the hard phases and Cu, Ni, Co as the soft catalyst phases
- Optimized deposition parameters with respect to temperature, deposition rate, bias voltage, and sample rotation in order to achieve highly uniform coating thickness and structure
- Completed structural, chemical, and mechanical characterization of the optimized coatings and correlated conditions with the tribological performance

Future Directions

Basefluids:

- Downselect the most advanced mineral oil-based fluid as a baseline for the mixed fluid development effort (Yubase 4 and Yubase 4+)
- Evaluate friction and wear performance of fluid mixtures with optimized rheological properties in comparison with the Yubase baseline fluids with and without additives
- Develop thermodynamic model to predict rheological properties of binary and ternary fluid mixtures, including fuel dilution

Additives:

- Evaluate scuffing performance of colloidal additive systems
- Analyze nano-structure of tribo-chemical films formed from colloidal systems using TEM with a focused ion beam
- Evaluate the thermal properties and behavior of colloidal lubricant and measure nanoscale mechanical properties of the tribo-chemical films formed from the systems

Coatings:

- Complete remaining bench tribological studies and develop friction and wear maps illustrating operational ranges of optimized coatings
- Confirm durability and effectiveness under conditions that are typical of actual engine components
- Complete surface and structural characterization of carbon-based boundary films and elucidate their lubrication mechanism
- Confirm performance in engines ■

Introduction

Friction, wear, and lubrication affect fuel economy, durability, and emissions of engines used in ground transportation vehicles. Total frictional losses alone, in typical engines, may account for more than 10% of the total fuel energy (depending on the engine size, driving conditions, etc.). The amount of emissions produced by these engines is related to the fuel economy of each specific engine. In general, the higher the fuel economy, the lower the emissions. Higher fuel economy and lower emissions in future diesel engines may be achieved by the development and widespread use of novel materials, lubricants, and coatings. For example, with increased use of lower viscosity oils (that also contain lower amounts of sulfur- and phosphorous-bearing additives), the fuel economy and environmental performance of future engine systems can be dramatically improved. Furthermore, with the development and increased use of smart surface engineering and coating technologies, even higher fuel economy and better environmental soundness are feasible.

The major objective of this project is to develop novel approaches to reduce parasitic friction losses in engines and drivelines while maintaining or improving reliability and durability of critical components. Three pathways are explored: one that mitigates hydrodynamic losses—losses that occur by shearing in viscous fluids; a second that mitigates boundary friction losses—losses that occur with metal-on-metal contact of surface asperities; and a third approach that mitigates boundary friction while at the same time provides a hard wear-resistant surface.

This project has tasks related to coatings, additives, and basefluids. The coatings task focuses on the development of hard nitride coatings doped with catalytically active elements that promote the formation of a low friction carbon film. The additives task focuses on the development of colloidal compounds that reduce friction during boundary lubrication regimes. The basefluids task focuses on developing composite fluids (mixtures of automotive synthetic fluids, e.g., PAOs, with high-performance polyol ester fluids used in aerospace applications) to minimize hydrodynamic shear losses.

Hybrid Basefluids

Introduction

Lower viscosity engine oil will result in significant overall engine friction reduction and fuel economy improvement. However, there are problems with low viscosity oils in terms of friction and wear protection; hence, there is a need for excess levels of antiwear and extreme pressure additives that exacerbate the performance of friction modifiers [1]. Another problem is the increased evaporation rate. The development of a synthetic, low viscosity hybrid basestock with optimized rheological properties can reduce friction in the hydrodynamic regime without compromising performance in the boundary regime. This will enable fuel economy improvements and ensure reliability of engine components. This task develops a composite basestock consisting of two low viscosity synthetic fluids (PAO and ester) to minimize viscous shear losses. The rheological, traction, and various tribological (friction, wear, and scuffing) properties of the composite fluids will be determined. The same attributes will be also evaluated for the composite basefluids in the presence of conventional AW and FM additives to lubricants.

Results

During FY 2015, low viscosity hybrid basestock fluids consisting of different molecular structures of ester (different diester and polyol ester) and PAO4 were blended. Rheological properties (kinematic, CCV, and HTHS viscosity) of the hybrid basestock were determined. Measurements showed that the hybrid fluids exhibited superior rheological properties compared to PAO alone.

In earlier reported results, friction and wear under unidirectional and reciprocating sliding were reported, with the composite basefluid exhibiting significantly superior performance compared to PAO. In this reporting year, tribological performance under the more severe contact condition of four-ball wear and scuffing tests was determined. As shown in Figure 1, the mixed fluid produced significant wear reduction (four-ball) and substantial increase in scuffing resistance.

Reciprocating and unidirectional sliding friction and wear performance was evaluated with hybrid basefluids and PAO containing AW and FM additives. As indicated in Figure 2, the friction for all the fluids containing additives was about the same and substantially lower than that of fluids without additives. Also, additives were more effective in reducing wear in hybrid fluids compared to pure PAO (Figure 2).

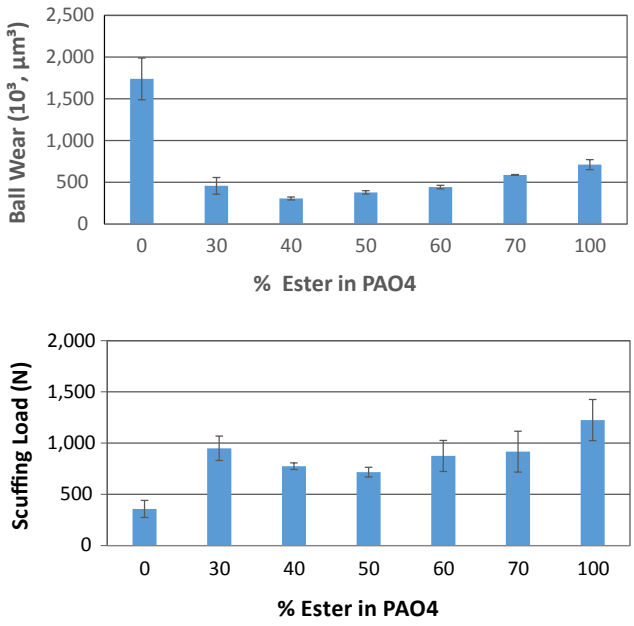
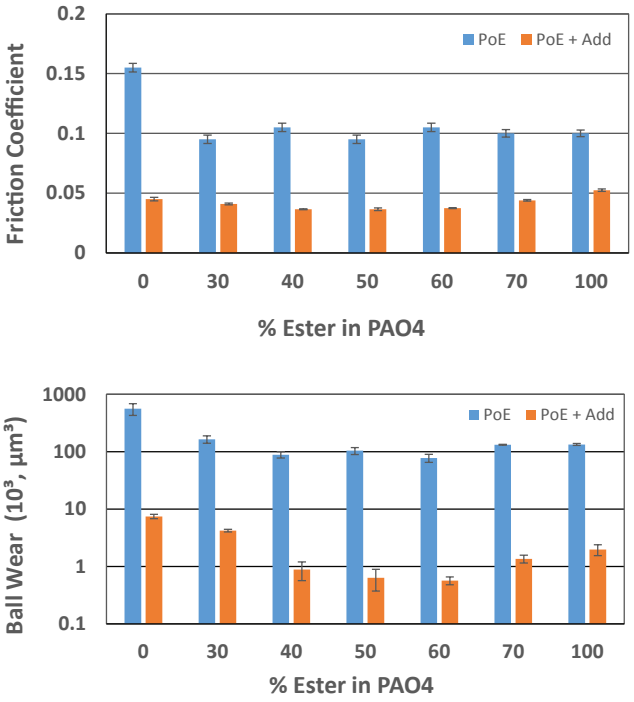


Figure 1. Four-ball wear volume (top) and average scuffing load (bottom) of hybrid fluids



PoE – polyolester

Figure 2. Friction (top) and wear (bottom) under reciprocating sliding for hybrid fluids

Advanced Additives

Introduction

The main goal of this task is to develop and deploy novel lubricant additive systems that can provide sustainable

friction reduction in legacy and new vehicle engines over an extended duration. The additive systems will also be designed to mitigate 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 plus lower viscosity engine oils.

The new additive systems will be based on a nano-technology platform, invoking both physical and chemical mechanisms for their tribological attributes. Compared with the chemically-based state-of-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. Nano-particulate systems with friction-reducing characteristics will be identified and synthesized. These will most likely be based on inorganic layer structures and/or soft metal in a core-and-shell morphology. Particulate systems that reduce wear and prevent scuffing will also be designed and synthesized based on materials that can form a durable surface layer. Using the same approach, systems for chemical and thermal stability and control can also be designed and synthesized. (Note that some of the current additive systems are based on a nano-particulate platform as proposed here, e.g., detergents in diesel engine formulation.)

Results

In the previous year, efforts were devoted to establishment of a tribological performance benchmark for the new additive system. Figure 3 shows the average boundary friction coefficients for six state-of-the-art engine and gear oils. Many candidate nano-additives showed tribological performance comparable and sometimes superior, and other times worse, than the benchmark performance requirements.

Based on input from industrial stakeholders, the focus of the project was shifted to colloidal systems in which the particle size should be less than 20 nm. With this shift, new candidate particulate additives with appropriate tribological performance attributes were identified (five AW, four FM, and five extreme pressure compositions). During this reporting period, we characterized, by analytical TEM, these candidate particulate systems as well as the rheological properties of low viscosity PAO containing the particulate additives. Furthermore, friction and wear behavior of the colloidal lubricants was determined under reciprocating sliding conditions.

Figure 4 shows a high-resolution TEM micrograph of the graphitic particulate additive system used for the

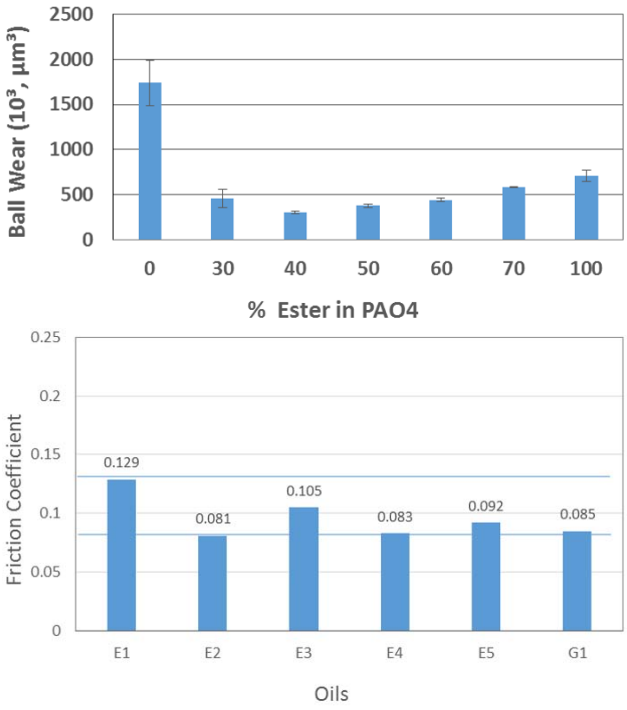


Figure 3. Average boundary friction for advanced commercially available lubricants (project benchmark)

formulation. Electron energy loss spectroscopy indicated that the particulate consists of both layer graphite and nano-diamond constituents. Similar analysis, including energy dispersive X-ray spectroscopy to determine elemental constituents, was done for all the particulate systems. The kinematic viscosity at 100°C of various colloidal lubricants containing 0.1% particulate additive is shown in Figure 5. The data indicate that the addition of particulate additives had a minimal or no effect on viscosity.

Preliminary friction and wear data from reciprocating sliding tests with 0.1% colloidal lubricants indicate that several FM particulate additives reduced the friction coefficient from 0.14 to 0.08, while the AW additives systems did not reduce friction. In some cases antiwear additives actually increased friction slightly. More comprehensive tribological performance evaluation of various colloidal additives under different contact conditions is ongoing.

Optimization of Non-Ferrous Coatings

Introduction

At present, several tribological coatings, such as diamond-like carbon, CrN, etc., are being used to reduce friction and wear of various engine parts [2]. These coatings appear to function best in the presence

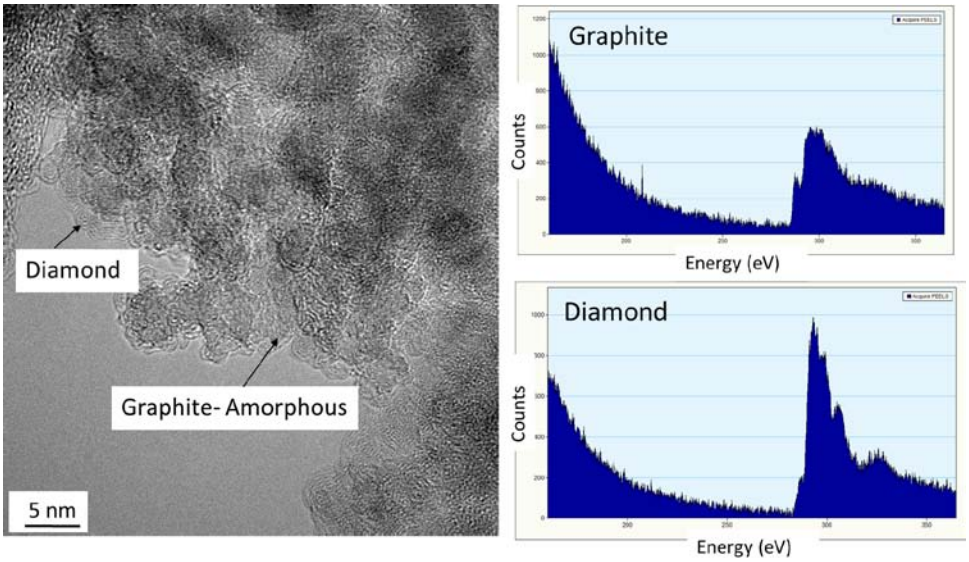
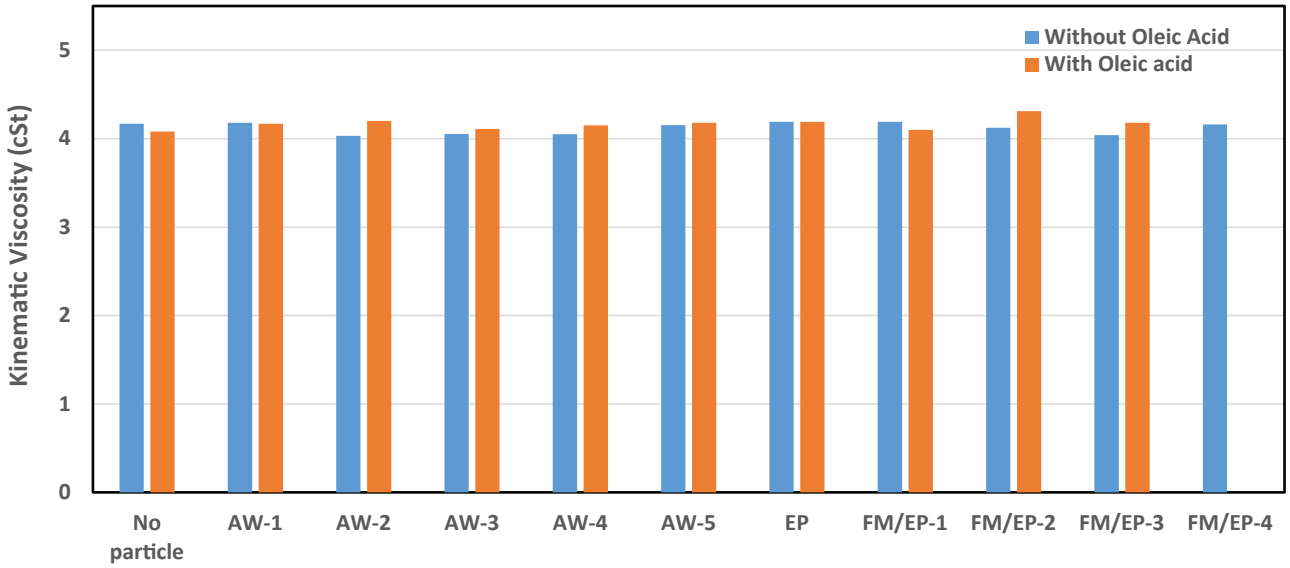


Figure 4. TEM and electron energy loss analysis for friction-reducing graphite colloidal particles



EP – extreme pressure

Figure 5. Kinematic viscosity for colloidal additive systems with and without encapsulation

of certain additives; otherwise, their friction coefficients under boundary conditions are comparable to uncoated components. In this project, a new breed of catalytically active non-ferrous coatings that can provide much superior lubrication even without the use of additives in oils is being investigated. It was discovered that such composite coatings can catalytically crack or split long-chain hydrocarbon molecules of lubricating oils and then deposit them on rubbing surfaces as low shear, carbon-based boundary films. Accordingly, the major goals of this project are to design, develop, and optimize such non-ferrous coatings for use in critical engine parts and implement them in engine applications to further improve their performance, efficiency, and durability.

Results

Figure 6 compares the typical friction coefficients of control and VN-Ni-coated test pairs under boundary-lubricated sliding conditions. As evident, coated surfaces suffer no wear while uncoated surfaces wear out severely. Friction is also significantly reduced despite severe boundary conditions and high temperature (i.e., 100°C). Figure 7 shows a piston-and-ring assembly coated with a non-ferrous coating for further evaluation under rig

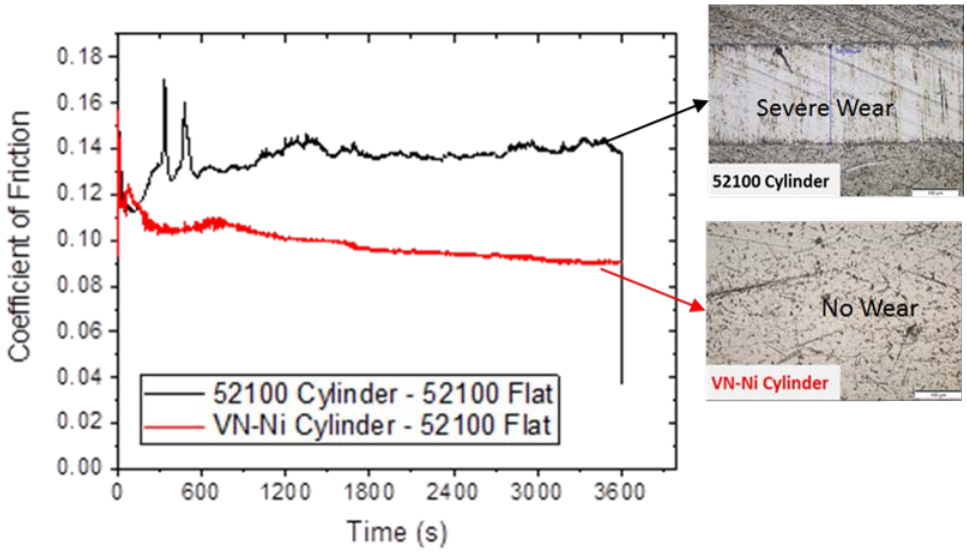


Figure 6. Typical friction coefficients of uncoated (control) and VN-Ni-coated American Iron and Steel Institute 52100 steel test samples under boundary-lubricated sliding conditions

Figure 7. Piston-and-ring assembly coated with Argonne's catalytically active non-ferrous coating.

engine testing in FY 2016. Initial surface analytical studies of rubbing surfaces confirmed severe oxidative wear for the uncoated steel surfaces while a carbon-rich boundary film was found on the rubbing surfaces of VN-Ni coated surfaces.

Conclusions

Basefluids:

- Hybrid fluids showed superior kinematic, CCV, and HTHS viscosity, as well as traction behavior, compared to current mineral oil basefluids.
- Under severe contact conditions, hybrid fluids showed superior performance as indicated in four-ball wear and scuffing test results.
- Incorporation of AW and FM additives was not detrimental to the tribological performance of composite fluids. Indeed, additives were more effective in reducing wear in hybrid fluids.

Additives:

- Friction and wear performance benchmarks were established by evaluating the performance of advanced commercially available lubricants. Specifically, the friction coefficient for these advanced lubricants was 0.08–0.13 under the boundary lubrication regime.
- Five antiwear, four FM, and five extreme pressure particulate additives were synthesized and characterized.
- Various viscosity measurements showed that particulate additive did not change the kinematic viscosity of PAO-based fluids. Preliminary friction and wear results under reciprocating sliding indicated that FM additives are indeed effective in reducing friction while the AW additives are equally effective in preventing wear through the formation of a protective surface layer.

Coatings:

- The ability to form carbon-based tribofilms was confirmed with a series of non-ferrous coatings, which demonstrated as much as 50% reduction in friction while wear was virtually eliminated in pure base oils.

Overall, these novel coatings may have significant positive impact on the environmental cleanliness, durability, and efficiency of future engine systems.

References

1. M. Covitch et al., "Oil Thickening in the Mack T-7 Engine Test—Fuel Effects and the Influence of Lubricant Additives on Soot Aggregation," SAE Technical Paper 852126, doi:10.4271/852126 (1985).
2. S-C. Cha and A. Erdemir, eds., *Coating Technology for Vehicle Applications*, Springer, New York (2015).

FY 2015 Publications/Presentations

1. C. Lorenzo-Martin, O.O. Ajayi, A. Erdemir, and G.R. Fenske, "Hybrid Base-Stocks Fluids for Fuel Efficient Lubricants," FY 2014 Annual Progress Report, DOE Office of Vehicles Technologies, Fuels & Lubricant Program (2014).
2. C. Lorenzo-Martin, O.O. Ajayi, A. Erdemir, and G.R. Fenske, "Scuffing Performance of Mixed Synthetic Base Fluids," Annual Meeting STLE 2016, Las Vegas, NV, May 15–19, 2016.
3. O.O. Ajayi, C. Lorenzo-Martin, D. Singh, and G.R. Fenske, "Advanced Lubrication Additives for Improved Fuel Efficiency," FY 2014 Annual Progress Report, DOE Office of Vehicles Technologies, Fuels & Lubricant Program (2014).
4. C. Lorenzo-Martin, O.O. Ajayi, K.L. Hartman, R.A. Erck, and G.R. Fenske, "Effect of Particle Size on the Performance of Anti-wear Nano-oxides Additives," Society of Tribologists and Lubrication Engineers Annual Meeting, May 17–21, 2015, Dallas, TX.
5. S-C. Cha and A. Erdemir, eds., *Coating Technology for Vehicle Applications*, Springer, New York (2015).
6. V. Sharma, A. Erdemir, and P. B. Aswath, "An Analytical Study of Tribofilms Generated by the Interaction of Ashless Anti-wear Additives with ZDDP using XANES and Nano-indentation," Tribology International, 82 (2015) 43–57.
7. A. Erdemir, "Low-friction Materials and Coatings," in *Multifunctional Surfaces and Materials for Tribological Applications*, (invited chapter) R. Wood, ed., Pan Stanford Publishing, pp. 259–289 (2015).
8. O. Eryilmaz and A. Erdemir, "Frontiers of Nanomaterials and Coatings in Automotive Applications," (Plenary) International Workshop on Superlubricity in the Automotive World: Searching for Ultra-low Friction with Combined Coating/Lube/Surface, Sao Paulo, Brazil, May, 5–7, 2015.
9. G. Ramirez, O.L. Eryilmaz, R. Mirabal, O. Depablos-Rivera, S.E. Rodil Posada, Y. Liao, and A. Erdemir, "Development and Tribological Characterization of Ni-doped Vanadium Nitride Coatings," 42nd International Conference on Metallurgical Coatings and Thin Films, San Diego, CA, April 20–24, 2015.
10. A. Erdemir, "Nanomaterials and Coatings for Friction and Wear Control," (Invited Colloquium), Department of Aerospace Engineering, University of Illinois at Urbana-Champaign, April 6, 2015.

III.11 Impact of Engine Lubricant and Fuel Properties on LSPI

Overall Objectives

- Improve the understanding that engine lubricants and fuel properties have in low speed pre-ignition (LSPI) phenomena with a fundamentally focused thermo-chemical parametric fuel and lubricant study
- To better understand the in-cylinder conditions required for LSPI with a variety of engine lubricant properties

Fiscal Year (FY) 2015 Objectives

- Analyze and report on proof of concept top ring zone liquid measurements
- Evaluate fuel properties on LSPI such that two fuels can be used for parametric LSPI lubricant study
- Demonstrate initial interactions between engine operating conditions, lubricant formulation, and fuel properties on LSPI
- Isolate lubricant properties of interest for LSPI parametric study

FY 2015 Accomplishments

- Gas chromatography–mass spectrometry measurements of top ring zone liquid illustrate that liquid fuel species are proportional to fuel boiling point, with mass concentration measurements corresponding to approximately 20% fuel in the top ring zone under steady state operation
- Determined that LSPI propensity and event frequency are directly proportional to fuel boiling point, where increased intermediate fuel boiling point increased LSPI tendency
- Demonstrated that in-cylinder thermodynamic conditions and fuel–air mixing during charge preparation are critical to LSPI event promotion, where reduced mixing or increased top dead center temperature increased LSPI tendency
- Formed strategic partnerships with industry to isolate specific lubricant detergents, antioxidants, and antiwear properties of interest for parametric lubricant property study of LSPI; lubricants formulated and delivered to ORNL for FY 2016 testing

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Future Directions

- Evaluate parametric lubricant study of lubricant detergent types on LSPI with two fuels
- Provide unused and used sump lubricant to National Renewable Energy Laboratory for Ignition Quality Tester analysis; if successful, couple Ignition Quality Tester results with statistical LSPI results from engine studies
- Develop an understanding of lubricant and fuel chemistry through batch reactor studies to explore aging and chemistry effects on lubricant and fuel formulations of interest; couple aged liquid properties to engine studies with LSPI event count
- Fully formulate a test ionic liquid lubricant and evaluate ionic lubricant effects in LSPI ■

Introduction

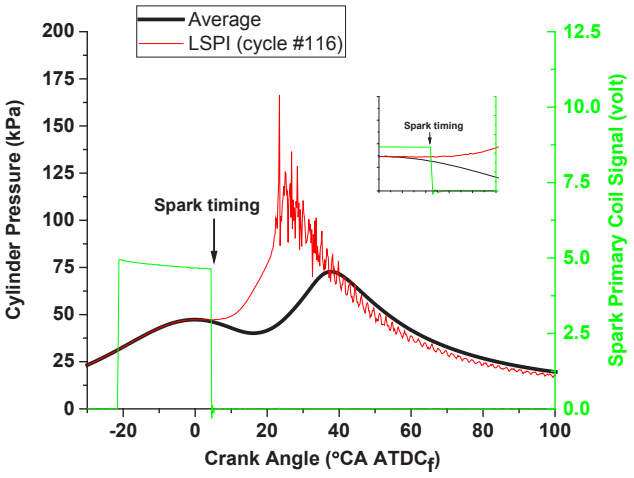
Currently, the United States light-duty market is evolving through downsizing and downspeeding [1], as evidenced by increased continually variable transmission or 6+ speed transmissions, gasoline direct injection (GDI), and turbocharging within the marketplace [2]. Regardless of the final powertrain configuration, it has been shown that smaller displacement, high output engines can reduce the relative effects of friction and pumping losses, improving powertrain efficiency and associated vehicle fuel economy [2–6]. Although these studies show fuel economy benefits from small displacement, high output engines, recent findings in research and in the field with these powertrains have illustrated the presence of an abnormal stochastic and extreme combustion process, known as low speed pre-igntion (LSPI). LSPI results

in either a singular or short burst of undesirable or uncontrolled combustion events, exhibiting extreme in-cylinder pressure, see Figure 1. The result of extended operation with LSPI can be engine damage or failure, therefore practically limiting the downsizing potential of high efficiency small displacement powertrains.

To reduce LSPI tendency and improve the fuel economy potential of future powertrains, research on understanding the chemical–physical relations governing LSPI has been evolving. A leading and developing theory suggests that fuel–lubricant interactions and liquid rejection from the piston top ring land under high-load, low-speed operating conditions are responsible for creating an LSPI ignition source [7,8]. The present work explores this theory through a combination of engine experiments aimed at improving the understanding of fuel and lubricant properties responsible for promotion of LSPI. Through improved understanding of the chemical–physical relation of lubricants and fuels, solutions and avoidance strategies of LSPI could become accelerated, in turn improving vehicle fuel economy.

Approach

To date, this project has used three engine designs to study LSPI phenomena at ORNL. All three engines have been used to explore and better understand how fuel and lubricant interact within the combustion chamber to promote LSPI. The most basic engine was a sacrificial air cooled utility engine, which was used to develop a liquid sampling diagnostic to directly acquire liquid from the top ring zone of a running engine. Sampled liquid was analyzed with gas chromatography–mass spectrometry



°CA – degrees crank angle; $ATDC_f$ – after top dead center firing

Figure 1. Cylinder pressure traces, average (black) LSPI (red), and spark coil discharge command (green).

analysis to isolate chemical species of interest present in the top ring zone under fired engine operation.

The other two engines are single-cylinder versions of modern turbocharged GDI engines, which employ in-cylinder pressure based diagnostics of LSPI event characteristics of fuels and lubricants of interest. One single-cylinder engine is based on a General Motors 2.0 L LNF, which is a side-mounted GDI engine. The other single-cylinder engine is based on a Ford 1.6 L EcoBoost engine, which is a center-mounted GDI engine. Both engines are operated with a fully open and flexible engine controller, and have laboratory-grade control of all pertinent engine operating parameters (i.e., fuel timing, fuel mass, spark timing, cam phaser positon, backpressure, etc.). Conditions explored with the two single-cylinder engines were at steady engine speed of 2,000 rpm, with loads in excess of 1,800 kPa gross indicated mean effective pressure ($IMEP_g$) and crank angle at 50% mass fraction burned (CA50) phasing of ~30°CA $ATDC_f$.

Results

Experiments published this year from the utility engine [9] illustrated that the liquid composition in the top ring zone varies with engine operating condition, and temperature. Liquid was sampled from behind the top ring in the engine, as indicated in Figure 2, where gas chromatography–mass spectrometry-based speciated results of the liquid are shown in Figure 3. Data showed that under the tested conditions, the liquid was approximately 20% by mass fuel and 80% by mass lubricant. Moreover, fuel species concentrations were proportional to load, inversely proportional to engine temperature, and strongly correlated with species boiling point, see Figure 3. Thus, these results suggest that under LSPI conditions, there could be increased propensity for fuel species of elevated boiling point mixing with lubricant in the top ring zone, potentially facilitating an

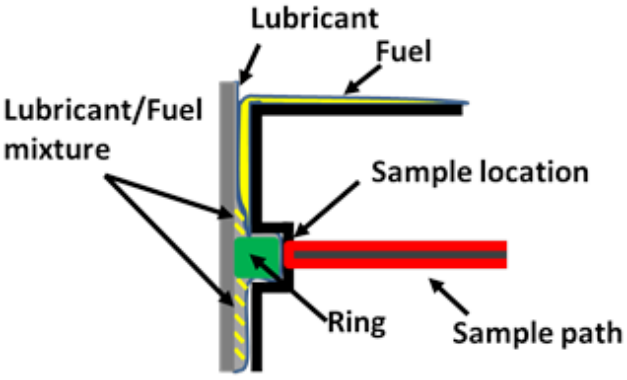


Figure 2. Schematic of top ring zone sampling location.

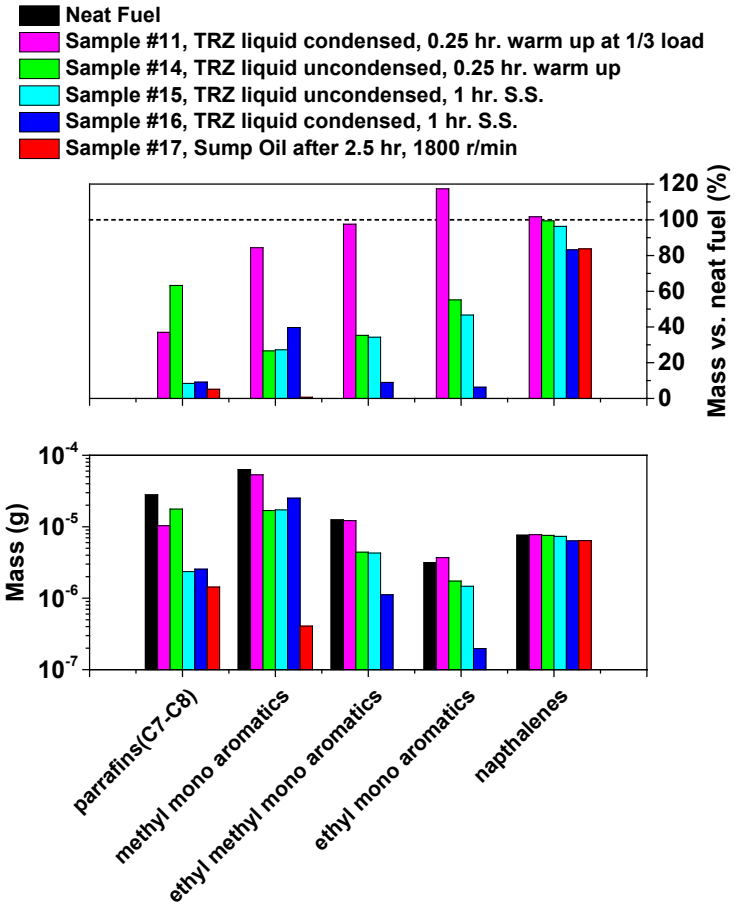


Figure 3. Gas chromatography–mass spectrometry determined mass of different top ring zone (TRZ) componets grouped by molecular type (bottom) and relative mass of compared neat fuel (top).

ignition source of LSPI. This finding is in agreement with fuel distillation effects on LSPI as documented by others by varying fuel aromatics content [10].

To further test the theory of fuel boiling point effects on LSPI, engine experiments were conducted on the General Motors LNF single-cylinder engine. In this preliminary study three fuels were selected, where the boiling curves are illustrated in Figure 4. The fuels were gasoline (87 AKI E0), a 23% by volume mixture of cyclopentanone with the 87 AKI E0 gasoline (CPN 23), or 30% by volume mixture of ethanol with the 87 AKI E0 gasoline (E30). Results at 2,000 rpm showed that the 87 Anti-Knock Index (AKI) fuel exhibited LSPI events beginning at a load of 2,000 kPa $IMEP_g$ with a knock limited CA50 combustion phasing of 30°CA $ATDC_f$. The CPN 23 and E30 fuels did not exhibit LSPI at these conditions, but they were also not knock limited at combustion phasing of 30°CA $ATDC_f$. Load was increased with 23% CPN to 2,250 kPa $IMEP_g$, where knock limited operation was achieved at 30°CA $ATDC_f$, where LSPI was observed at a high frequency. With E30 LSPI was not observed at 2,250 kPa $IMEP_g$, so load was increased until 2,570 kPa $IMEP_g$ where CA50 was knock limited at 30°CA $ATDC_f$; however, at this condition E30 did not illustrate LSPI events. The results showed that LSPI tendency was a function of knock limited operation at late combustion phasing, and at least proportional to the intermediate temperature range of the fuel boiling curve, where oxygenates in the fuel (CPN 23 or E30) showed little effect.

Using the knowledge from the LNF experiments, initial testing in the Ford 1.6 L single-cylinder engine commenced, to explore thermodynamic and fuel preparation effects on LSPI. The center mounted GDI configuration of the 1.6 L single-cylinder engine has an extremely efficient fuel–air mixing process. It was found that the production engine fuel delivery strategy was not excessively LSPI prone, with operation in excess of 2,600 kPa $IMEP_g$ with knock limited CA50 timings in excess of 30°CA $ATDC_f$. To explore in-cylinder effects on LSPI, a port fuel injection (PFI) injection system was added to the engine and the GDI injector was used to direct inject water. The approach enabled two independent effects to be explored. First the PFI system degraded the quality of the fuel–air mixing, and LSPI was achieved at a load as low as 1,800 kPa $IMEP_g$ where combustion was knock limited at a CA50 phasing of 30°CA $ATDC_f$. This finding demonstrated that in-cylinder fuel–air mixing is critical for LSPI promotion. Although the PFI system reduced fuel–air mixing, it also results in increased in-cylinder temperatures due to more of the fuel vaporization processes occurring in the intake manifold, not in-cylinder. To alter the in-cylinder temperature history without affecting the PFI fuel vaporization process, water was direct injected to the combustion chamber through the GDI. It was found that with a small amount of water injection the LSPI events were suppressed, with several water injection timings explored. Then at one water injection timing, the load was increased until operation became knock limited at a CA50 phasing of 30°CA $ATDC_f$ (matched to no water injection PFI fuel only operation), this occurred at 2,600 kPa load. Interestingly no LSPI events were recorded with the GDI operation at matched conditions, suggesting again that LSPI is not governed entirely by knock limited operation, but potentially more importantly dependent on in-cylinder fuel–air mixing and maximum temperature, see Figure 5 for the results.

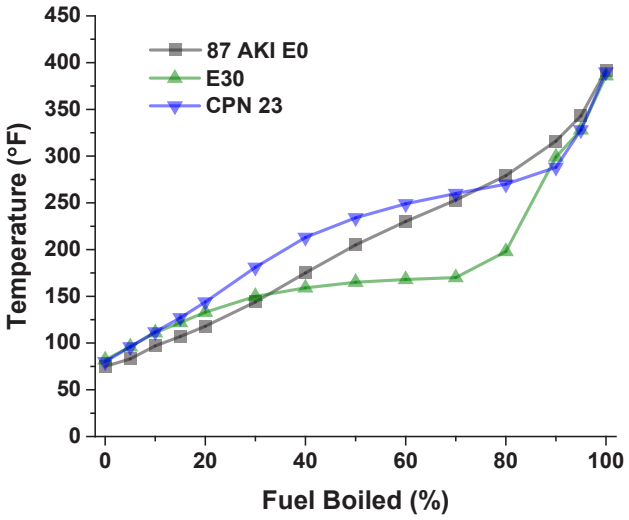


Figure 4. ASTM D86 fuel distillation curve for gasoline and gasoline/oxygenate fuel blends.

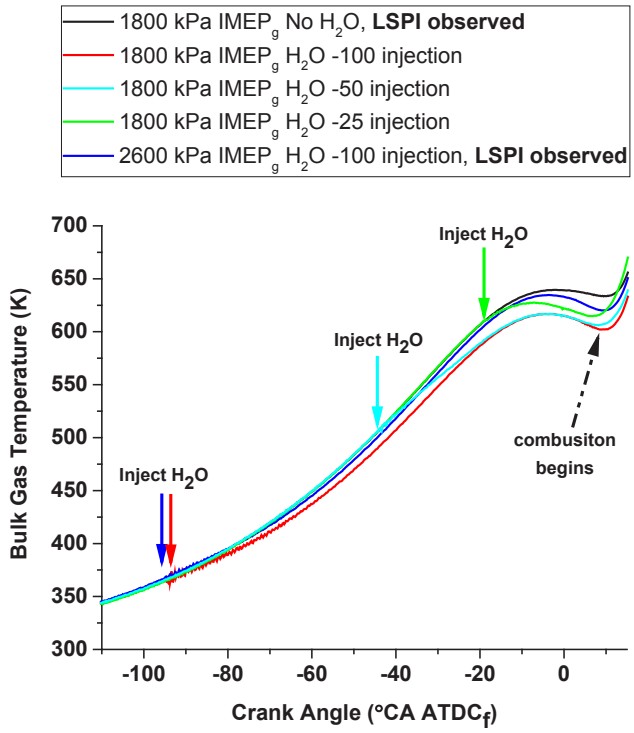


Figure 5. In-cylinder temperature history with and without direct water injection (PFI fueling of Tier II EEE premium grade certification fuel); LSPI events were registered at knock limited spark advance operating conditions where top dead center temperatures were very similar.

Using the aforementioned studies on LSPI fundamental process and governing factors, a parametric lubricant based study was initiated, and currently is underway. Industry partners and lubricant formulation support from Driven Racing Oil was integrated into the project.

Besides two production lubricants, Driven has supplied multiple custom lubricants formulations, all utilizing a common Group II base stock and viscosity. Variations in detergent concentration, detergent type, and antioxidant were formulated, see Figure 6. Preliminary literature and findings have suggested that lubricant additive formulation, and specifically detergent type, could influence LSPI [11]. The current work is embarking on improving the fundamental understanding of these effects.

Conclusions

- Gas chromatography–mass spectrometry measurements of top ring zone liquid illustrate that the liquid can be in excess of 20% fuel, and the liquid fuel species are proportional to fuel boiling point, and operation.
- LSPI propensity and event frequency was found to be directly proportional to fuel boiling point, with little effect from oxygenates.
- ORNL demonstrated that where reduced in-cylinder mixing or increased top dead center temperature increased LSPI tendency.
- ORNL formed strategic partnerships with industry to isolate specific lubricant detergents, antioxidants, and antiwear properties of interest for parametric lubricant property study of LSPI. Lubricants were formulated and delivered to ORNL for testing at the end of FY 2015, which is continuing into FY 2016.

References

1. Pawlowski, A., & Splitter, D. (2015). SI Engine Trends: A Historical Analysis with Future Projections (No. 2015-01-0972). SAE Technical Paper, doi:10.4271/2015-01-0972.

2. Alson J., Hula A., and Bunker A., (2014) Light-Duty Automotive Technology, Carbon Dioxide Emissions, and Fuel Economy Trends: 1975 through 2014 (EPA-420-R-14-023), U.S. Environmental Protection Agency, Ann Arbor, Michigan, Available at, http://www3.epa.gov/fueleconomy/fetrends/1975-2014/420r14023a.pdf, accessed June 10, 2015.

3. Fraser, N., Blaxill, H., Lumsden, G., & Bassett, M. (2009). Challenges for Increased Efficiency through Gasoline Engine Downsizing. SAE International Journal of Engines, 2(1), 991–1008, doi: 10.4271/2009-01-1053.

4. Shahed, S. M., & Bauer, K. H. (2009). Parametric Studies of the Impact of Turbocharging on Gasoline Engine Downsizing. SAE International Journal of Engines, 2(1), 1347–1358, doi:10.4271/2009-01-1472.

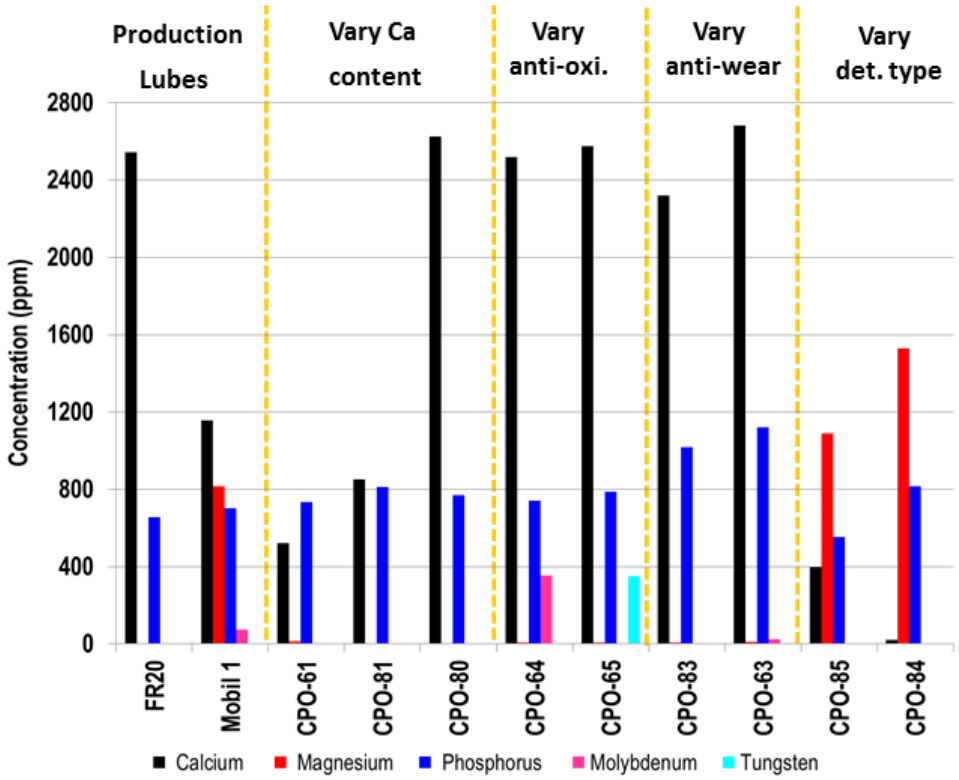


Figure 6. Initial lubricant properties investigated. CPO-XX lubricants span the range of production lubricants, and are custom blends from Driven Racing Oil where all non-displayed properties and additives held constant between the CPO-XX lubricants.

5. Turner, J. W. G., Popplewell, A., Patel, R., Johnson, T. R., Darnton, N. J., Richardson, S., et. al, (2014). Ultra Boost for Economy: Extending the Limits of Extreme Engine Downsizing. SAE International Journal of Engines, 7(1), 387–417. 2014, doi:10.4271/2014-01-1185.

6. Thomas, J. (2014). Drive Cycle Powertrain Efficiencies and Trends Derived from EPA Vehicle Dynamometer Results. SAE International Journal of Passenger Cars-Mechanical Systems, 7(4), 1374–1384, doi:10.4271/2014-01-2562.

7. Dahnz, C, Kyung-Man Han, Ulrich Spicher, Max Magar, Robert Schießl, and Ulrich Maas. "Investigations on Pre-Ignition in Highly Supercharged SI Engines." SAE International Journal of Engines 3, no. 1 (2010): 214–224.

8. Zahdeh, A., Rothenberger, P., Nguyen, W., Anbarasu, M. et al., "Fundamental Approach to Investigate Pre-Ignition in Boosted SI Engines," SAE Int. J. Engines 4(1):246–273, 2011, doi:10.4271/2011-01-0340.

9. Splitter, D., Burrows, B., and Lewis, S., "Direct Measurement and Chemical Speciation of Top Ring Zone Liquid During Engine Operation," SAE Technical Paper 2015-01-0741, 2015, doi:10.4271/2015-01-0741.

10. Chapman, E., Davis, R., Studzinski, W., and Geng, P., "Fuel Octane and Volatility Effects on the Stochastic Pre-Ignition Behavior of a 2.0L Gasoline Turbocharged DI Engine," SAE Int. J. Fuels Lubr. 7(2):379–389, 2014, doi:10.4271/2014-01-1226.

11. Smith A.G., Pearson R.J., Williams J., Yates R., and Mayer M., Effects of lubricant composition on low-speed pre-ignition in direct-injection spark-ignition engines, oral only presentation SAE Naples 2015, September 2015, Capri, Italy.

FY 2015 Publications/Presentations

1. Splitter, D., Burrows, B., and Lewis, S., "Direct Measurement and Chemical Speciation of Top Ring Zone Liquid During Engine Operation," SAE Technical Paper 2015-01-0741, 2015, doi:10.4271/2015-01-0741.

2. Splitter, D., Burrows, B., and Lewis, S., *Direct Measurement and Chemical Speciation of Top Ring Zone Liquid During Engine Operation*, SAE World Congress April 21, 2015, Cobo Hall, Detroit, Michigan.

III.12 Phenomenological Modeling of Lubricant Film Formation and Performance

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 the durability limits and interactions of tribochemical films with basestock oil
- Determine and develop a model for the failure mechanisms in lubricated systems in engines
- Validate performance in both bench-top testing and engine environment tests

Fiscal Year (FY) 2015 Objectives

- Assess and study the mechanisms of the impact of base fluid viscosity on the frictional performance and nature of pertinent tribochemical surface films
- Initiate the study of tribochemical film formation and failure mechanisms in engine components, with particular focus on scuffing mechanisms
- Determine the mechanical properties and durability of tribochemical surface films in engine components

FY 2015 Accomplishments

- Observed peculiar frictional variation with temperature for low viscosity mineral and ester base fluids containing zinc dialkyldithiophosphate (ZDDP) antiwear and molybdenum dialkyldithiocarbamate (MoDTC) friction modifier additives
- Identified the possible mechanisms for the peculiar friction behavior for low viscosity base fluids using high-resolution transmission electron microscopy of tribochemical films
- Completed initial analysis of scuffing and wear mechanisms for ring and liner components in engines

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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 lubricated interfaces
- Verify the peculiar friction behavior for low viscosity base fluid for other additive systems
- Develop empirical relationship between base fluid viscosity and boundary regime frictional behaviors ■

Introduction

Most critical components in engines and transportation vehicle subsystems 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, antiwear 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. The key to friction reduction is design and engineering of these tribochemical surface films while maintaining reliability and durability. The main goal of the current project is the development of mechanistic understanding, plus optimization, of lubricant additives and tribochemical films for sustainable friction reduction and consequent improvement in fuel economy for transportation vehicles. Another congruent goal of this project is the determination of the basic mechanisms of failure, especially scuffing in engine components, and the development of predictive model for such failures.

Approach

To take full 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 effort is to develop this understanding. The overall goal is to advance the science and technology of in situ-generated surface layer films with low friction to the point of commercialization. This will involve development of a controlled method of production, characterization of tribological properties, and performance optimization for a variety of pertinent components. Detailed modeling and validation studies (bench-top and engine tests) will also be performed.

The approach for this project involves 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 the Massachusetts Institute of Technology. An additional component is the study of basic mechanisms and the development of a predictive model for scuffing in piston ring and liner systems of internal combustion engines, based on input from original equipment manufacturers. Briefly, this will involve the following tasks:

- Development of a technique for low friction tribo-film deposition
- Detailed characterization of the composition and structure of the film by various analytical techniques
- Detailed characterization of the nano-mechanical properties of the films
- Tribological performance evaluation of the film by bench-top friction and wear testing
- Determination of mechanisms and development of a 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 FY 2014 report [1] presented results on the thermal and mechanical durability of tribochemical surface films formed from a variety of advanced, commercially available lubricants. In general, tribo-films with a crystalline phase or a mixture of crystalline and amorphous phases exhibited very high load-carrying capacity. These films were able to sustain a 3 GPa contact pressure under reciprocating sliding contact without failure. In these durable films, failure occurred by gradual wear or surface removal. Films with all-amorphous phase were less durable mechanically and failed by sudden removal and consequent increase in friction and severe surface damage. Under thermal loading, two failure modes were observed in the tribo-films, namely, sudden increase in friction due to a sudden removal of the tribo-films and onset of frictional instability as a result of increased oxidation.

During this reporting period, efforts were devoted to more in-depth study of the peculiar frictional behavior of low viscosity basefluid as a function of temperature reported for polyalfaolefin (PAO) last year. Both low viscosity mineral and ester basefluids were evaluated with the same model additive (ZDDP and MoDTC mixture) as a function of temperature. As shown in Figure 1, the same peculiar friction behavior was observed in both the mineral oil and the ester fluids. Essentially, the test started at room temperature with a friction coefficient of about 0.1, which is typical of the boundary lubrication region. As the temperature increased, the friction decreased followed by an increase at about 75°C, reaching a peak at about 110°C, followed again by a decrease at higher temperature. The behaviors of mineral base fluid (Figure 1a) are very similar to that of PAO. Ester fluids exhibit a similar trend (Figure 1b).

To elucidate the possible mechanisms for this frictional peculiar behavior, three tests were conducted with PAO and the model additives. The tests were terminated at different stages of frictional behavior, as shown in Figure 2. The repeatability of the behavior was very good for different positions of test termination, as

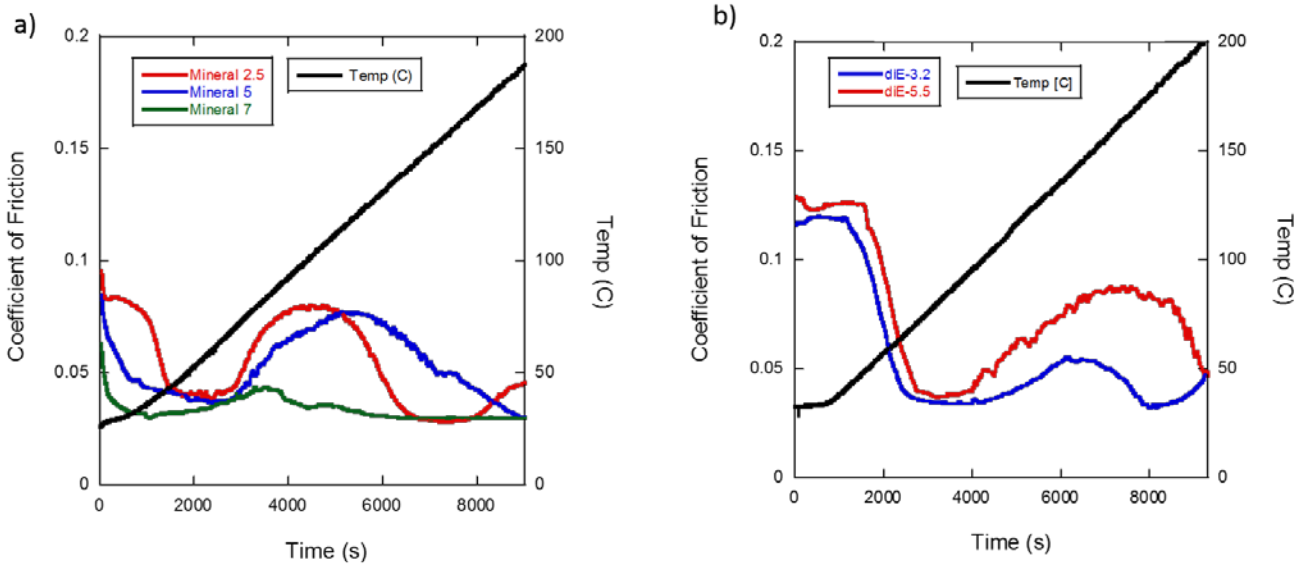

Figure 1. Friction coefficient as function of time and temperature for low viscosity (a) mineral and (b) ester basefluids containing the same performance additives.

indicated in the figure. Based on observations from numerous tribochemical films, the nanostructure of the films usually determines their frictional behavior. No tribochemical films were observed in the test terminated at Position 0. The nanostructure of the tribo-films from positions 1 and 2 were characterized by a focused ion beam/high-resolution transmission electron microscopy. Figure 3 shows the cross-sectional transmission electron microscopy (TEM) micrograph of a tribochemical film from Position 1 (high friction). The tribochemical film at this stage is only about 10 nm thick. Local energy-dispersive X-ray spectroscopy indicated that the film contains mainly Fe and O with no elemental constituent of additive present. Figure 4 shows the cross-sectional TEM micrograph of the tribo-film from Position 2, which is the high temperature, low friction stage. The film has a thickness of about 70 nm and has an amorphous structure, as indicated in Figure 4. Energy-dispersive X-ray spectroscopy analysis of the film showed that it consists of element from the additives. This nanostructural analysis is consistent with our previous observation that tribo-films with amorphous structure usually exhibit low friction behavior.

Based on this analysis of the films formed from tests with low viscosity PAO and model additives, it appears that friction behaviors at different temperatures are controlled by different mechanisms. Tribo-film analysis results at different stages suggest that the initial decrease in friction is due to a combination of reduction of limiting shear strength of the lubricant fluid film and adsorption of some molecular species in the additives to minimize interaction between surface asperities. At some temperature, the films for low viscosity fluid can no longer provide load support, and desorption of surface-separating molecules can also occur, resulting in friction increase. At high enough temperatures, formation of tribochemical films from an additive with the appropriate nanostructure can lead to friction reduction. Although this observation could have a major implication for lubricated component performance, there are still many outstanding questions. Is the observation peculiar only to the additive combination used in this study? Can the same behavior occur in fully formulated lubricants if the base fluid viscosity is low enough?

In response to the request and input from the original equipment manufacturer members of the Massachusetts Institute of Technology engine lubrication consortium, a study was initiated on the scuffing mechanisms in the internal combustion engine ring and liner system. Also conducted was a preliminary analysis of surface damage mechanism in used ring and liner components as well as laboratory bench-top specimens. Results show different levels of surface shear–strain evolution during the scuffing process. Figure 5 indicates a different level of strain on the cast iron liner surface from engine components. Analytical quantification and calculation of surface shear strains will provide the basis for scuffing model development for a ring and liner system.

Conclusions

The peculiar frictional behavior for low viscosity base fluid containing a ZDDP and MoDTC additive mixture that was observed in the PAO base fluid was also

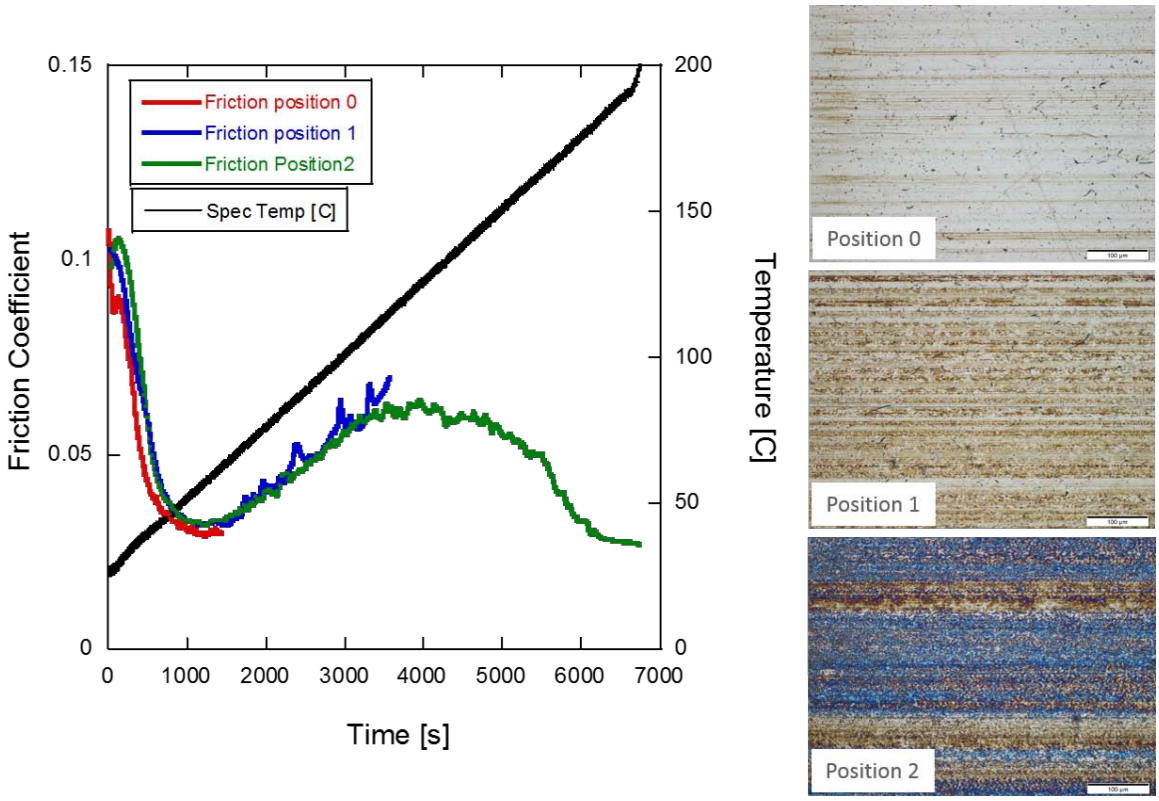

Figure 2. Friction coefficient as function of time and temperature for low viscosity PAO interrupted at different stages.

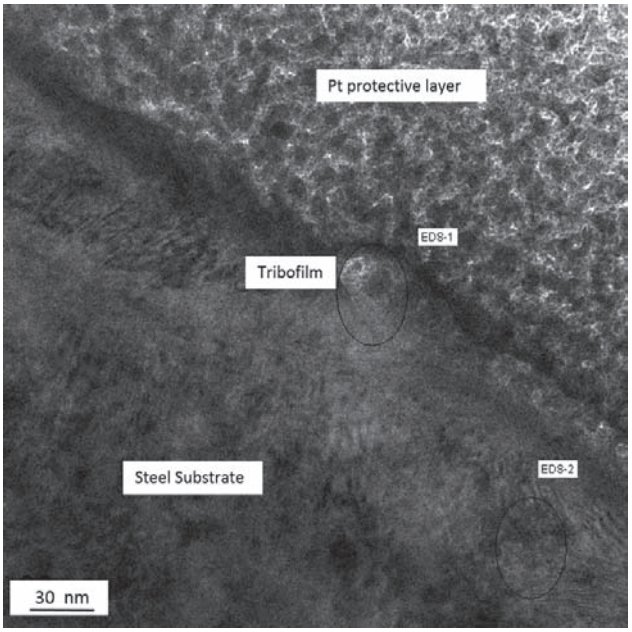

Figure 3. Cross-sectional TEM micrograph of tribochemical film from Position 1 (high friction)

observed in mineral oil and ester base fluids. Possible mechanisms for this behavior were investigated through nanostructural analysis of tribochemical films formed at different stages of friction behavior. The initial friction increase in the mid-temperature range coincided with the presence of a very thin tribo-film containing mostly Fe and O, suggesting it is an iron oxide layer. The friction drop at higher temperatures coincided with the formation of an amorphous tribochemical surface film. Although the implications of this peculiar observation for engine and lubricated components are obvious, it is not clear yet if they are peculiar to the combination of additives used in this study or valid for fully formulated lubricants. In a preliminary analysis, liner scuffing was observed to involve a significant local plastic strain pattern at the honing plateau of the liner surface. Further characterization of the strain pattern in engine and test specimens will be conducted and used as the basis for scuffing model formulation.

Reference

1. O.O. Ajayi, C. Lorenzo-Martin, and G.R. Fenske, “Advance Lubrication Additives for Improved Fuel Efficiency,” FY 2012 Annual Progress Report, DOE

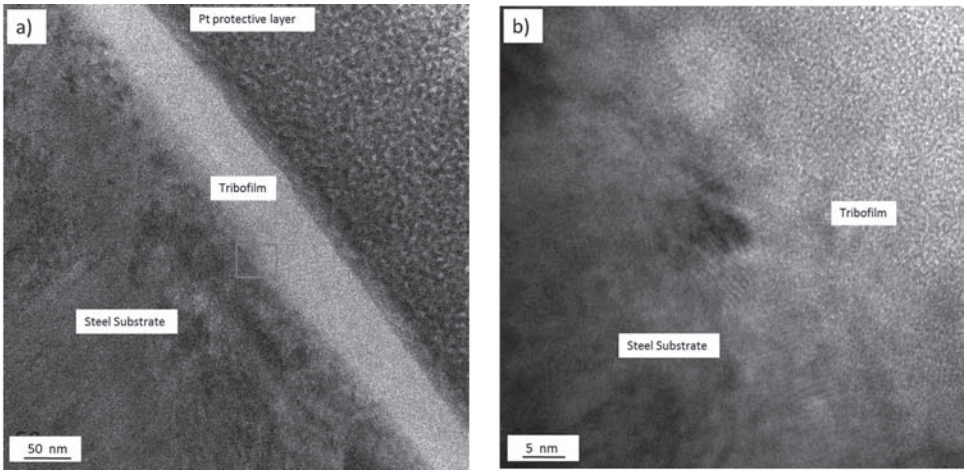

Figure 4. Cross-sectional TEM micrograph of tribochemical film from Position 2 (low friction)

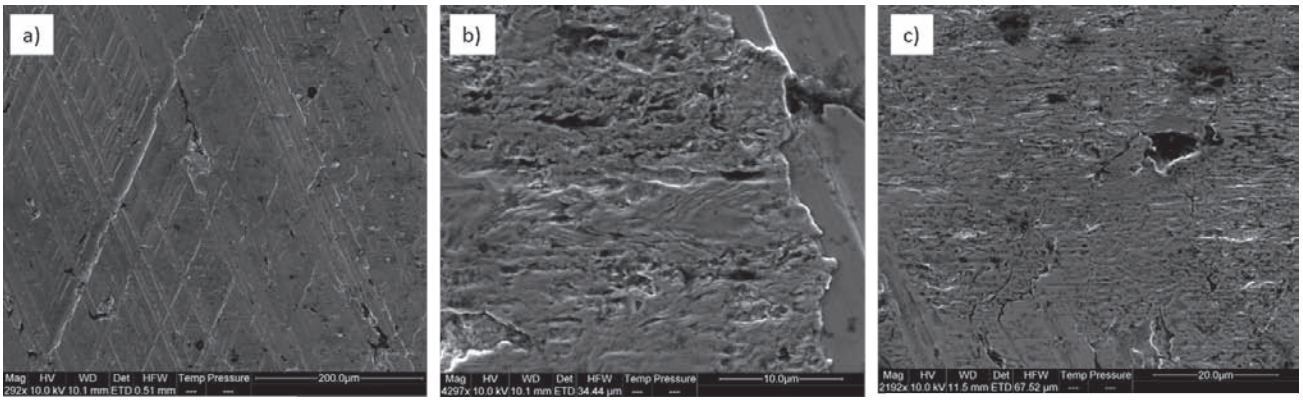

Figure 5. Scanning electron micrographs of wear track of liner components from laboratory tests: (a) boundary of wear track and (b) and (c) different levels of surface shear strain evolution during the scuffing process.

Office of Vehicles Technologies, Fuels & Lubricant program, II-18-20 (2013).

FY 2015 Publications/Presentations

1. B. Olofinjana, C. Lorenzo-Martin, O.O. Ajayi, and E.O. Ajayi, "Effect of Laser Surface Texturing (LST) on Tribochemical Films Dynamics and Friction and Wear Performance," Wear 332-333 (2015) 1225–1230. doi:10.1016/j.wear.2015.02.050.

2. C. Lorenzo-Martin, O.O. Ajayi, S. Torrel and G.R. Fenske, "Friction and Wear Behavior of Thin-Film Ceramic Coatings under Lubricated Sliding Contact," Thin Film Solid 569 (2014) 70–75. DOI: 10.1016/j.tsf.2014.08.008

3. C. Lorenzo-Martin, O.O. Ajayi, R.E. Cook, R. Arenal, and J. Mabon, "Durability of Tribochemical Surface Films under Severe Contact Conditions," Tribology Frontiers Conference, October 26–28, 2014, Chicago, IL, USA.

4. C. Lorenzo-Martin, O.O. Ajayi, and K. Hartman, "Effect of Base Fluid Viscosity on Friction and Wear Behavior under Boundary Lubrication Regime," Society of Tribologists and Lubrication Engineers Annual Meeting, May 17–21, 2015, Dallas, TX.

5. Oyelayo Ajayi, Cinta Lorenzo-Martin, and George Fenske, "Phenomenological Modeling of Lubricant Film Formation and Performance," Fuels and Lubricants, FY 2014 Annual Report.

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: US20150087566A1.

III.13 Compatibility of ZDDP and Ionic Liquid Anti-Wear Additives with Hard Coatings for Engine Lubrications

Overall Objectives

- Investigate the compatibility of engine lubricant anti-wear (AW) additives, specifically conventional zinc dialkyldithiophosphate (ZDDP) and newly developed ionic liquids (ILs), with selected commercial hard coatings
- Provide fundamental understanding to guide future development of engine lubricants

Fiscal Year (FY) 2015 Objectives

- Further understand the tribochemical interactions between AW additives and non-metallic coatings in boundary lubrication regime, and investigate the AW coating compatibility in mixed lubrication regime
- Reveal the wear process and tribofilm formation via wear debris characterization

FY 2015 Accomplishments

- Oak Ridge National Laboratiry Significant Event Award
- Five journal papers
- Five conference presentations
- New wear mechanism discovered for the excessive material removal on the steel counterface against diamond-like carbon (DLC) coating, DLC-catalyzed tribocorrosion
- Evolution of wear debris generation revealed and correlated to the wear process and tribofilm formation

Future Directions

This task of AW coating compatibility has successfully been concluded and we are shifting the efforts to investigate the compatibility between AW additives and non-ferrous engine bearing alloys, specifically bronze and aluminum alloys, in FY 2016. ■

Introduction

Current engine lubricants and their additive packages were designed for ferrous alloy bearing surfaces. The compatibility between oil AW additives and non-metallic hard coatings is little known. Fundamental understandings gained in this study will help guide future development of engine lubricants. A synergistic lubricant–coating combination will potentially maximize the benefits in fuel economy.

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Approach

We experimentally studied the friction and wear behavior for selected non-metallic hard coatings lubricated by selected AW additives using tribological bench tests in well-defined conditions. The tribochemical interactions between the AW additives and the coating surfaces were investigated via comprehensive tribofilm characterization.

Results

Investigate the Compatibility between AW and Hard Coatings

In FY 2014, we had reported a significantly increased wear on the steel ball that rubbed against a hydrogenated DLC (a-C:H) coating in a base oil containing 1% ZDDP or phosphonium-organophosphate IL (IL-A), as shown in Figure 1b [1]. In contrast, a boride coating, $AlMgB_{14}$-TiB_2, was tested in the same condition as that for a-C:H DLC, but showed no detrimental impact on the steel ball. In FY 2015, we further explored the increased wear phenomenon for the steel ball rubbing against a non-hydrogenated DLC coating (ta-C DLC). A similar trend

was observed; the addition of 1% ZDDP into the base oil resulted in an 80% increase in the ball wear. On the other hand, when 1% of a non-phosphate IL, phosphonium–carboxylate (IL-B, Figure 1a), was used instead, no such wear increase was occurred on the steel ball (see Figure 1b) [1]. Results clearly indicate incompatibility between phosphate-based AW additives and DLC coatings.

Here we propose a new mechanism for such excessive wear of the steel ball when rubbing against DLC; DLC catalyzes tribochemical reactions between the phosphate AW additives and the steel ball surface, causing tribocorrosion. Both sp2 C [2] and sp3 C [3] have been reported with catalytic effects. Without catalysis, the phosphate-based AW additives (ZDDP or IL) form a dense, protective tribofilm on the steel surface as normally observed. However, in presence of sp2 and/or sp3 C, tribochemical reactions would occur at an unacceptably high rate, as illustrated in Figure 1c, which is expected to generate a porous tribofilm. If no AW, the compressed wear particles are likely to be removed from the surface due to poor bonding. Further illustrated in Figure 2a, when an AW is present, the wear particles react with AW molecules and transform to a dense protective layer. When tribocorrosion occurs, a primitive, porous tribofilm containing larger debris is expected to form. Figure 2b presents the transmission electron microscope cross-sectional images of two tribofilms on the steel ball against the DLC and steel flats, respectively. The tribofilm on the ball against steel has a double layer structure containing a top porous layer of fine nanoparticles and a bottom dense amorphous layer. In contrast, the tribofilm on the ball against DLC contains only a porous layer of nanoparticles, which supports our hypothesis of tribocorrosion [1].

Stribeck curves were generated using a steel cylinder sliding against steel, DLC (a-C:H), and TiB_2 flats in polyalphaolefin (PAO) 4 cSt base oil, PAO + 1% ZDDP, and PAO + 1% IL by using a variable load-speed bearing tester. DLC exhibited little changes between cycles, while the TiB_2 surface, on the other hand, produced a lower friction after running-in. The TiB_2 flat surface was observed with some material transferred from the steel

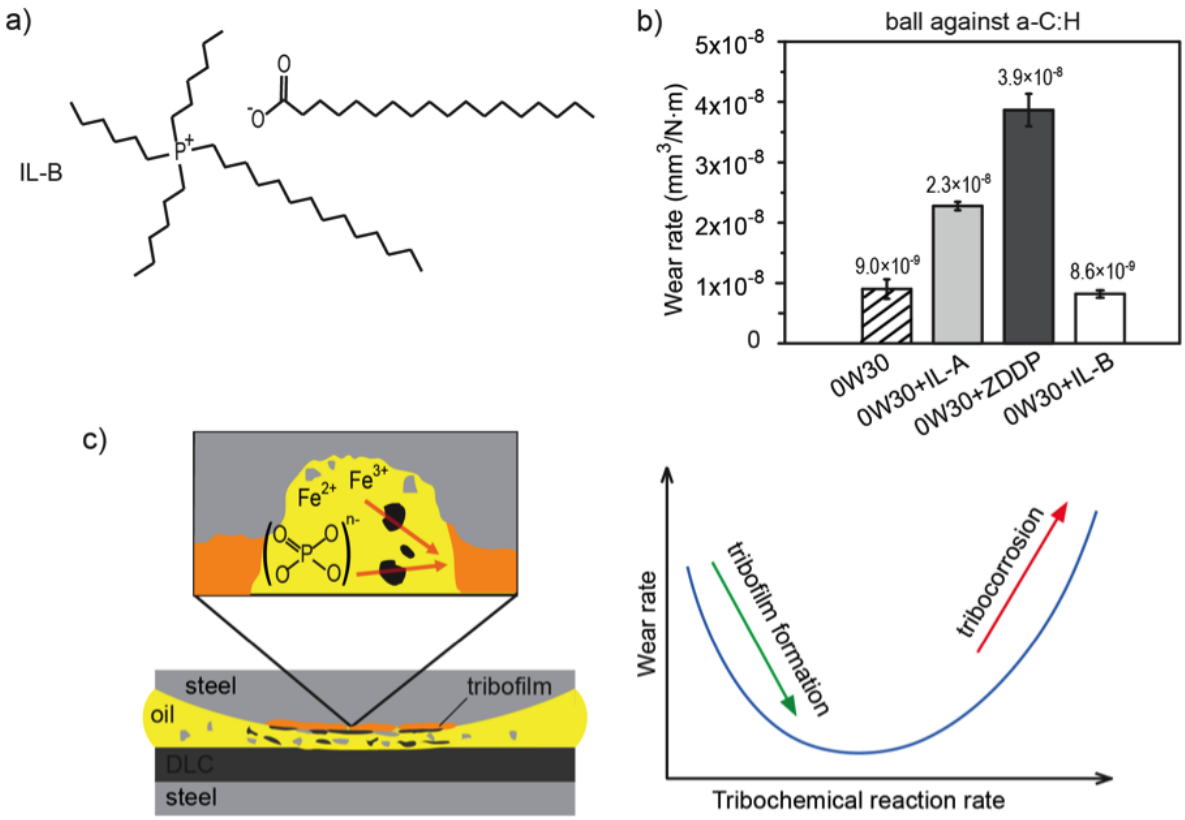

Figure 1. Unlike ZDDP or phosphonium–phosphate IL (IL-A), phosphonium–carboxylate IL (IL-B) does not cause increased wear on the steel ball against DLC. (a) Molecular structure of IL-B. (b) Wear rates of the steel balls against a-C:H DLC in oils containing three different additives. (c) Proposed mechanism: phosphate additives (ZDDP or IL-A) normally react with the steel ball surface to form a protective tribofilm; however, when catalyzed by sp2 and/or sp3 C, tribochemical reactions occur at an unacceptably high rate to cause rapid material removal [1].

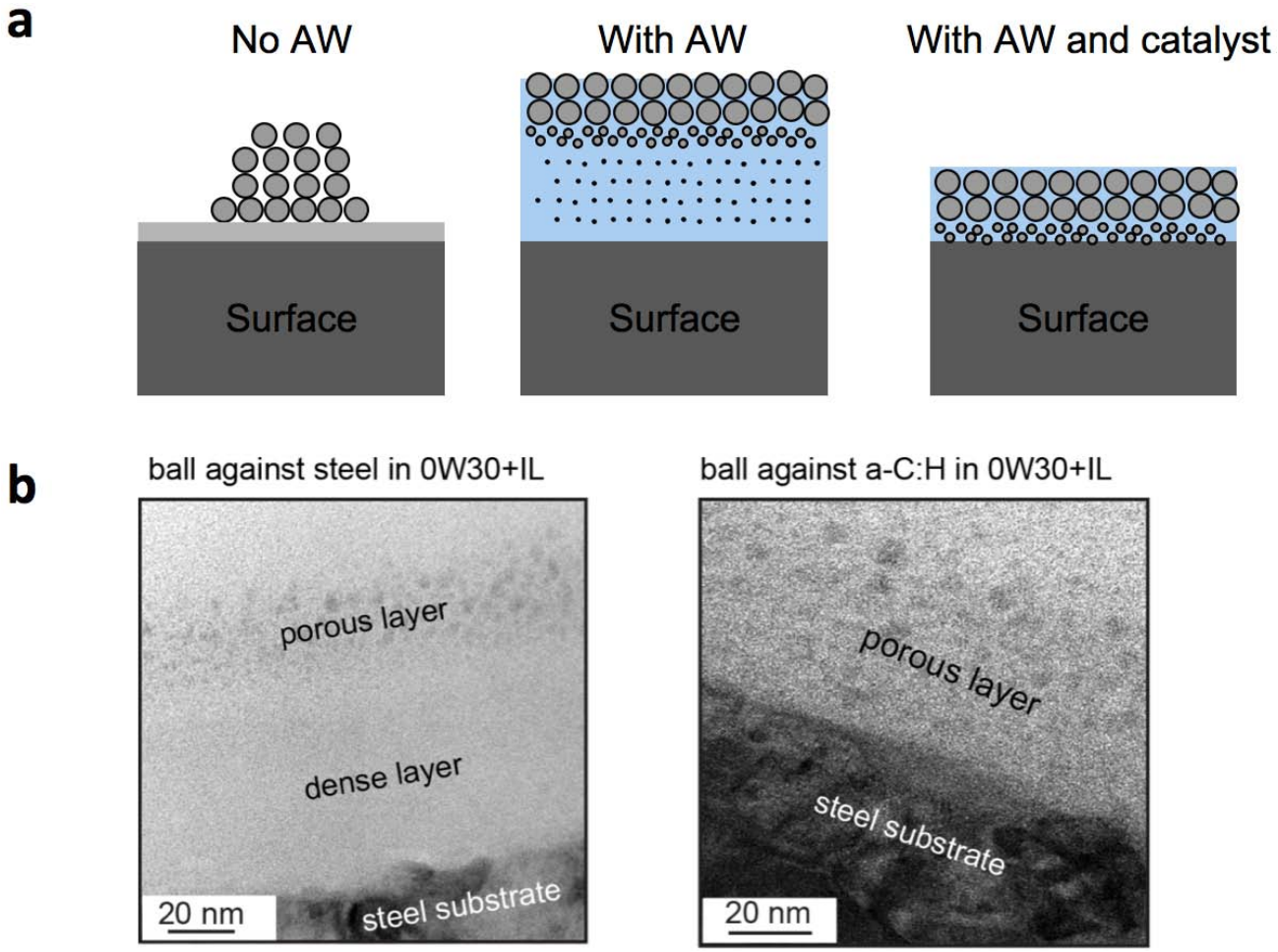

Figure 2. (a) Schematic representation of tribofilms (not in scale) under different conditions. (b) Cross-sectional bright field transmission electron microscopy images of the sample lubricated by 0W30+IL-A trihexyltetradecylphosphonium bis(2-ethylhexyl) phosphate ([P_{66614}][DEHP]).

ball, but there is neither measurable material loss nor transfer on the DLC flat.

Reveal Wear Debris Evolution to Correlate with Wear Process and Tribofilm Formation

Figure 3a shows the scanning electron microscope images of the wear scar of the steel ball. The worn surface shows three distinctive regions. Region 1 is relatively smooth and takes the most of the wear scar, and Region 2 is rather rough. Region 3 is a stripe of dark patches that runs parallel to the direction of the sliding. The two-dimensional profile corresponds to the marked line after subtracting ball curvature and shows grooving and protrusion of Regions 2 and 3, respectively. In Figure 3b, focused ion beam-aided cross-sectional scanning transmission electron microscope (STEM) images illustrate an oxidation layer of 5 nm that has a continuous coverage of the surface of Regions 1 and 2. The patches of Region 1 are part of a discrete adhesive tribofilm with its thickness up to 250 nm with randomly embedded nanoparticles. The stresses encountered by the three regions and the difficulties of wear debris removal both are ranked as 2 > 3 > 1. Region 1 is much smoother than the other two regions because of the little trapped wear debris and low contact stress. For Region 2, the highest contact stress worked collectively with the large amount of trapped wear debris, resulting in three-body abrasive wear that was accompanied by micro-scuffing. The high contact stress also reduced the longevity of adhered tribofilm, causing it to be removed swiftly and leaving only the natural oxidation layer of steel. For Region 3, wear debris particles were regularly removed while some of them were able to adhere to the surface, due to the medium contact stress. Cross-sectional energy dispersive X-ray spectroscopy (EDS) elemental maps in Figure 3b confirm that the tribofilms formed in the base oil are mainly composed of iron oxides.

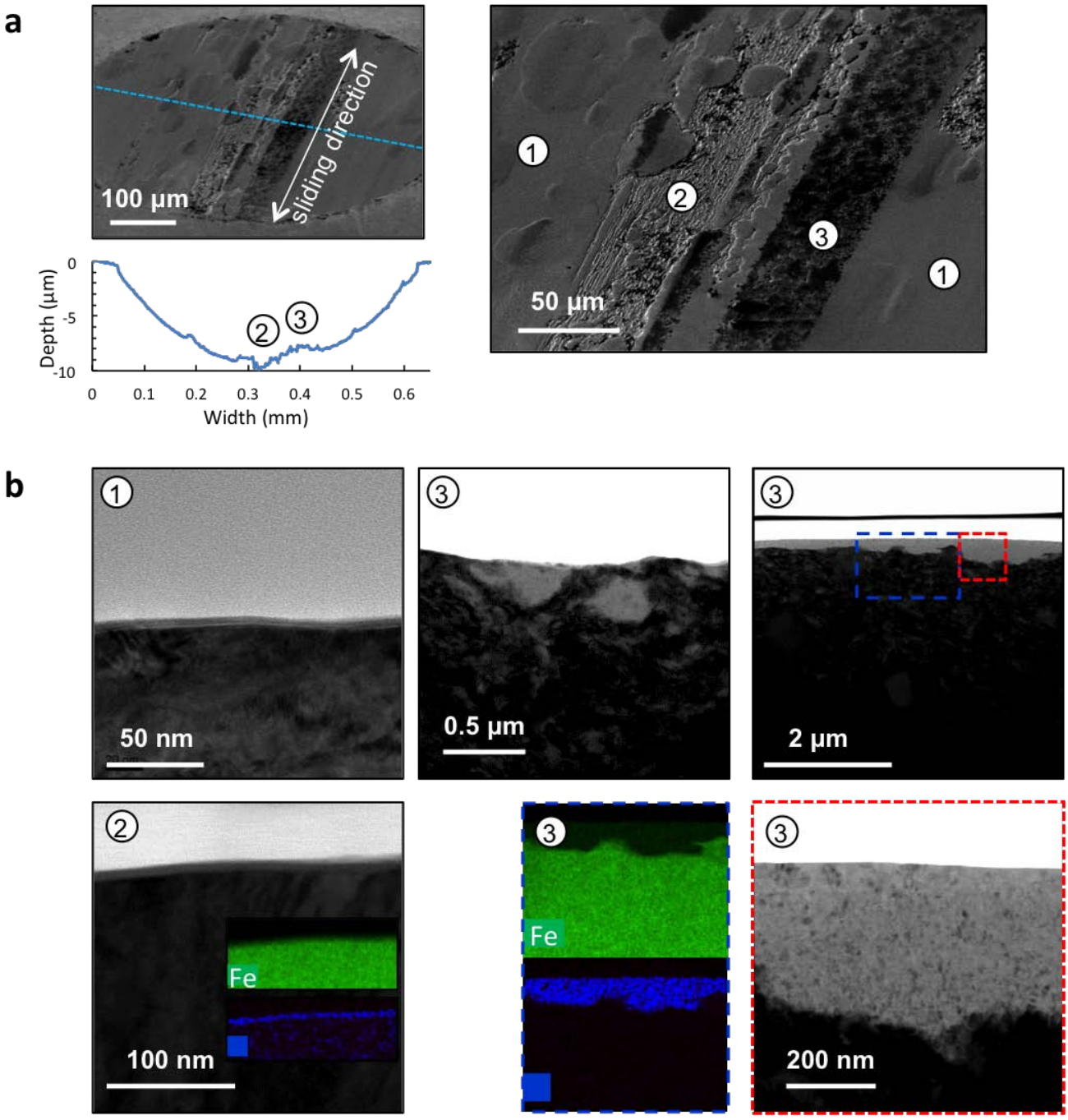

Figure 3. (a) Scanning electron microscope images of the wear scar on a steel ball against a steel flat lubricated by SAE 0W-30 base oil. (b) Cross-sectional STEM images and EDS elemental maps.

Wear debris analysis complements the characterization of worn surface and tribofilm. Figure 4a shows the STEM images of aggregates of wear debris particles from the steel–steel contact in 0W-30. Metallic clusters (magnified image) and spindle-like particles (indicated by the arrow) are scattered in the aggregate. The spindle-like particle contains Fe and O, indicated by EDS mapping. The morphological change of wear debris reflects a dynamic and evolutionary process. The size of wear particles is inversely proportional to the received energy during sliding, and the big wear particles are ground down during tribotests, as illustrated in Figure 4b. The collision between asperities generates wear debris particles of varied sizes. The grinding process removes edges and vortexes of debris particles and reduces their size. When the particles get small enough, the tribofilm would

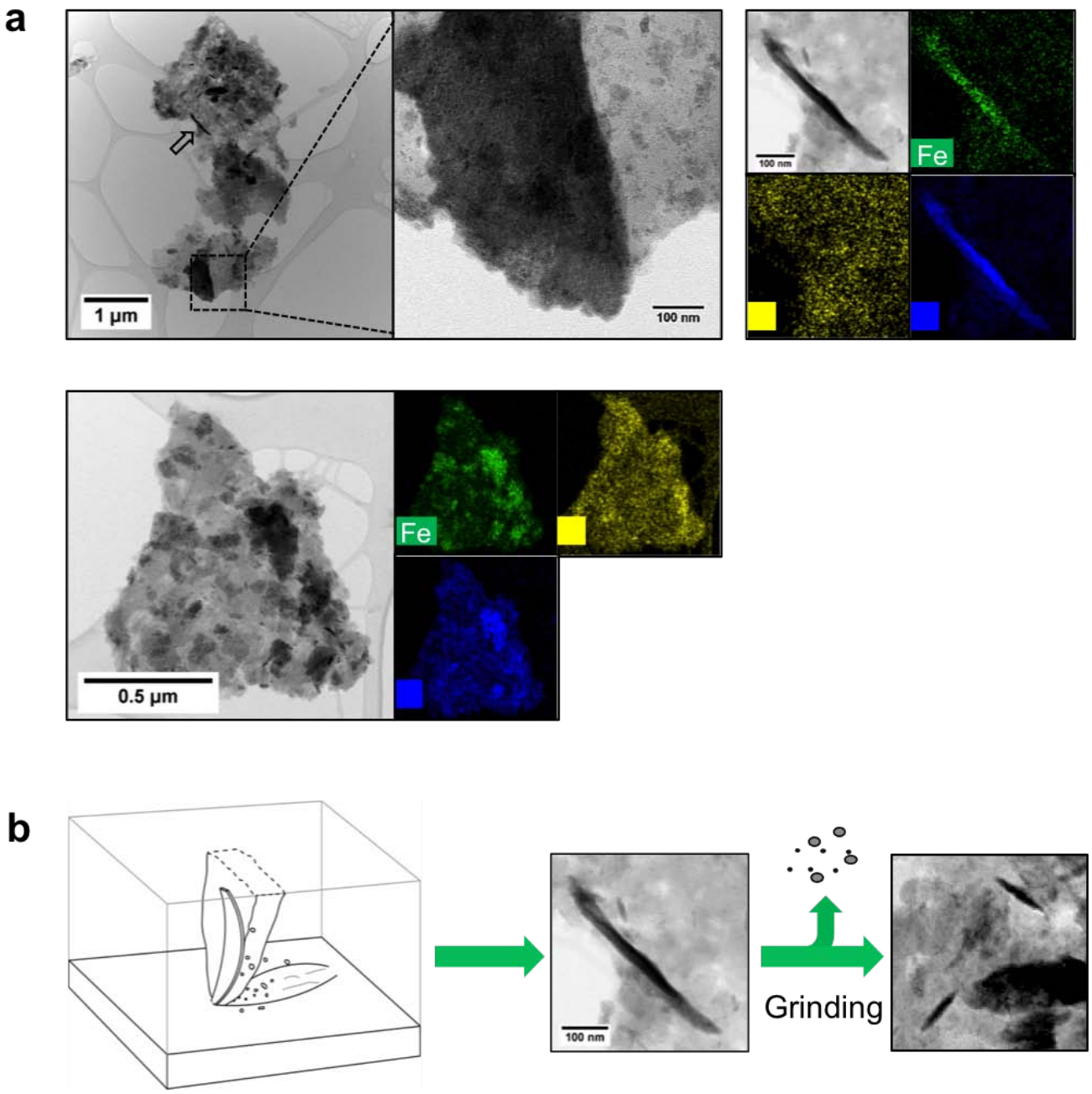

Figure 4. (a) STEM images and EDS elemental maps of the aggregates of wear particles from steel-steel contact in the base oil; (b) Evolution of wear debris from large to small with edges and vortexes lost in the process.

incorporate them by embedding with the matrix. When an AW is present at the interface, the AW molecules chemically react with the wear debris to incorporate and bind the reaction products and particles to form a protective tribofilm.

Conclusions

- A significantly increased wear rate was observed on a steel ball when it was rubbed against a DLC coating in the presence of an organophosphate AW additive. Such detrimental effects do not apply to non-carbon hard coatings or non-phosphate additives. The ball wear is proposed to be accelerated by DLC-catalyzed, high-rate tribochemical reactions with the phosphate additives.
- The compatibility results between non-metallic coatings and lubricant AW additives provide new insights for future development and implementation of advanced lubricants and materials.

- The wear debris characterization deepens fundamental understanding if the wear process and the dynamics of tribofilm formation.

References

1. Y. Zhou, D.N. Leonard, H.M. Meyer, H. Luo, J. Qu, *Advanced Materials Interfaces* (2015) 2(15) DOI: 10.1002/admi.201500213.

2. H. Huang, J. Huang, Y.M. Liu, H.Y. He, Y. Cao, K.N. Fan, *Green Chem* 2012, 14, 930; H.L. Fei, R.Q. Ye, G.L. Ye, Y.J. Gong, Z.W. Peng, X.J. Fan, E.L.G. Samuel, P.M. Ajayan, J.M. Tour, *Acs Nano* 2014, 8, 10837.

3. Y. Cao, X. Luo, H. Yu, F. Peng, H. Wang, G. Ning, *Catalysis Science & Technology* 2013, 3, 2654; D.S. Su, N. I. Maksimova, G. Mestl, V. L. Kuznetsov, V. Keller, R. Schlogl, N. Keller, *Carbon* 2007, 45, 2145.

FY 2015 Publications/Presentations

1. Y. Zhou, D.N. Leonard, H.M. Meyer, H. Luo, J. Qu, "Does the use of diamond-like carbon coating and organophosphate lubricant additive together causes excessive tribochemical material removal?" *Advanced Materials Interfaces* (2015) 2(15) DOI: 10.1002/admi.201500213.

2. J. Qu, H.M. Meyer III, Z.-B. Cai, C. Ma, H. Luo, "Characterization of ZDDP and ionic liquid tribofilms on boride and DLC coatings," *Wear* 332-333 (2015) 1273–1285.

3. Z.-B. Cai, Y. Zhou, J. Qu, "Effect of oil temperature on tribological behavior of a lubricated steel−steel contact," *Wear* 332-333 (2015) 1158–1163.

4. Y. Zhou, J. Dyck, T. Graham, H. Luo, D.N. Leonard, J. Qu, "Ionic liquids composed of phosphonium cations and organophosphate, carboxylate, and sulfonate as lubricant anti-wear additives," *Langmuir* 30 (2014) 13301–13311.

5. Z.-B. Cai, H.M. Meyer III, C. Ma, M. Chi, H. Luo, J. Qu, "Comparison of the tribological behavior of steel-steel and Si_3N_4-steel contacts in lubricants with ZDDP or ionic liquid," *Wear* 319 (2014) 172–183.

6. Y. Zhou, D. Leonard, H. Luo, J. Qu, "Characterization of wear debris generated in steel-steel and steel-DLC contacts lubricated by an ionic liquid additized oil," *2015 STLE Tribology Frontiers Conference*, Denver, October 25–27, 2015.

7. Y. Zhou, H.M. Meyer III, D.N. Leonard, H. Luo, J. Qu, "Compatibility of ZDDP and ionic liquid with DLC and boride coatings," *STLE 70th Annual Meeting*, Dallas, May 17–21, 2015.

8. J. Qu, H.M. Meyer III, Z.-B. Cai, C. Ma, H. Luo, "Characterization of ZDDP and ionic liquid tribofilms on boride and DLC coatings," *20th International Conference on Wear of Materials,* Toronto, Canada, April 12–16, 2015.

9. Z.-B. Cai, Y. Zhou, J. Qu, "Effect of oil temperature on tribological behavior of a lubricated steel−steel contact," *20th International Conference on Wear of Materials,* Toronto, Canada, April 12–16, 2015.

10. J. Qu, H.M. Meyer III, Y. Zhou, Z.-B. Cai, C. Ma, H. Luo, "Tribofilm Characterization for Understanding the Compatibility Between Lubricant Anti-Wear Additives and Non-Metallic Coatings," *2014 STLE Tribology Frontiers Conference*, Chicago, October 26–28, 2014.

Special Recognitions and Awards/ Patents Issued

1. J. Qu, Y. Zhou, D.N. Leonard, H.M. Meyer, H. Luo, ORNL Significant Event Award, "Discovery and fundamental understanding of incompatibility between diamond-like-carbon coatings and lubricant additives provide new insights for future materials development," 2015.

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.

IV.1 Cellulosic Biomass-Derived Oxygenates as Drop-In Fuel Blend Components

Overall Objective

- 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) 2015 Objectives

- Research the knock resistance properties of biomass oxygenates in more detail, including temperature effects on autoignition and kinetics
- Evaluate particle mass (PM) and number (PN) emissions from a broader range of oxygenate structures and fuel properties
- Assess dimethylfuran (DMF) oxidative instability and determine if antioxidant additives can mitigate this issue for this promising high octane gasoline oxygenate

FY 2015 Accomplishments

- The oxygenates ethanol, isobutanol, anisole, 4-methylanisole (4-MA), 2-phenylethanol (2-PE), 2,5-DMF, and 2,4-xylenol were blended into a blendstock for oxygenate blending (BOB) at levels ranging from 10 to 25 volume percent (vol%). The base gasoline and its blends with p-xylene and p-cymene were tested as controls. Gasoline properties including Research Octane Number (RON), Motor Octane Number (MON), distillation curve, and vapor pressure were measured. Detailed hydrocarbon analysis was used to estimate heat of vaporization (HOV) and particulate matter index (PMI).
- Knock-limited spark advance (KLSA), PM, and PN were measured in a gasoline direct injection engine.
- Oxidation of the promising high-RON oxygenate 2,5-DMF at 100°C in the presence of oxygen was confirmed and studied in additional detail.

Future Directions

The project "Evaluation of Cellulosic Biomass-Derived Oxygenates as Drop-In Fuel Blend Components" was completed in 2015. Work to evaluate fuel performance properties and combustion of a wider range of biomass-derived oxygenates and hydrocarbons will continue under the New Fuels and Vehicle Systems Optima program in 2016, a collaboration among several DOE national laboratories. The National Renewable Energy Laboratory will:

- Evaluate the performance properties of a wide range of oxygenate classes that can be produced from biomass by thermochemical, chemical, biochemical, or hybrid means.
- Determine how RON and HOV interact in terms of extending knock limits, and determine if or how HOV can interact with aromatics to increase PM emissions; develop improved methods for measuring HOV ■

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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 approaches produce a high oxygen content product (40–60 weight percent [wt%]) that must be upgraded. Hydroprocessing at high pressures, high temperatures, and low space velocities is required to remove the oxygen from these crude products. There is a clear economic advantage to removing only a portion of the oxygen from the pyrolysis oil [1]. The projected cost of hydroprocessing nearly doubles when the targeted oxygen content in the final product is reduced from 5 wt% to 0.02 wt% oxygen. This project examined the fuel performance of oxygenates observed in partially hydroprocessed biomass pyrolysis oils [2] and oxygenates produced by depolymerization or biochemical

means. Critical fuel properties were measured for pure component oxygenates and their blends with gasoline. Blends with gasoline were tested in a gasoline direct injection engine to assess performance.

Approach

Oxygenated compounds were reagent grade chemicals obtained from commercial suppliers. These were blended into a 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 PN and particle size distribution measurements. An AVL Micro-Soot Sensor was used to measure PM mass from the raw exhaust in real time.

Results

KLSA was measured in spark timing sweep experiments at a nominal load of 925 kPa net mean effective pressure (NMEP), 1,500 rpm, and intake air temperature of 35°C (measured at the intake port). Relatively low engine speed was used because longer combustion duration increases exposure of the unburned end-gas to heat and pressure making the engine more sensitive to knock. The load and intake air temperature were selected to ensure the engine could operate on the 88 RON hydrocarbon base gasoline. Figure 1 plots KLSA versus RON. In the octane index (OI) proposed by Kalghatgi [5] (Equation 1 where K is a constant at a given engine operating conditions and S-RON-MON). RON is the case where K = 0 and linear regression produced a correlation coefficient, $R^2 = 0.870$. A very slightly improved correlation is obtained for K = 0.25. From this analysis, it appears that K for this engine and operating condition approximates the RON method. This is reasonable given the low intake air pressure and temperature, near-maximum brake torque spark advance, and modest compression ratio [6,7].

$$OI = RON - K_* S \quad (1)$$

Figure 2 shows the correlation between PM concentration and PMI, while Figure 3 shows the correlation between

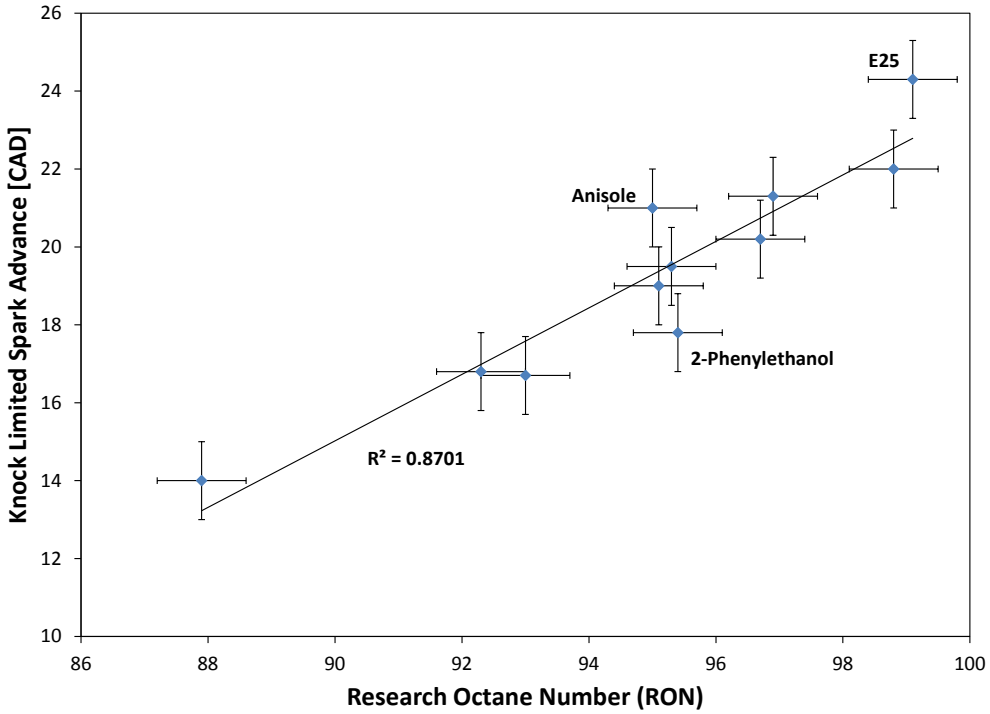

Figure 1. KLSA vs. RON for oxygenate-BOB blends. X-axis error bars are ±0.7 RON units (D2699 stated reproducibility for the RON range 90–100). Y-axis error bars are ±1.0 crank angle degrees (CAD) based on results of repeated measurements.

PN concentration and PMI. For most fuels there was good correspondence of PM-mass and PN emissions with PMI; however, in both cases results for p-cymene, 2,4-xylenol and 2-PE were not included in the linear regression as they fall significantly away from the trend for other fuels ($R^2 = 0.95$), emitting less PM than predicted by PMI. The lowest PM-mass and PN emissions were observed for E50, which also had the lowest PMI (0.58) and the highest fuel oxygen content. Isobutanol and DMF slightly increased PM-mass and PN over the base gasoline at 2,500 rpm/13 bar despite having slightly lower PMIs (0.92 and 1.0, respectively) which may simply reflect small measurement errors in both PM emissions and in the parameters used to estimate PMI. However, higher isobutylene emissions have been measured from an isobutanol–gasoline fueled vehicle, so it is possible that in-cylinder isobutylene formation contributed to molecular weight growth, and therefore to PM [8]. In the case of DMF, once the furan ring opens, reactive olefins are likely produced, which similarly may lead to molecular weight growth.

The difference in results between 4-MA and p-cymene, which have the same PMI, was also unexpected because they have nearly identical boiling points and vapor pressures (at 443 K). Yet 4-MA produced higher PM and PN emissions. Studies of anisole pyrolysis show that its decomposition proceeds through homolysis of the O–CH_3 bond to the phenoxy radical. This further decomposes to cyclopentadienyl radical, which can couple to form naphthalene-initiating molecular weight growth [9,10]. No similar route to phenoxy exists for aromatic hydrocarbons, which must add oxygen to the ring, so p-cymene may be substantially inert under similar thermal conditions. Thus, while the points we chose to include in the regression suggest that p-cymene falls below the trend indicated by PMI; given that PMI was developed for hydrocarbons, this may be fortuitous, and in reality 4-MA falls above the trend. Taken as a whole, these observations for isobutanol, DMF, and 4-MA suggest that combustion effects may exist for blending some oxygenates with gasoline that are not captured by the current PMI relationship (Equation 2),

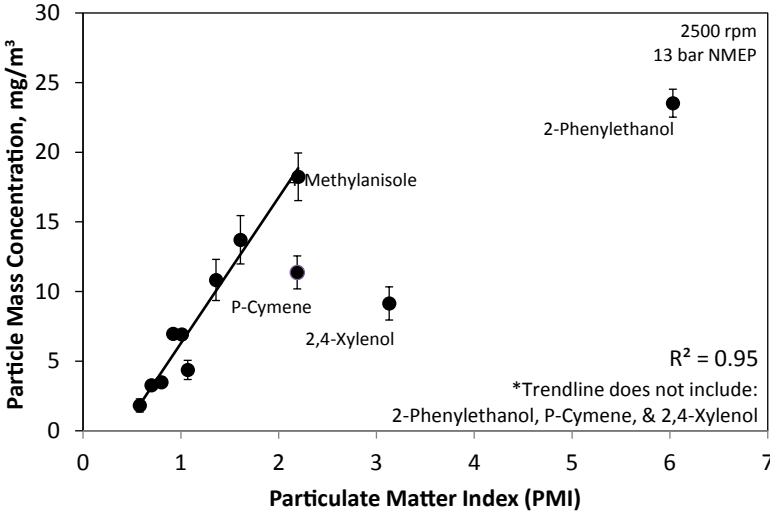

Figure 2. PMI correlation with PM-mass from 2,500 rpm and 13 bar NMEP.

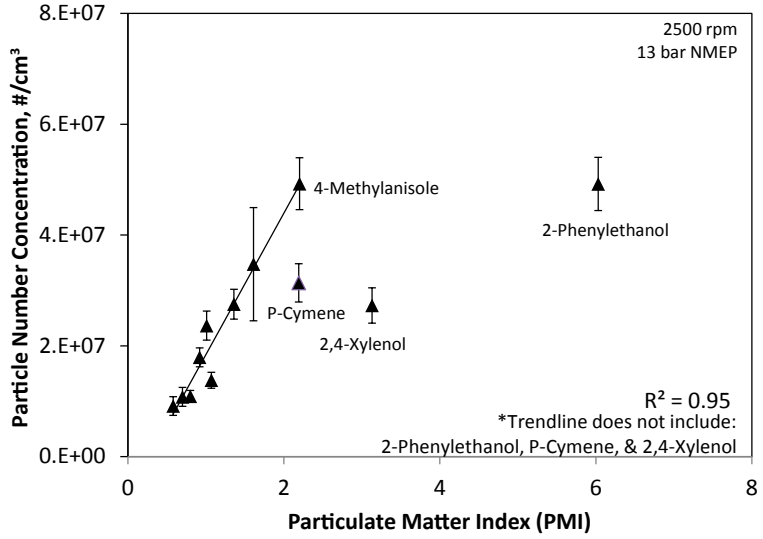

Figure 3. PMI correlation with total PN concentration from 2,500 rpm and 13 bar NMEP.

$$PMI = \sum_{i=1}^{n}\left[\frac{(DBE_i + 1)}{VP(443K)_i} \times Wt_i\right] \qquad (2)$$

where DBE is the double-bond equivalent and VP is the vapor pressure at 443 K. In comparing results for both PM and PN to the PMI predicted trend, both 2-PE (PMI = 6.0) and 2,4-xylenol (PMI = 3.1) are not as high as expected. Both blend components boil above 200°C, significantly increase blend the 90% distillation temperature (T_{90}), and have the lowest vapor pressures (at 443 K) of all oxygenates tested. The T_{90} for the 2-PE blend is well above the allowable T_{90} limit for gasoline in ASTM D4814. The reason for the lower than expected PM and PN emissions for 2-PE and 2,4-xylenol may be that they

do not fully evaporate and burn. The T_{90} limit for gasoline exists, in part, to protect engines from accumulation of unburned fuel in the lubricant. While anecdotal, we observed by smell that the engine lube oil retained the four lowest vapor pressure fuels, which all have a distinctive odor.

DMF has been considered as a highly promising biomass-derived high-octane gasoline component [11] whose combustion kinetics and engine combustion performance have been studied in detail [12,13]. We initially tested a 13 vol% blend of DMF in BOB on the ASTM D873 test, which provides a quantitative measure of the tendency for fuels to form gums under accelerated thermal and oxidative aging conditions. In this test the fuel is held at 100°C under 700 kPa of oxygen for 16 hours, and the mass of insoluble material (gum) formed is determined. The DMF blend produced over 700 mg/100 mL (insoluble gum). This experiment was replicated with similar results. The gum is likely formed by an oxidation reaction because a 20 vol% DMF–gasoline blend can fail the ASTM D525 stability test. D525 uses the same apparatus and conditions as D873, but the pressure is measured over time to determine the oxidation induction time. Fuels with induction times exceeding 240 minutes meet the ASTM D4814 specification requirements. The reaction was also shown to occur at 100°C and atmospheric pressure.

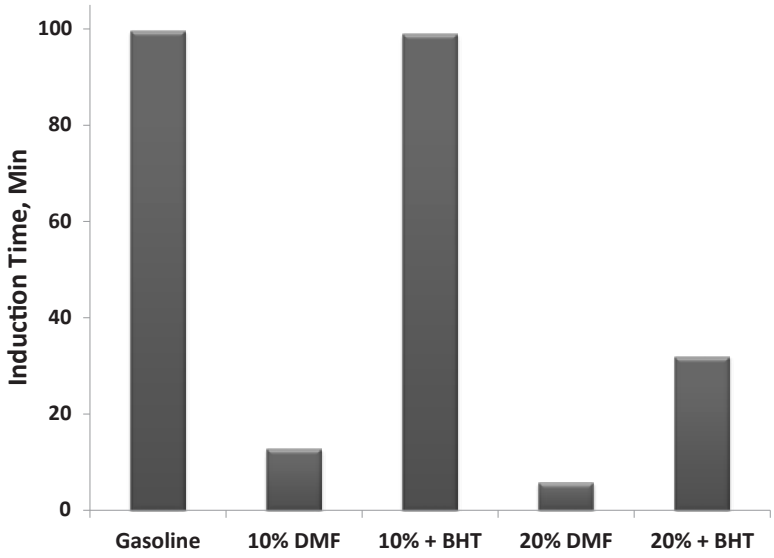

Figure 4. Effect of 1,000 ppm of BHT on stability of 10 vol% and 20 vol% DMF blends.

The residue or gum formed was observed to be an insoluble liquid. Analysis by gas chromatography–mass spectrometry and C^{13} nuclear magnetic resonance demonstrated that the liquid consisted almost entirely of 3-hexene-2,5-dione, a product of the DMF ring opening after addition of oxygen. In some cases, this compound appears to have undergone polymerization to form higher molecular weight species. Experiments with 2-methylfuran and furan show that these compounds can add oxygen to form gasoline-insoluble lactones, but do not undergo ring opening under these conditions. Because the furans appear to react stoichiometrically with oxygen rather than in a peroxidation chain reaction, antioxidant additives are expected to be relatively ineffective. We observed that 1,000 ppm of butylated hydroxy toluene (BHT) was required to preserve the stability of a 10 vol% DMF-isooctane blend (Figure 4) but was insufficient for a 20 vol% blend. A typical butylated hydroxy toluene treat rate in gasoline is less than 100 ppm. Automobile fuel systems commonly achieve temperatures of 100°C, suggesting that there will be significant practical difficulties in utilization of DMF and other furanics as gasoline blend components.

Conclusions

Measurement of KLSA for oxygenate–gasoline blends shows a range of knock resistance that correlates well with RON for the 1,500 rpm/925 kPa engine operating condition.

Molecules with relatively a low boiling point, high vapor pressure, and lack of unsaturation had little effect on PM or PN emissions. The biomass-derived aromatic oxygenates caused a significant increase in both PM and PN (by a factor of 2 to 3) relative to the base 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.

For most fuels, PMI was well correlated with PM and PN. However, high boiling, low vapor pressure oxygenates such as 2-PE produced less PM and PN than predicted by PMI, likely because they do not fully evaporate and are swept into the lube oil.

Oxidation of the high RON oxygenate 2,5-DMF at 100°C in the presence of oxygen was confirmed. The decomposition product is 3-hexene-2,5-dione, which is insoluble in gasoline and also appears to polymerize to secondary products. 2-methylfuran and furan were also shown to decompose into gasoline-insoluble lactones.

References

1. Arbogast, S., Bellman, D., Paynter, J.D., Wykowski, J. *Fuel Proc. Techn.* **104** 121–127 (2012).

2. Christensen, E., Chupka, G., Luecke, J., Alleman, T.L., Iisa, K., McCormick, R.L., Franz, J.A., Elliott, D.C. *Energy Fuels* **25**(11), 5462–5471 (2011).

3. Christensen, E., Yanowitz, J., Ratcliff, M., McCormick, R.L. *Energy Fuels* **25** 4723–4733 (2011).

4. He, X., Ratcliff, M.A., Zigler, B.T. *Energy Fuels* **26** 2014−2027 (2012).

5. Kalghatgi, G.T. SAE Technical Paper 2001-01-3585, 2001, doi:10.4271/2001-01-3585..

6. Mittal, V., Heywood, J.B. SAE Technical Paper 2009-01-2622, 2009, doi:10.4271/2009-01-2622.

7. Amer, A., Babiker, H., Chang, J., Kalghatgi, G., Adomeit, P., Brassat, A., Gunther, M. *SAE Int. J. Fuels Lubr.* **5**(3):2012, doi:10.4271/2012-01-1634.

8. Ratcliff, M., Luecke, J., Williams, A., Christensen, E., Yanowitz, J., McCormick, R.L. *Environ. Sci. Technol.* **47** 13865–13872 (2013).

9. Pecullan, M., Brezinsky, K., Glassman, I. *J. Phys. Chem. A* **101** 3305–3316 (1997).

10. Scheer, A.M., Mukarakate, C., Robichaud, D.J., Ellison, G.B., Nimlos, M.R. *J. Phys. Chem. A* **114** 9043–9056 (2010).

11. Qian, Y., Zhu, L., Wang, Y., Lu, X. *Renewable and Sustainable Energy Reviews* **41** 633–646 (2015).

12. Sirjean, B., Fournet, R., Glaude, P.A., Battin-Leclerc, F., Wang, W., Oehlschlaeger, M.A. *J. Phys. Chem. A* **117** 1371−1392 (2013).

13. Zhong, S., Daniel, R., Xu, H., Zhang, J., Turner, D., Wyszynski, M.L., Richards, P. *Energy Fuels* **24** 2891–2899 (2010).

FY 2015 Publications/Presentations

1. Ratcliff, M.A., Burton, J., Sindler, P., Christensen, E., Chupka, G.M., Fouts, L., McCormick, R.L. "Knock Resistance and Fine Particle Emissions for Several Biomass-Derived Oxygenates in a Direct-Injection Spark-Ignition Engine," submitted.

2. Baumgardner, M.E., Vaughn, T.L., Lakshminarayanan, A., Olsen, D., Ratcliff, M., McCormick, R.L., Marchese, A.J. "Combustion of Cellulosic Biomass Based Oxygenated Components in a Compression Ignition Engine," *Energy Fuels* **29** 7317–7326 (2015).

3. McCormick, R.L., Ratcliff, M., Christensen, E., Fioroni, G.M., Burton, J., Alleman, T., Marchese, A., Olsen, D., Tian, M. "Performance of Biofuels and Biofuel Blends," DOE/VTO Annual Peer Review, June 11, 2015; Arlington, VA.

4. McCormick, R.L., Ratcliff, M., Christensen, E., Fouts, L., Luecke, J., Chupka, G.M., Yanowitz, J., Tian, M., Boot, M.D. "Properties of Oxygenates Found in Upgraded Biomass Pyrolysis Oil as Components of Spark and Compression Ignition Engine Fuels," *Energy Fuels* **29** 2453–2461 (2015).

5. Ratcliff, M., Burton, J., Sindler, P., Christensen, E., Fouts, L., McCormick, R.L. "Particle Emissions from a Direct Injection Spark Ignition Engine Fueled with Biomass Oxygenates," 25th CRC Real World Emissions Workshop, March 24, 2015; Long Beach, CA.

IV.2 Unconventional and Renewable Hydrocarbon Fuels

Overall Objectives

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

Fiscal Year (FY) 2015 Objectives

- Utilize one- and two-dimensional nuclear magnetic resonance (NMR) spectroscopy, and gas chromatographic techniques to correlate fuel's chemical substructures, i.e., types of chemical bonds, with fuel properties
- Contribute to Analytical Working Group Meetings to foster a collaborative relationship and information exchange with groups such as CanmetENERGY and the Coordinating Research Council (CRC)

FY 2015 Accomplishments

- Continued development of new NMR approaches for identifying structure–property relationships of diesel fuels, focusing on data extraction from one-dimensional NMR spectra and the two-dimensional NMR technique, single-bond proton-carbon correlation (heteronuclear single quantum coherence, or HSQC)
- PNNL and CanmetENERGY continued collaboration and further refined structure–property relationships for diesel fuel lubricity using NMR and gas chromatography–field ionization mass spectrometry data
- Developed a method for testing fuels at pressures up to 380 MPa (~55 ksi) to assess fuel phase behavior at pressures, which reflect those found in modern common rail diesel fuel injection systems
- Continued collaborative efforts with CRC through participation in the Fuels for Advanced Combustion Engines (FACE) Working Group, and contributions to CRC Advanced Vehicle/Fuel/Lubricants (AVFL) Projects: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling (AVFL-18/18a), Characterization of Advanced Alternative and Renewable Fuels (AVFL-19a), Data Mining of FACE Diesel Fuels (AVFL-23), and Measuring Fuel Heat of Vaporization (AVFL-27)

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Future Directions

- Continue to develop signal processing and correlation approaches to relate fuel properties and chemical structures
- Refine structure–property correlations for lubricity and develop additional structure–property correlations using current fuel sets
- Identify key molecular structures in unconventional fuels, which have the greatest impact on fuel properties and performance
- Introduce additional fuel sets, including diesel, gasoline, and bio-derived fuels/fuel components, to broaden the applicability of fuel structure–property correlations
- Continue to coordinate the interaction with Natural Resources Canada (CanmetENERGY) on analytical correlation of fuel properties and material compatibility investigations
- Continue collaborative work with members of the CRC's Working Group and the Alternative and Surrogate Fuels projects ■

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. Future advanced combustion and aftertreatment 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 supplement the costly and empirically derived bench tests with tests that will better represent the properties of new engine fluids, as well as to develop predictive capabilities based upon molecular structure regarding fuel properties and performance.

Approach

PNNL examined fuel-related samples, such as crude oils, diesel, diesel surrogate, gasoline, and gasoline-like samples, as well as components thereof, some of which were from bio-derived processes. Also examined were ten FACE gasoline fuels; research fuels designed to meet targeted research octane numbers, sensitivities, as well as aromatic and *n*-paraffin contents.[†] These samples were obtained through a variety of mechanisms, most notably through our collaborations with other national laboratories and with AVFL committee members.

[†]Fuels for Advanced Combustion Engine (FACE) gasoline blends were developed as research fuels under guidance from the Coordinating Research Council (CRC). A report detailing these gasoline blends may be found on the CRC website, http://www.crcao.com/publications/advancedVehiclesFuelsLubricants/index.html.

A series of analyses were undertaken with an emphasis on quantitative NMR measurements, and a secondary focus on applying analytical capabilities to fuels for the purpose of linking specific molecular substructures to fuel physical and performance properties. Analytical capabilities under development include the use of two-dimensional NMR techniques such as HSQC; two-dimensional gas chromatography; and NMR signal extraction techniques such as Complete Reduction to Amplitude-Frequency Table (CRAFT). 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. NMR signal extraction techniques, such as CRAFT, provide a quantitative assessment of individual components in complex mixtures. 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 fuel 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 2014 efforts which utilized one and two-dimensional NMR techniques to elucidate more detailed structural information from fuel samples, PNNL has continued to apply NMR spectroscopy 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 and the overall analyses have been undertaken jointly, leveraging the capabilities provided by each collaborator. 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 assigned 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. Carbons without protons attached

(such as internal, and alkyl- or naphthene-substituted aromatic carbons) are not shown in HSQC spectra, and these regions are expected to be blank. NMR resonances observed in these regions of the HSQC spectra, therefore must contain an attached hydrogen, and clearly demonstrate a limitation of relying only on discrete spectral regions in one-dimensional NMR. Figure 1 shows a side-by-side comparison of the aromatic regions of two HSQC spectra for a commercially available Saudi light crude oil (1a), and a stabilized shale oil provided by Red Leaf Resources, Incorporated (1b) with example structures shown next to each region [1]. In this figure, there are clear differences in the populations of fused-ring aromatic species, such that the overall quantities of polyaromatics are lower in the Saudi crude oil (note the relative peak intensities and increased noise level in the spectrum), and species such as phenanthrenes and pyrenes are effectively absent (regions outlined by blue, dotted lines). Present in the shale oil, but not the Saudi crude, are resonances which may be attributed to polyunsaturated species, as shown by the absence of resonances in the U-shaped region at the top of the left spectrum (1a). Additionally, both samples have very similar monoaromatic species, but the concentrations are much higher in the shale oil. Understanding the compositional differences between crude oils from conventional and unconventional sources may assist in making processing decisions that will enhance or suppress the production of specific chemical substructures.

PNNL has also been contributing to the simplified, or "surrogate," fuel project under development as part of CRC Project AVFL-18/18a [2]. Using the surrogate fuels developed as models containing known concentrations of individual components, some of which present complex NMR spectra, PNNL has been adapting the CRAFT technique for application to fuels analysis. CRAFT utilizes NMR time and frequency domain data, coupled with a Bayesian approach, to yield quantitative analyses of complex mixtures, and is an analysis method being used in metabolomics research [3]. It is hoped that by adapting this approach, individual fuel component molecules might be identified quantitatively within complex fuel NMR spectra, yielding results similar to those obtained from a detailed hydrocarbon analysis. Figure 2a shows a $^{13}C\{^{1}H\}$ NMR spectrum for a surrogate diesel fuel, and directly below Figure 2b shows the stacked, graphic output of the CRAFT analysis. Each resonance is deconvolved from the NMR free induction decay, individually Fourier transformed, and curve fit. Individual traces are compared to a spectral library, and combined to quantitate each component. Initial results suggest that there is promise for this approach, but additional development must be undertaken before reliable application to realistic fuels is possible.

PNNL has also undertaken the investigation of the high-pressure phase behavior of the CRC diesel fuel surrogates. Because of the small number of components and the high pressures attained in diesel fuel injectors,

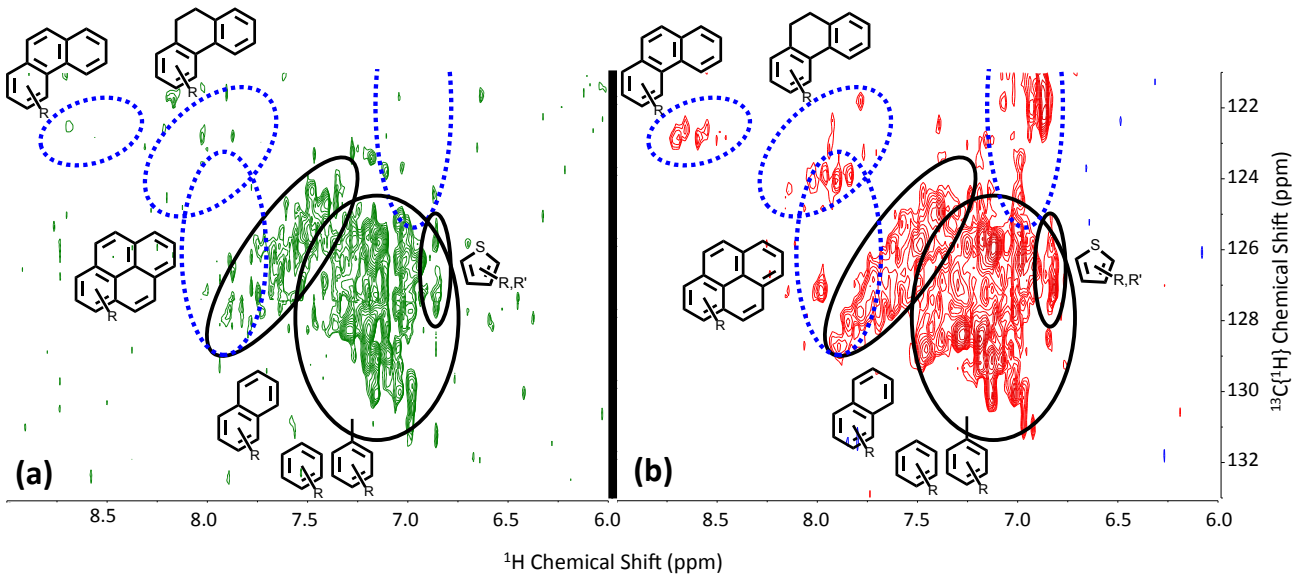


Figure 1. Side-by-side HSQC NMR spectra of a Saudi light crude oil (a) and stabilized shale oil (b). These two-dimensional NMR spectra are contour plots showing the correlation of protons attached directly to aromatic carbon atoms of the fuel components. The horizontal axis represents the ^{1}H NMR and the vertical axis represents the $^{13}C\{^{1}H\}$ NMR. The spectra highlight differences (outlined by blue dots) and similarities (outlined by black lines) in the carbon types contained within the two crude samples. Chemical structures containing representative carbon types are shown for each region.

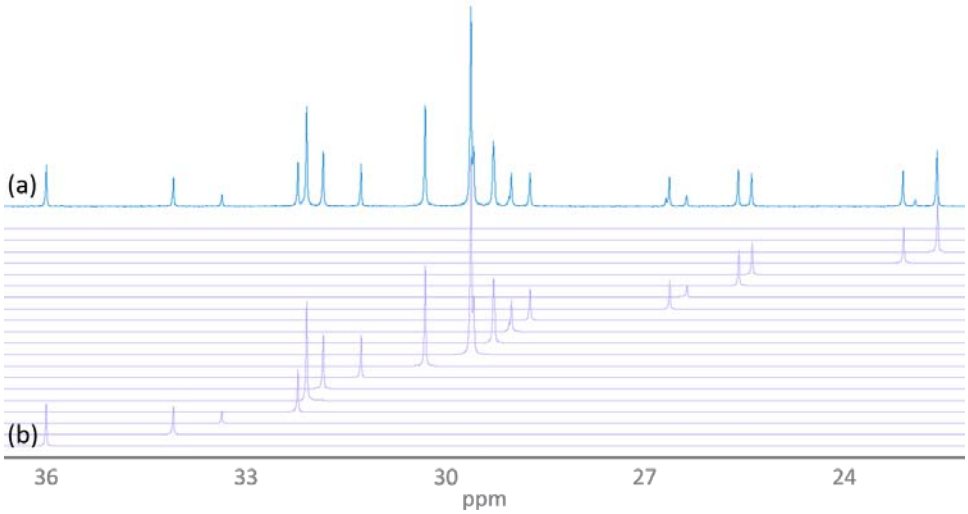


Figure 2. CRAFT analysis of a surrogate diesel fuel. (a) The aliphatic region of a $^{13}C\{^{1}H\}$ NMR spectrum from a surrogate diesel fuel, and (b) the graphic output of the CRAFT analysis, showing each resonance deconvolved from the NMR free induction decay, individually Fourier transformed and curve fit. Individual traces are compared to a spectral library, and combined to quantitate each component.

there was concern that fuel solidification may occur at certain temperatures and pressures, blocking the flow of fuel to the engine, or changing the composition of the fuel surrogate. To assess whether fuel solidification is a problem in surrogate fuel mixtures, an apparatus was developed to assess the phase behavior of fuels at temperatures and pressures likely to be experienced in the fuel system. The system pressurizes a small amount of sample in a fused-silica capillary, while maintaining tight temperature control. The sample is supercooled slightly to induce freezing, and the temperature is slowly raised to melt the solid. The final melting point temperature and pressure represent a point of solid–liquid equilibrium for a pure material, or what may be a single component of a multicomponent material. Figure 3 shows a series of photos of a diesel surrogate inside the capillary slowly melting as the temperature is increased, with the final melting point determined when the solid has melted. To validate system performance, points of solid–liquid equilibria were determined for *n*-hexadecane, and found to be in close agreement with published data (Figure 4) [4]. Figure 4 also shows a series of solid–liquid equilibria obtained for four surrogate diesel fuels and a reference diesel fuel. While this study remains ongoing, the implications for the diesel surrogates are that heated fuel delivery systems may be needed to maintain the integrity of the surrogate when system temperatures and pressures fall near or below the solid–liquid equilibrium line [2b].

In collaboration with researchers at CanmetENERGY, PNNL continued a comprehensive statistical analysis of the $^{13}C\{^{1}H\}$ and ^{1}H NMR data for four diesel fuels and distillate cuts from each fuel. This analysis addresses two questions. First, do certain NMR features attributable 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 ultralow sulfur content, and combinations of high and low diaromatic content. These fuels were fractionated into boiling point cuts to isolate viscosity effects on lubricity. Lasso regression was performed on the $^{13}C\{^{1}H\}$ NMR data for these and other test fuels. Only five $^{13}C\{^{1}H\}$ NMR regions were selected as significant for the prediction of WSD: CH_3-α-to-hydroaromatics, CH_3 in *n*-paraffins/CH_3-γ-to-aromatics, iso-paraffins, aliphatic carbons, and substituted aromatic carbons. Results of the lasso regression procedure using these five regions are provided in Figure 5. In the figure, the actual WSD is shown on the x-axis, and the corresponding predicted WSD is shown on the y-axis. Points plotted as "x" are data values used to develop the lasso model, while points plotted as "o" are values used to test the model. As indicated in the figure, the model error is 87.0 mm, while the prediction error is 92.5 mm. This represents a slightly higher error than the previous model constructed using partial least squares regression; however, the lasso regression model is simpler and easier to interpret. Namely, where the partial least squares regression model uses more than 80 H and C NMR integration regions, the lasso regression uses only five. This error is near that of the ASTM-specified reproducibility value of 90 µm,

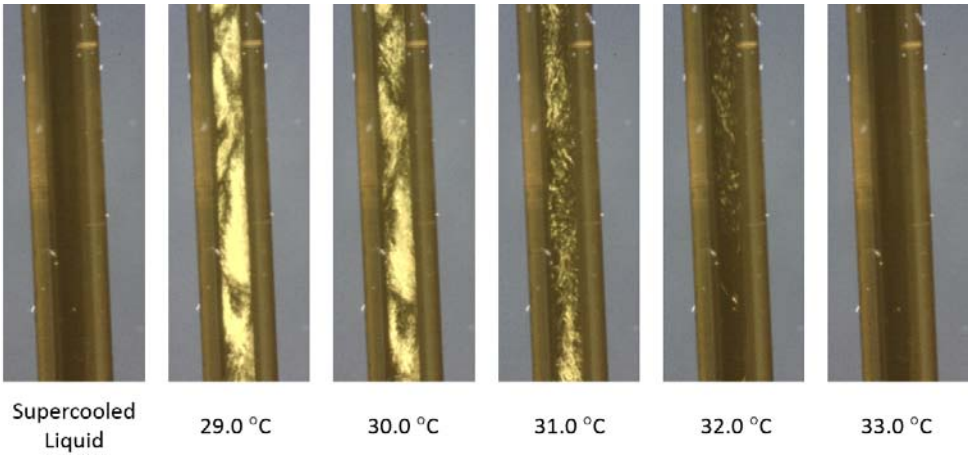


Figure 3. Determination of the final melting point of a diesel surrogate at 68.9 MPa (10,000 psi). The photos above show a fused silica capillary containing a diesel surrogate and solid derived from the surrogate. Frozen solid/crystalline material from the surrogate appears as light, highly reflective areas in each image. To determine the final melting point, the sample is slightly supercooled (left), and then warmed slowly until the solids formed from freezing have melted (right). Temperatures are listed below each image. The dark color results from a polyimide coating that protects the capillary from damage.

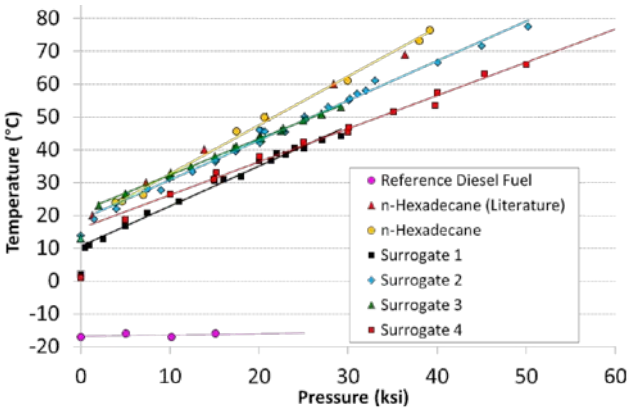
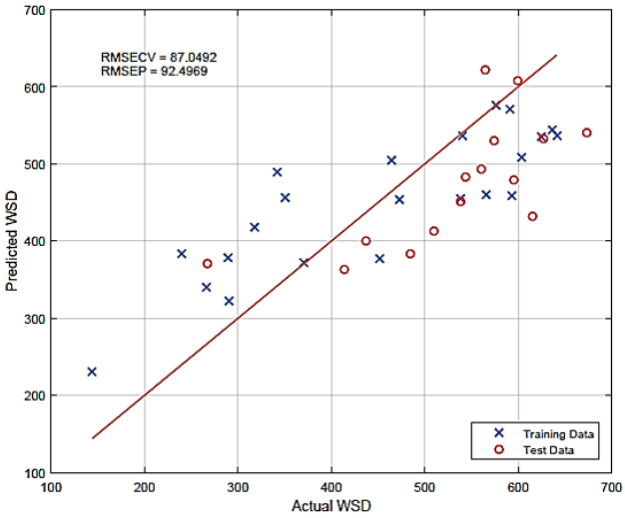


Figure 4. Chart showing the final melting points and trends for four diesel fuel surrogates, a reference diesel fuel, and *n*-hexadecane. Data points for each material are shown as indicated, as well as the trendlines resulting from the data. *n*-Hexadecane (yellow circles) was used to validate the results obtained in the high-pressure system, and compared to literature results (red triangles) [4]. Each material can be expected to remain a liquid at temperatures and pressures above its respective trendline. Below its respective trendline, a pure material will solidify, and a multicomponent material will have at least one component freeze out.

suggesting this lasso regression may be used to predict WSD with accuracy sufficient for practical application. PNNL will continue to seek correlation between chemical sub-structures and physical or performance properties in order to better predict the behavior of fuel components.



RMSECV – root mean squared error cross validation; RMSEP – root mean squared error predicted

Figure 5. Predicted versus measured WSD. Lasso regression results predicting WSD is predicted from $^{13}C\{^{1}H\}$ spectral regions corresponding to molecular substructures of interest having either strong positive or negative correlations. WSD was found to correlate strongly to regions indicative of CH_3-α-to-hydroaromatics, CH_3 in *n*-paraffins/CH_3-γ-to-aromatics, iso-paraffins, aliphatic carbons, and substituted aromatic carbons. The actual WSD is shown on the x-axis, and the corresponding predicted WSD is shown on the y-axis. Points plotted as "x" are data values used to develop the lasso model, while points plotted as "o" are values used to test the model.

Conclusions

- PNNL has continued developing a "toolkit" of NMR approaches, data analysis techniques, and statistical analyses 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, can provide quantitative structural and substructural information that is not able to be resolved in using one-dimensional NMR techniques.
- Understanding the high pressure phase behavior of simple and complex surrogate mixtures will allow the surrogates to be used by researchers to provide a standardized fuel for engine testing without questioning the chemical integrity of the surrogate system.

References

1. (a) Bays, J.T.; King, D.L.; Franz, J.A.; Gallant, T.R.; O'Hagan, M.J.; Linehan, J.C.; Patten, J.W.; Bunger, J.W., 1H and 13C NMR characterization of oil shale crude at various process stages of distillate fuel production. *Prepr. - Am. Chem. Soc., Div. Energy Fuels* **2014,** *59* (2), 767–768; (b) Bays, J.T.; King, D.L.; Franz, J.A.; Gallant, T.R.; O'Hagan, M.J.; Linehan, J.C.; Patten, J.W.; Bunger, J.W. In *1H and 13C NMR characterization of oil shale crude at various process stages of distillate fuel production*, American Chemical Society: 2014; pp ENFL-347.
2. (a) Mueller, C.J.; Cannella, W.J.; Bruno, T.J.; Bunting, B.; Dettman, H.D.; Franz, J.A.; Huber, M.L.; Natarajan, M.; Pitz, W.J.; Ratcliff, M.A.; Wright, K., Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics. *Energy & Fuels* **2012,** *26* (6), 3284–3303; (b) Mueller, C.; Cannella, W.; Bays, J.T.; Bruno, T.; DeFabio, K.; Dettman, H.; Gieleciak, R.; Huber, M.; Kweon, C.-B.; McConnell, S.; Pitz, W.; Ratcliff, M., Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties. *Energy & Fuels* **2015**, Submitted.
3. Krishnamurthy, K., CRAFT (complete reduction to amplitude frequency table) - robust and time-efficient Bayesian approach for quantitative mixture analysis by NMR. *Magnetic Resonance in Chemistry* **2013,** *51* (12), 821–829.
4. Domanska, U.; Morawski, P., Influence of size and shape effects on the high-pressure solubility of n-alkanes: Experimental data, correlation and prediction. *Journal of Chemical Thermodynamics* **2005,** *37* (12), 1276–1287.

FY 2015 Publications/Presentations

1. Bays, J.T.; King, D.L.; Jarman, K.H.; Sorenson, C., "Unconventional Hydrocarbon Fuels," *FY 2014 Progress Report for Fuel & Lubricant Technologies*, DOE Office of Vehicle Technologies Annual Report, 2014.
2. Bays, J.T.; King, D.L.; Jarman, K.H.; Linehan, J.C.; O'Hagan, M.J.; Sorenson, C., Unconventional Hydrocarbon Fuels, Project ID: FT027, presented at the U.S. Department of Energy's (DOE's) 2015 Annual Merit Review and Peer Evaluation Meetings (AMR) for the Vehicle Technologies Office, June 11, 2015 in Arlington, Virginia.
3. Bays, J.T.; King, D.L.; Linehan, J.C.; Smurthwaite, T.D. A NMR-Based Carbon-Type Analysis of Renewable Gasoline-Type Fuel Components, Draft PNNL Report, elements of which will be incorporated into a CRC Report.

IV.3 E85–Diesel Premixed Compression Ignition (EDPCI)

Overall Objectives

- Use a dual-fuel engine to reduce the petroleum usage of a Class 8 vehicle by at least 50%
- Develop and demonstrate an advanced, highly integrated combustion/aftertreatment system to achieve 2010 heavy-duty emissions compliance
- Maintain comparable vehicle performance and drivability based on system implementation into a demonstrator vehicle
- Develop the system architecture to accommodate on-board diagnostics regulations from the design state to better enable product commercialization

Fiscal Year (FY) 2015 Objectives

- Design cylinder head to integrate the port fuel injection (PFI) system and in-cylinder pressure sensors
- Design a dual-fuel combustion system capable of meeting emissions and performance targets
- Perform engine testing to support and validate combustion and control system development

FY 2015 Accomplishments

- Demonstrated 54% petroleum reduction over Supplemental Emissions Test (SET) modes
- Demonstrated a full torque curve and operation over the entire engine map
- Successfully integrated PFI system and in-cylinder pressure sensors into cylinder head
- Designed dual-fuel combustion system to meet program goals

Future Directions

- Validate analysis-led combustion system design through engine testing
- Develop steady-state calibration to meet program goals on demonstration hardware
- Develop transient calibration to meet program goals on demonstration hardware
- Complete vehicle build of dual-fuel engine demonstrating 50% petroleum reduction ■

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Introduction

The successful development of a high efficiency dual-fuel engine could significantly reduce the petroleum usage of on-highway heavy duty Class 8 vehicles by more than 50% as well as improve the thermal efficiency of the engine. By utilizing a domestically producible and renewable fuel (85% ethanol, 15% gasoline blend [E85]) the security of the nation's energy supply can be increased. The dual-fuel platform could also provide a pathway to reduced dependence on oxides of nitrogen (NO_x) exhaust aftertreatment devices.

Approach

The approach integrates advances in the areas of combustion, air handling, fuel systems, closed loop controls, and aftertreatment to create a high efficiency, low emission dual-fuel engine, suitable for both consumer and commercial applications. Dual-fuel combustion can enable premixed low temperature combustion resulting in improved engine efficiency and reduced formation of NO_x and particulate matter. The program examines the use of PFI of a low-reactivity fuel (E85) and direct injection of a high-reactivity fuel (diesel) in a lean fuel–air mixture. The combustion phasing is controlled by a combination of in-cylinder fuel reactivity stratification, direct injection fuel injection timing and in-cylinder temperature and oxygen concentration. A unique and innovative model-based controller utilizing in-cylinder pressure feedback is being implemented to transiently control the combustion phasing.

Results

System Design

A key design effort this year was to finalize the design for the integration of a vertically oriented in-cylinder pressure sensor (ICPS) into the cylinder head to support combustion phasing control. Discussions with the sensor supplier ensured the application of their sensor was acceptable and met installation guidelines to ensure peak performance. The sensor integration was designed to include the standard length sensor, which the supplier could provide very rapidly. The design concept assembly is shown in a cross-section in Figure 1.

Combustion Computation Fluid Dynamics (CFD) Analysis

The combustion development of a new dual-fuel premixed compression ignition engine is being conducted using three-dimensional CFD simulation. The analysis-led design process employed seeks to optimize the combustion system design elements such as the compression ratio, piston bowl shape, in-cylinder charge motion, fuel injector configuration and fuel injection strategy to minimize petroleum usage while simultaneously achieving low emissions and operation over the entire engine map. During 2015, extensive CFD work focused on understanding the sensitivity and impacts of these elements to provide a robust combustion system design.

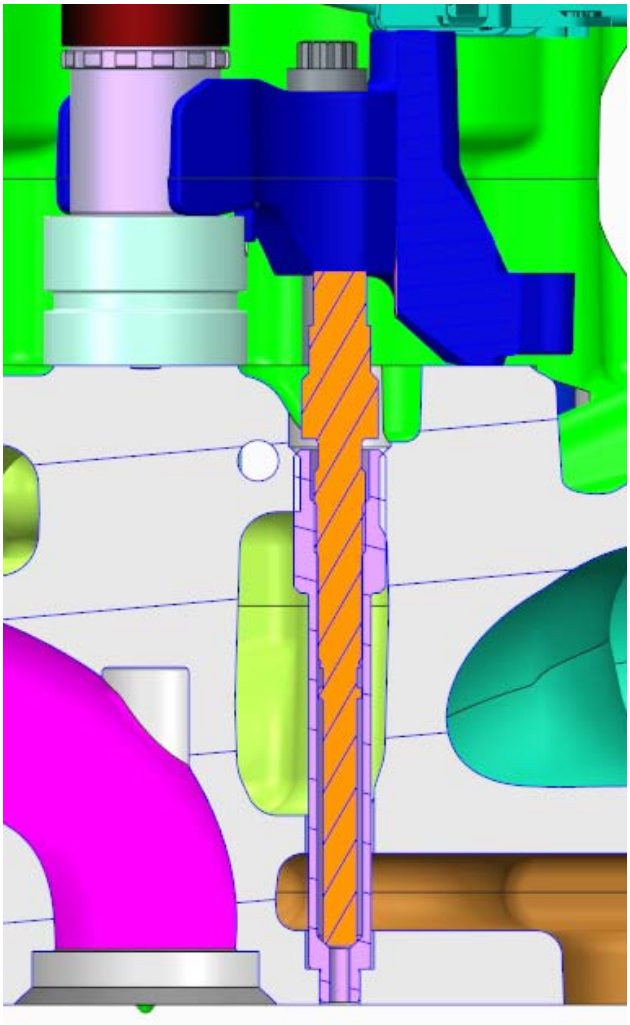


Figure 1. ICPS assembly integration

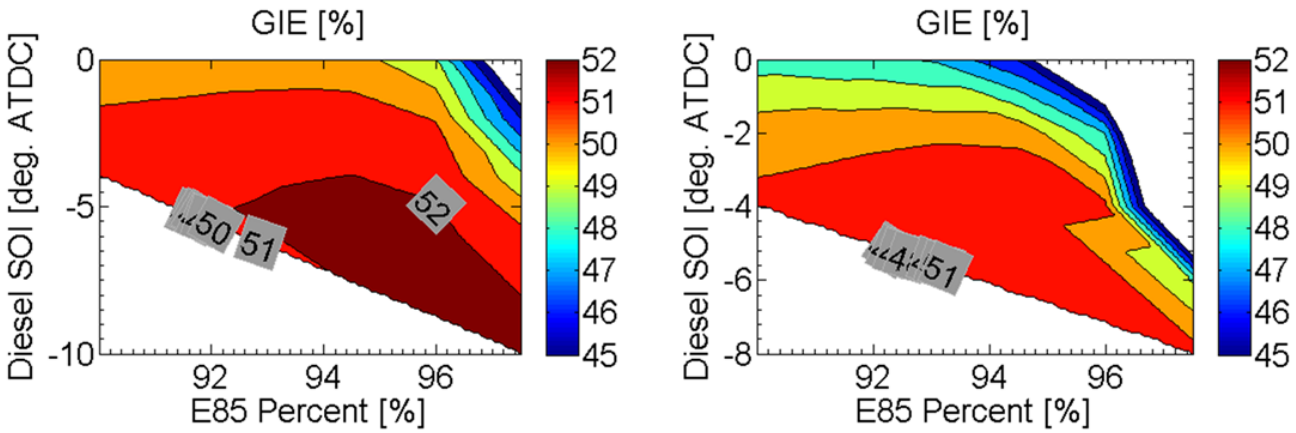
One potential pitfall for a highly premixed combustion system is the tendency for uncontrolled autoignition of fuel at high engine loads. This often leads to reduced load capability compared to traditional diesel engines. In order to make sure that the new EDPCI engine will operate robustly at high loads without abnormal autoignition, several combustion design elements were analyzed to create a system to meet the objective. A compression ratio sweep was conducted to determine the optimal compression ratio to avoid autoignition while maximizing the expansion ratio for efficiency. An in-cylinder charge motion study was also performed to study the effect of the flow field on combustion. Finally, the piston bowl shape and fuel injector configuration were analyzed concurrently to determine the most robustly performing system. An example of the impact of the piston bowl shape is shown in Figure 2 for two different shapes at the same compression ratio and same injector configuration. The piston bowl shape on the left operates with higher peak gross indicated efficiency (GIE) and has larger islands of high efficiency performance.

Controls Development

A key enabler for the EDPCI program is closed-loop control of the combustion phasing. As such, great effort is placed in developing the architecture and algorithms to ensure robust performance of the engine. Key components of controls system include the ICPS processing system, engine control unit, PFI control module, and dSPACE controls system. Each component was developed and bench tested in the laboratory before being deployed at the test cell. The dSPACE system is the central component of the controls system. It implements advanced controls technologies to control combustion phasing, as shown in Figure 3, by interfacing with other components. It also monitors the status of components for diagnostics and communicates with the test cell system for safety during tests. High speed data logging capability is also configured to collect cycle-based data during tests.

System Analysis

A system tool was created to provide targets for emissions and petroleum usage for upfront analysis (CFD, system level analysis, and bench controls development). The tool



SOI – start of injection; ATDC – after top dead center

Figure 2. Piston bowl shape optimization results

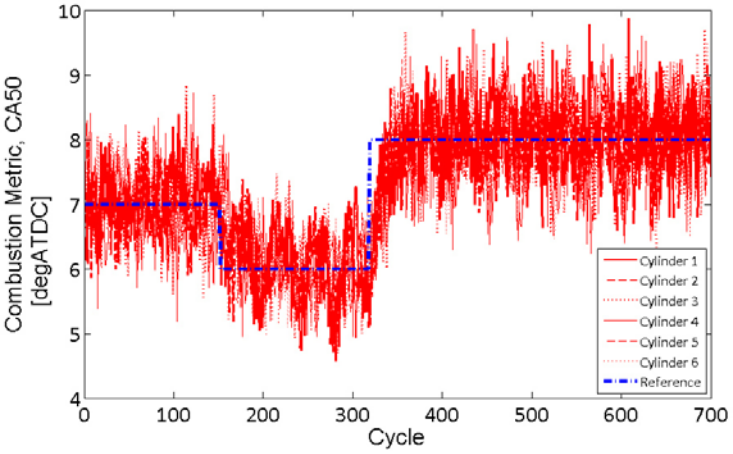


Figure 3. Cycle response of the crank angle at which 50% of the fuel energy has been released (CA50)

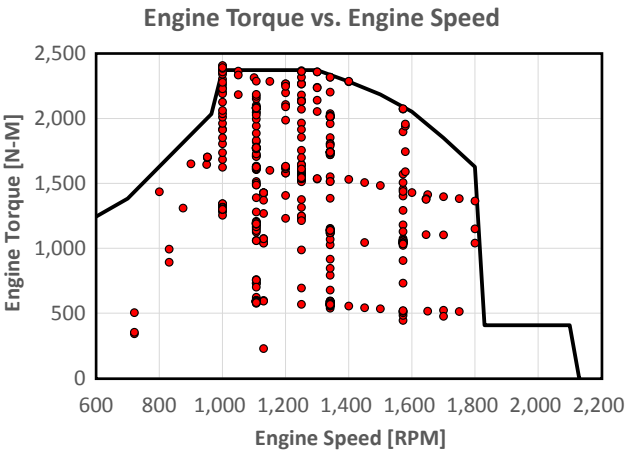


Figure 4. Demonstrated EDPCI operating range

is intended to stay updated regularly, as new information and test data becomes available. Additionally, a full engine system model was created and calibrated in GT-POWER. The model supports air handling optimization efforts as well as controls development. The model is calibrated to test data collected during the testing phase.

Engine Testing

During the Cummins SuperTruck program [1], the 55% brake thermal efficiency (BTE) Alternative Fuel Compression Ignition program had shown that it was possible to run EDPCI combustion up to 10 bar brake mean effective pressure at 1,000 rpm with a demonstrated BTE of 49.4%. However, higher load operation was limited by a late autoignition caused by concentration of ethanol in the squish region of the combustion chamber. This late autoignition would cause the engine to knock, thereby limiting the operating range. Based on combustion CFD results, the compression ratio was reduced from 17.1 to 14.2 to lower in-cylinder temperature and pressure and additionally the bowl shape was modified to further prevent the late autoignition. The resulting engine configuration demonstrated the ability to operate across the entire operating space of the engine as seen in Figure 4.

To demonstrate certification cycle performance, the 13-mode SET rollup is used to quantify emissions performance. The rollup shown in Table 1 was compiled from engine test data. The current petroleum reduction is at 54% over a production engine while demonstrating improved BTE and NO_x emissions. These results are very promising as further petroleum reduction and BTE improvement will be achieved with further optimization. Future experimental work will include validation of the proposed analysis-led combustion design piston bowl

shape and injector configuration. The analysis suggests the optimized solution to perform better and more robustly than the results to date.

Table 1. EDPCI SET 13-mode rollup

% Petroleum Reduction	54.0%
BTE [%]	45.2
bsfc [g/kW-hr]	250.0
bsNOx [g/kW-hr]	1.31
bsHC [g/kW-hr]	2.07
bsDPM [g/kW-hr]	0.09

bsfc – brake specific fuel consumption; bsNOx – brake specific NO_x; bsHC – brake specific hydrocarbon; bsDPM – brake specific diesel particulate matter

Conclusions

The Cummins EDPCI E85–diesel dual-fuel engine program has successfully completed the first year of the two-year program. The following conclusions have come from the first year:

- A dual-fuel engine can be designed and developed to demonstrate a 50% petroleum reduction over the SET.
- A dual-fuel engine can be designed and developed to demonstrate comparable engine performance and full load capability compared to a diesel engine.
- Additional optimization opportunities are available to improve the results demonstrated to date through further combustion system development.
- A production-viable in-cylinder pressure transducer can be integrated into the cylinder head and provide adequate capability to support closed-loop combustion control.

References

1. David Koeberlein, Lyle Kocher, *Cummins SuperTruck Program - Technology and System Level Demonstration of Highly Efficient and Clean, Diesel Powered Class 8 Trucks*, Cummins, 2015 DOE Vehicle Technologies Program Annual Merit Review, Arlington, Virginia, June 12, 2015.

IV.4 Dual-Fuel Technology Development for Heavy-Duty Long Haul Applications in 2014 and Beyond

Overall Objectives

- Demonstrate a compressed or liquefied natural gas Class 8 heavy-duty Dual-Fuel 13 L compression ignition engine that utilizes an average of 60–75% natural gas ignited by a pilot of 25–40% diesel for use in heavy-duty commercial on-road applications
- Work with a wide cross-section of fleets to demonstrate the Dual-Fuel 13 L engine, collecting performance and operational data to help refine and more effectively commercialize an alternative fuel engine product that fills an existing gap in the marketplace
- Refine the ultra-low NO_x emission engine that secures initial Environmental Protection Agency and California Air Resources Board emission certification at 0.2 g/bhp-hr NO_x
- Develop heavy-duty on-board diagnostics (HD OBD) compliant and compatible Dual-Fuel engines
- Provide a low incremental cost option for fleets interested in Class 8 heavy-duty natural gas operations, allowing fleets to recognize long-term fuel cost savings with a shorter payback timeframe on upfront vehicle costs

Fiscal Year (FY) 2015 Objectives

- Initial Dual-Fuel system design and development – development of system requirements and the preliminary development and testing of the Dual-Fuel system in both engine and vehicle platforms
- Dual-Fuel engine management system (EMS) engine manufacturer diagnostics enhanced (EMD+) concept definition
- Complete software requirements specification (SWRS) describing the EMD+ diagnostics
- Define concept-level countermeasures to avoid activation of original equipment manufacturer (OEM) HD OBD system while operating in Dual-Fuel mode

FY 2015 Accomplishments

- A model year (MY) 2015 vehicle with a Volvo/Mack 13 L engine was procured during the first quarter of 2015, the installation of the Dual-Fuel system was completed and the vehicle was commissioned to operate on natural gas.
- An assessment was made of the EMD+ requirements during the first quarter time period. This assessment was used in the second quarter time period to form the basis of the SWRS.
- The SWRS to update the existing software to ensure compliance with new EMD+ requirements for system monitoring was completed.
- Concept-level countermeasures to avoid activation of the OEM HD OBD system while operating in Dual-Fuel mode were developed.
- A list of support (information, hardware, etc.) that will be requested from an OEM partner was produced.

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Future Directions

- Procure an MY 2016 Volvo/Mack D13/MP8 engine and vehicle; install the CAP Dual-Fuel system on the engine and vehicle; investigate any differences between the MY 2016 configuration and previous MY engines and implement required revisions to the CAP Dual-Fuel system
- Complete the development and the calibration of the new EMD+ software using the MY 2016 engine and vehicle
- Conduct market readiness demonstration of the HD OBD compliant Dual-Fuel system ■

Introduction

The technology being developed is a combination of Dual-Fuel combustion and combustion control to meet United States 2010 emission levels, including compatibility with the existing diesel systems full MY 2013 and beyond HD OBD requirements (shown in Figure 1) while maintaining overall efficiencies and performance of typical modern heavy-duty diesel vehicles. The concept retains the base engine's diesel fuel system and aftertreatment, which will allow emission certified operation on diesel fuel at full power. This feature allows for early market development of natural gas fuel stations and relieves concerns by fleet operators over range limitations from existing natural gas refueling infrastructure that would otherwise prevent the use of liquefied or compressed natural gas in true long haul applications.

This 425 hp heavy-duty engine provides 1,550 lb·ft of torque at economically competitive costs to diesel engines, and fills a critical role in natural gas engine product availability. The introduction of an HD OBD compliant and compatible natural gas Dual-Fuel Volvo/Mack D13/MP8 will solve a technology gap problem in the marketplace by offering a heavy-heavy-duty engine product suited to the needs of goods movement and Class 8 operators. While the existing 9 L spark ignited natural gas engine has been used in the regional hauling sector, its popularity is partly due to the fact that it is the only affordable natural gas engine. However, it is only certified for freeway speeds of up to 65 mph and is not appropriate for grades or hills. Also, there is a recently released 12 L spark ignited natural gas engine rated at 400 hp, but it has twice the incremental cost of Clean Air Power's Dual-Fuel technology and suffers serious weight and range penalties as well. With diesel-like performance and lower upfront capital cost, the CAP Dual-Fuel product offering will result in accelerated market adoption.

Approach

The project will utilize CAP's Dual-Fuel combustion technology to deliver a Class 8 heavy-duty alternative fuel engine that is fully compliant with the U.S. Environmental Protection Agency's and California Air Resource Board's current HD OBD regulations. The Volvo/Mack D13/MP8 engine will combine the innovation of CAP's Dual-Fuel technology with a uniquely and vertically integrated engine and truck product manufactured by Volvo/Mack. CAP's Dual-Fuel application enables diesel engines to operate on an average of 60–75% natural gas ignited by a pilot of 25–40% diesel. This Dual-Fuel technology is fitted onto a standard diesel engine, enabling a precisely metered quantity of natural gas to be injected with unthrottled air just before it enters the cylinder and is compressed to the same high levels as the air is in normal diesel-only operation, thus maintaining similar efficiencies. The Dual-Fuel engine uses a small injection of diesel fuel (around 25–40% of the normal diesel quantity) to ignite the main charge of natural gas and air.

Results

The first milestone for this project was a completed SWRS. The SWRS was completed and is now under change control. The SWRS describes the monitoring requirements by system/subsystem. The new 39 CAP fault codes identified for the EMD+ requirements are described in the SWRS along with the 122 carryover CAP fault codes. The SWRS document now represents the complete CAP diagnostic system and will be used to describe how the system meets the requirements of EMD+ for alternative fuel engines.

A MY 2015 Mack vehicle (equipped with a 2014 Model Year HD OBD compliant MP8 engine) was procured and the installation of the Dual-Fuel system was completed. A preliminary Dual-Fuel calibration was developed on the engine dynamometer and the validation of the OEM HD OBD fault codes by operating the vehicle in various driving conditions was completed. During the 2,091 miles of Dual-Fuel operation the OEM HD OBD fault codes shown in Table 1 were observed. The P001676 crankshaft/camshaft position fault along with the two piston cooling oil (P055B64 and P25AE00) faults were resolved with concept level corrective actions in the CAP EMS. An

HD Diesel Engine	EMD +		FULL HD OBD						
Alt Fuel Engines	EXEMPT		EMD +					FULL HD OBD	
	2011	2012	2013	2014	2015	2016	2017	2018	2019
	MODEL YEAR								

Figure 1. HD OBD requirements roll-out by model year

electrical wiring modification (addition of a resistor) on the CAP Dual-Fuel harness resolved the crankshaft/camshaft fault. A piston cooling oil sensor was added to the CAP EMS to monitor the piston cooling oil pressure. The other observed faults are controller area network communication issues that were resolved within the CAP EMS gateway communication modules.

Conclusions

With the completion of the SWRS, the successful installation of the Dual-Fuel system on a full HD OBD diesel vehicle, the identification and countermeasure development of the observed OEM fault codes, and the list of OEM support requirements, the deliverables were met for the Decision Point 1 review with Clean Air Power leadership. The outcome of the review was a decision to proceed to the next phase of the project. The concept phase has identified the requirements necessary to meet the EMD+ requirements for Dual-Fuel application on a full HD OBD diesel vehicle and has demonstrated the feasibility of completing the design, development, and validation of the Dual Fuel system successfully.

Table 1. Observed OEM fault codes during Dual-Fuel operation

Fault P number	Description
B100092	TGW2 GSM Modem, Performance or Incorrect Operation
P001676	Crankshaft Position – Camshaft Position Correlation, Wrong Mounting Position
P055B64	Piston Cooling Oil Pressure Sensor Range/Performance, Signal Plausibility Failure
P105594	Brake Switch Status, Unexpected Operation
P106074	Clutch Plate Load, Actuator Slipping
P25AE00	Piston Cooling Oil Pressure to Low, No Sub-type Information
PSID 201	Data Link, MID 144, FMI 9: Abnormal Update Rate
U008088	Vehicle Communication Engine Subnet, Bus off
U116C00	Lost Communication with TCM on Powertrain CAN, No Sub-type Information

TGW2 – Telematic GateWay; GSM – Global System for Mobile Communications; MID – message identification; FMI – failure mode identifiers; TCM – transmission control module; CAN – controller area network

IV.5 Efficiency-Optimized Dual Fuel Engine with In-Cylinder Gasoline–CNG Blending

Overall Objectives

- Optimize combustion concept with targeted in-cylinder natural gas (NG)–gasoline blending to achieve 10% efficiency improvement over gasoline baseline
- Demonstrate 10% improvement in NG power density over NG port fuel injection (PFI)
- Achieve 50% petroleum reduction and 36-month payback period while maintaining retrofitability and full emissions and on-board diagnostics compliance using standard three-way catalyst

Fiscal Year (FY) 2015 Objectives

- Characterize gaseous jets from NG direct injection (DI) using X-ray diagnostics
- Validate three-dimensional computational fluid dynamics (3D-CFD) simulation results of gaseous injection events against X-ray data
- Design, build, and integrate single-cylinder engine hardware to allow NG DI operation with central and side location as well as gasoline and NG PFI
- Establish baseline efficiency and performance with neat fuels using gasoline (E10) PFI, NG PFI as well as NG DI in central and side location
- Demonstrate concept potential of blended operation in terms of efficiency and power density
- Develop predictive simulation capability of mixture formation and combustion process using validated 3D-CFD tool

FY 2015 Accomplishments

- Successfully validated 3D-CFD simulations of the gaseous injection event against X-ray measurements and developed a best practice for engine simulations of the NG DI event
- Demonstrated 39.1% indicated efficiency with NG DI exceeding the efficiency in gasoline PFI operation by 5.9%, a ~17.8% relative improvement
- Achieved 11.3 bar indicated mean effective pressure (IMEP) at 1,500 rpm with NG DI, a 13% improvement in power density over NG PFI

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- Blended operation at part load shows a 0.5% efficiency benefit (1.3% relative improvement) due to improved exhaust gas recirculation (EGR) dilution tolerance

Future Directions

- Determine evaluation criteria and develop an optimized combustion system configuration to maximize the benefits of the in-cylinder gasoline–NG blending concept
- Experimentally evaluate the performance and efficiency potential of the optimized configuration
- Develop a vehicle level strategy with the goal to maximize the global benefits of the in-cylinder blending strategy

- Perform vehicle level simulations and a cost analysis evaluating progress towards the 50% petroleum reduction and 36-month payback period goals ■

Introduction

Advances in hydraulic fracturing and horizontal drilling have revolutionized the United States oil and gas industry increasing shale gas production sevenfold in five years (2007–2012) [1]. Increased supplies and subsequent low NG prices also resulted in renewed interest in introducing NG as a transportation fuel. However, using NG PFI in a dedicated spark-ignition engine vehicle reduces power density and engine efficiency relative to a comparable gasoline vehicle.

This project aims to demonstrate the potential of a novel combustion concept that is designed to take advantage of the beneficial properties of natural gas, in particular its high knock resistance while mitigating the challenges associated with the gaseous fuel, in particular its low density and reduced flame speed. To achieve this, gasoline and NG are blended in-cylinder where NG is injected directly into the combustion chamber while gasoline is introduced using conventional PFI hardware. The blend ratio is adjusted based on engine load and speed conditions as well as other parameters, such as remaining NG on-board storage. An optimized combustion concept employing this targeted in-cylinder NG–gasoline blending approach is expected to deliver a 10% efficiency improvement over neat gasoline operation while improving power density by 10% over NG PFI. The concept is also expected to achieve a 50% petroleum reduction and 36-month recovery period for retrofitting cost while maintaining full emissions and on-board diagnostic compliance using a standard three-way catalyst.

Approach

A multi-pronged technical approach combining experimental tasks and state-of-the-art computational modeling is employed to assure that the ambitious project goals are met and that the project remains on schedule. The approach is comprised of the (1) experimental characterization of the gaseous jet from a NG DI injector using Argonne's X-ray diagnostics in order to validate the predictive capabilities of 3D-CFD simulations followed by (2) experimental evaluation and optimization of the proposed dual-fuel approach on a single-cylinder research engine platform supplemented with and guided by CFD simulations and completed by (3) vehicle level simulations to develop high-level control strategies that maximize fuel property benefits, estimate the real-world fuel economy results and determine the amortization period for different vehicle types.

Results

X-ray Characterization of NG DI Jets and Validation of 3D-CFD Simulation

An outward opening injector is used to directly inject natural gas into the combustion chamber at injection pressures up to 16 bar. The high differential pressures and complex geometries of the injector nozzle, in particular the small flow area, present a challenging case for computational simulations. Validations of the 3D-CFD simulations were performed against X-ray measurements of the gaseous jet structures for a range of operating conditions, including free injection as well as impingement on a barrier, performed in a high pressure chamber. Figure 1 shows a comparison of X-ray measurements (left column) against simulations employing different computational mesh sizes for both free and impinging cases at an injection pressure of 15 bar. As can be seen, all simulations predict the general shape and penetration well, a more accurate prediction of the smaller scale jet structures and mass distribution within the jet is achieved with finer mesh resolution. These findings led to the development of a best practice for simulating the gaseous injection event in full engine simulations, where extremely fine mesh resolutions would be time prohibitive.

Experimental Evaluation of In-Cylinder Blending Concept

In order to allow for experimental evaluation of the proposed concept, a dedicated cylinder head was designed and built that can accommodate the NG DI hardware in the side as well as central location and also allows for PFI of gasoline and NG. Figure 2 shows a rendering of the cylinder head design with the NG DI hardware in the central and side location. The image on the right shows the cylinder head and injector hardware for DI and PFI operation installed on the single-cylinder research engine.

Baseline engine maps were established for gasoline (87 Anti-Knock Index E10) and NG PFI operation as well as NG DI in side and central location across the relevant engine speed and load range sweeping fuel injection timing as well as spark timing. Figure 3 shows differential efficiency maps depicting the efficiency differences between NG DI in the side location compared to E10 PFI (left) and NG PFI (right). Results are reported in absolute differences in indicated thermal efficiencies and positive values indicate higher efficiencies for NG DI operation compared to the respective PFI baseline. The higher knock resistance of NG allows for optimal

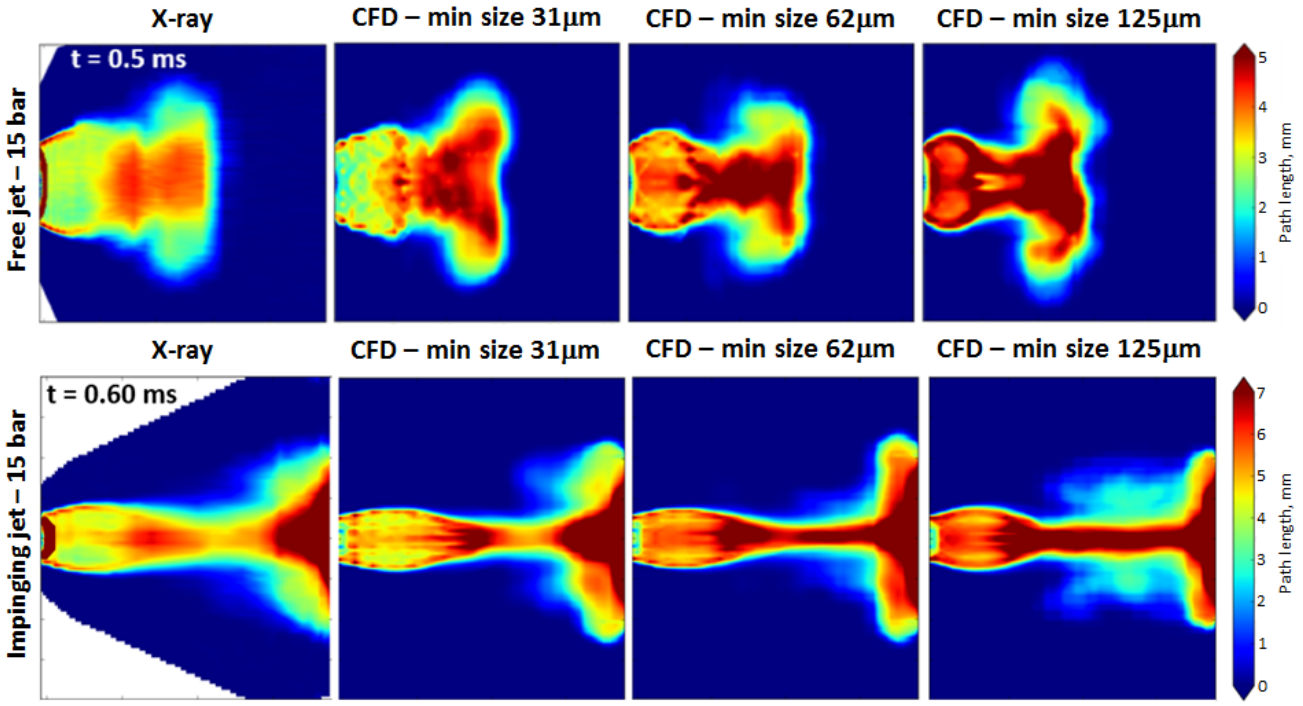
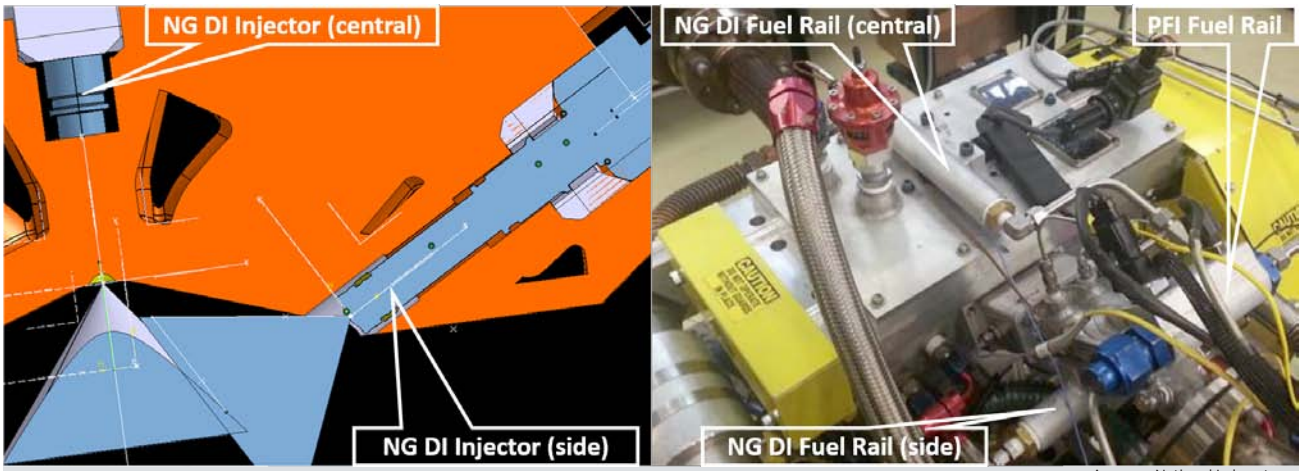


Figure 1. Comparison of gaseous jet development between X-ray and CFD data for free and impinging jets



Argonne National Laboratory

Figure 2. Rendering of the NG DI hardware and jet cones for central and side location (left) and image of the cylinder head with DI and PFI hardware installed on the single-cylinder research engine (right)

combustion phasing even at wide open throttle (WOT) operation resulting in efficiency benefits up to 5.9% (an ~17.8% relative improvement) compared to E10 PFI. Direct injection also significantly improves power density compared to the PFI operation resulting in an up to 1.2 bar increase in IMEP for NG DI compared to E10 PFI and up to 1.3 bar compared to NG PFI (relative improvements of 12% and 13%, respectively).

The efficiency benefits of NG DI compared to E10 PFI are limited to high load operation, while part load efficiencies were found to be equal or lower. Applying in-cylinder blending of E10 PFI with NG DI can provide benefits and improve EGR dilution tolerance and efficiency beyond the levels achieved with the neat fuels. Figure 4 shows the EGR dilution tolerance for E10 PFI, NG DI Side as well as blended operation at various blend levels. Engine efficiency and combustion stability are plotted as a function of EGR rate with engine stability expressed as coefficient of variation of indicated mean effective pressure (COV_{IMEP}). COV_{IMEP} values below 3%

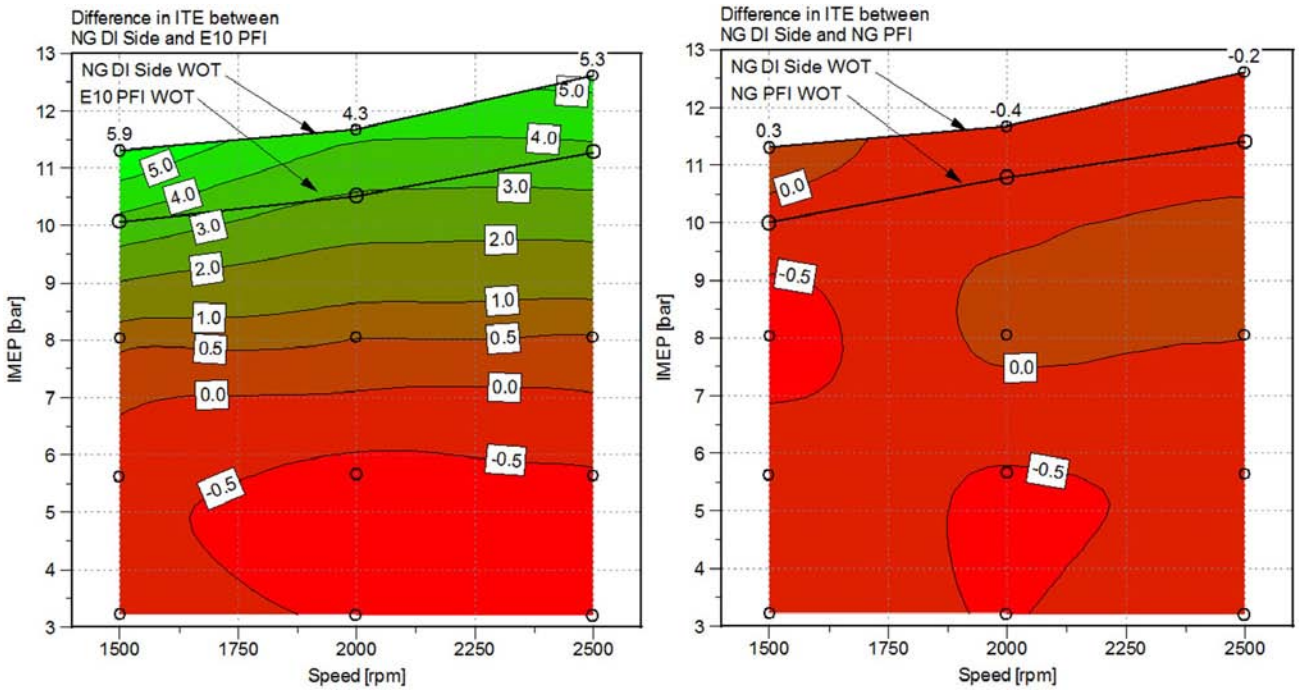
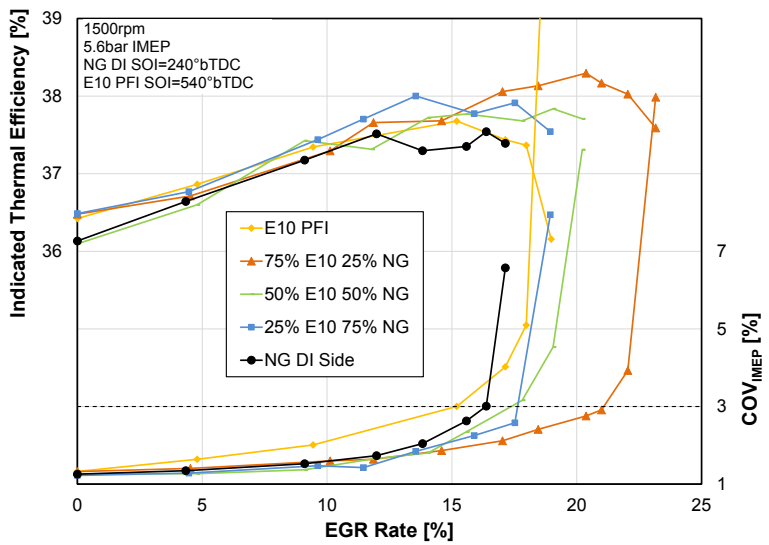


Figure 3. Differential indicated thermal efficiency (ITE) maps for NG DI side versus E10 PFI (left) and NG DI side versus NG PFI (right)



bTDC - before top dead center

Figure 4. EGR dilution tolerance comparison of E10 PFI and NG DI with blended operation

are typically deemed reasonable [2]. Operating the engine with 25% NG DI and 75% E10 PFI (on an energy basis) results in an extension of the EGR limit to 21% while maintaining a COV_{IMEP} below 3% compared to 15% and 16% for E10 PFI and NG DI, respectively. This improved dilution tolerance delivers NO_x emissions benefits of 1.9 g/kWh (30% relative improvement) as well as an improvement in engine efficiency of up to 0.5% (1.3% relative improvement) compared to E10 PFI.

Simulation of Mixture Formation and Combustion Process

The experimental results suggest that the proposed concept employing in-cylinder blending of gasoline and NG has the potential to meet and exceed the proposed efficiency and performance goals. Unlocking the full potential of the proposed concept requires an optimized combustion system design and 3D-CFD simulations are employed to evaluate design options. Figure 5 shows simulation results of the mixture formation process for NG DI in central compared to side location, for a late injection strategy (start of injection = 120º crank angle before top dead center). As can be seen, central NG DI results in an increased interaction of the gaseous jet with the pent-roof walls due to the Coanda effect [3]. This can significantly affect mixture stratification and therefore have a negative impact on thermal efficiency and exhaust emissions.

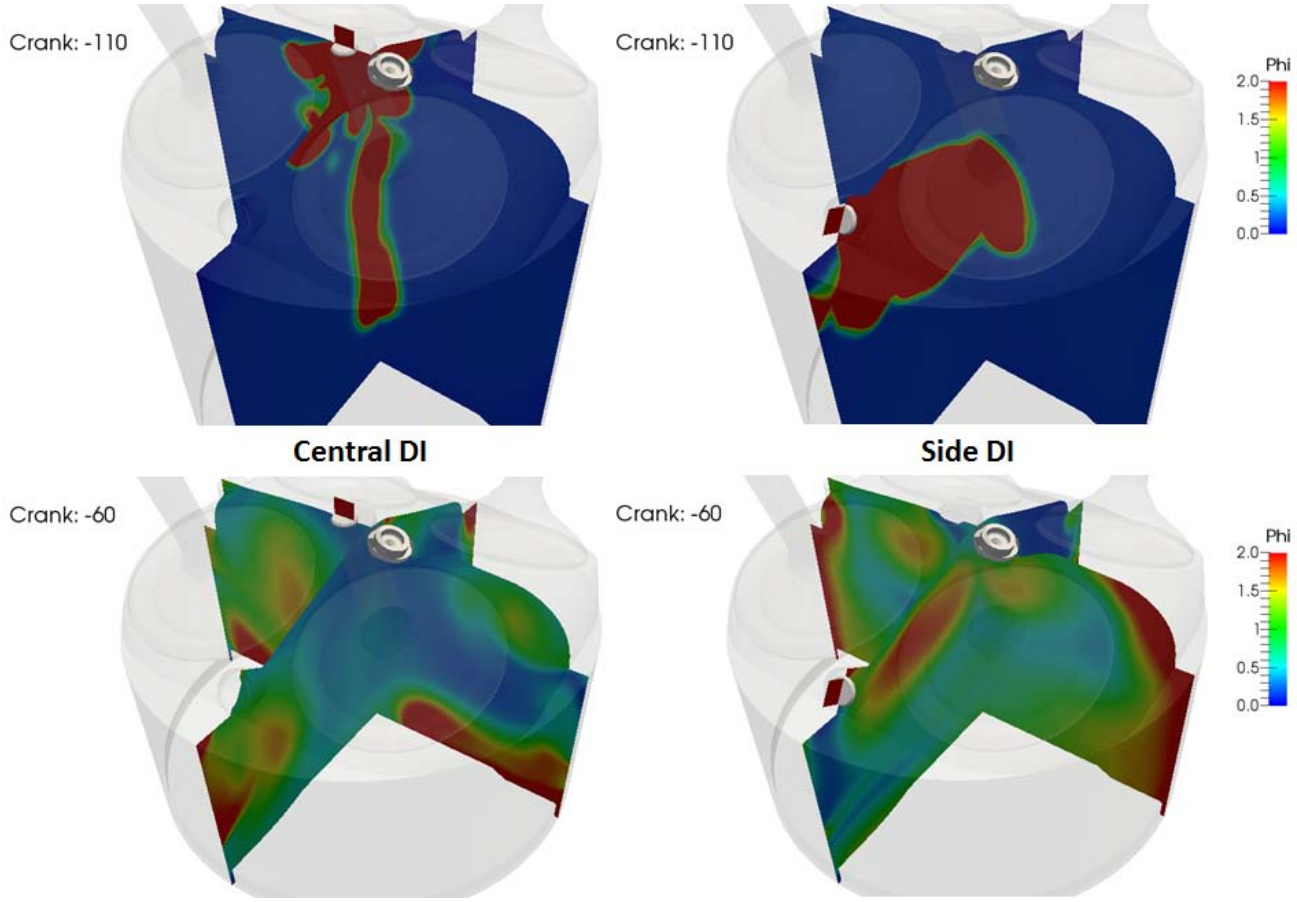


Figure 5. Comparison of the NG DI mixture formation process for central and side location and closed valve injection (start of injection = 120° crank angle before top dead center)

Conclusions

This project was designed to evaluate the potential benefits of targeted in-cylinder blending of NG with gasoline and has successfully met all first year milestones. Specific FY 2015 accomplishments include:

- Successfully validated 3D-CFD simulations of the gaseous injection event against X-ray measurements and developed a best practice for engine simulations of the NG DI event
- Demonstrated 39.1% indicated efficiency with NG DI exceeding the efficiency in gasoline PFI operation by 5.9%, a ~17.8% relative improvement
- Achieved 11.3 bar IMEP at 1,500 rpm with NG DI, a 13% improvement in power density over NG PFI
- Blended operation at part load shows a 0.5% efficiency benefit (1.3% relative improvement) due to improved EGR dilution tolerance

References

1. Energy Information Administration, 2013, North America leads the world in production of shale gas, https://www.eia.gov/todayinenergy/detail.cfm?id=13491

2. Sevik, J.; Scarcelli, R.; Wallner, T.; Pamminger, M.; Singleton, D.; Sanders, J.: "Extending lean and EGR-dilute operating limits of a modern GDI engine using a low-energy transient plasma ignition system." ASME Internal Combustion Engine Division: 2015 Fall Technical Conference. Houston, TX. 2015.

3. Tritton, D.J., Physical Fluid Dynamics, Van Nostrand Reinhold, 1977 (reprinted 1980), Section 22.7, The Coandă Effect.

FY 2015 Publications/Presentations

1. Sevik, J.; Pamminger, M.; Hall, C.; Wallner, T.; Scarcelli, R.; Miers, S.: "Performance, Efficiency and Emissions Comparison of Gasoline and Natural Gas Port-Fuel Injection with Central Natural Gas Direct Injection." Submitted for publication at the SAE World Congress. 2016.

2. Bartolucci, L.; Scarcelli, R.; Wallner, R.; Swantek, A.; Powell, C.: “Gaseous Direct Injection from an Outward Opening Injector: CFD and X-ray Analysis.” Submitted for publication at the SAE World Congress. 2016.

3. A.B. Swantek, D. J. Duke, A.L. Kastengren, N. Sovis, and C.F. Powell: “An Experimental Investigation of Gas Fuel Injection with X-ray Radiography.” Submitted to Experimental Thermal and Fluid Science.

V. 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.

V.1 Advanced Fuels Enabling Advanced Combustion in Multi-Cylinder Engines* Gasoline-Like Fuel Effects in Advanced Combustion Regimes†

Overall Objectives

- The Advanced Fuels Enabling Advanced Combustion in Multi-Cylinder Engines project will investigate the potential for direct substitution of biofuels for petroleum in advanced combustion technologies. Co-evolution of these emerging technologies and biofuels represents an opportunity to reduce petroleum consumption in future engines and vehicles in a mutually beneficial way.
- The Gasoline-Like Fuel Effects in Advanced Combustion Regimes project addresses fundamental pathways for increasing the efficiency of alternative gasoline-like fuels using multiple advanced combustion strategies as well as conventional spark-ignition (SI) combustion as appropriate for each load and fuel. The combination of direct petroleum displacement and higher efficiency while maintaining low tailpipe-out emissions will demonstrate the potential for alternative gasoline-like fuels to make a dramatic impact on petroleum displacement.

Fiscal Year (FY) 2015 Objectives

- Demonstrate the potential of biofuels to obtain efficiency target with advanced combustion reactivity controlled compression ignition (RCCI) combustion (second quarter Joule milestone)
- Conduct apples-to-apples comparison of dual-fuel RCCI and single-fuel gasoline compression ignition (GCI)
- Determine the extent and the causes of fuel-specific differences on exhaust gas recirculation (EGR) dilution tolerance at a light-load engine condition in an SI engine

FY 2015 Accomplishments

- Attained the 2015 technical target of demonstrating fuel effects enabling the 2020 U.S. DRIVE Advanced Combustion & Emissions Controls (ACEC) Tech Team goal of 36% brake thermal efficiency (BTE) at 2,000 rpm and 20% peak load

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- Comparison of RCCI with conventional fuels and GCI a variety of fuels spanning wide range in Research Octane Number (RON) for efficiency, load expansion, and controllability
- Concluded that EGR tolerance limits can be attributed to stochastic cycle-to-cycle instabilities; fuels with faster flame speeds are more resilient to the stochastic turbulence and are able to tolerate more dilution

Future Directions

- In the broader context, both of these projects are being brought into the Optima during the first quarter of FY 2016. Fuel effects on advanced combustion including effects on transient operation will continue to be explored with a variety of advanced and renewable fuels. The high efficiency SI project stands prepared to contribute understanding the fuel effects on dilution tolerance, and to test candidate fuels from the Optima project. Both of these projects will collaborate with other internal and external projects within the Optima. ■

Introduction

Many renewable and advanced fuels have unique properties which can enable increased efficiency for both advanced compression ignition (ACI) modes as well as high efficiency SI combustion modes. Understanding

the thermodynamics of internal combustion engines allows the pathways toward improved efficiency to be identified. Specifically of interest to these projects is to understand the role of fuels in maximizing the work extraction from the combustion products by maximizing the ratio of specific heat, utilizing a higher compression ratio, having combustion phased at the ideal timing, and decreasing the combustion duration. The role of fuel effects in allowing combustion modes that minimize the engine losses by reducing heat transfer and pumping work is also investigated. While these projects seek to help understand what makes engines more efficient, realizing these efficiency gains is not straightforward, and the limitations of fuel performance can frequently be what limits efficiency. These projects investigate which fuel properties are favorable for higher efficient operating regimes, and specifically whether the properties of renewable fuels can enable higher efficiency operating strategies. To this end, experiments and analysis on fuel effects of gasoline-range fuels is being conducted on multiple engine platforms at Oak Ridge National Laboratory.

Approach

Multiple paths are being pursued to understand and exploit the role that fuel properties can have on increasing the efficiency in engines. In the ACI focused project, fuel effects are being investigated on two advanced combustion strategies, RCCI and GCI, using a modern multi-cylinder diesel engine. This research platform brings with it all of the challenges that advanced combustion faces in the real world, such as air handling challenges and the compatibility of turbo machinery, as well as cylinder-to-cylinder balancing. In the SI focused project, activities in FY 2015 were focused on fuel effects on the EGR dilution tolerance for SI combustion using a modern direct injection gasoline engine. Both projects focused on experimental parametric investigations with fuel composition and properties, and used some elements of modeling to support and better understand the results. The focus of both projects is for greater understanding of the fuel effects on high efficiency combustion concepts to realize the goals of taking advantage of fuel properties for attaining a higher efficiency internal combustion engine.

Results

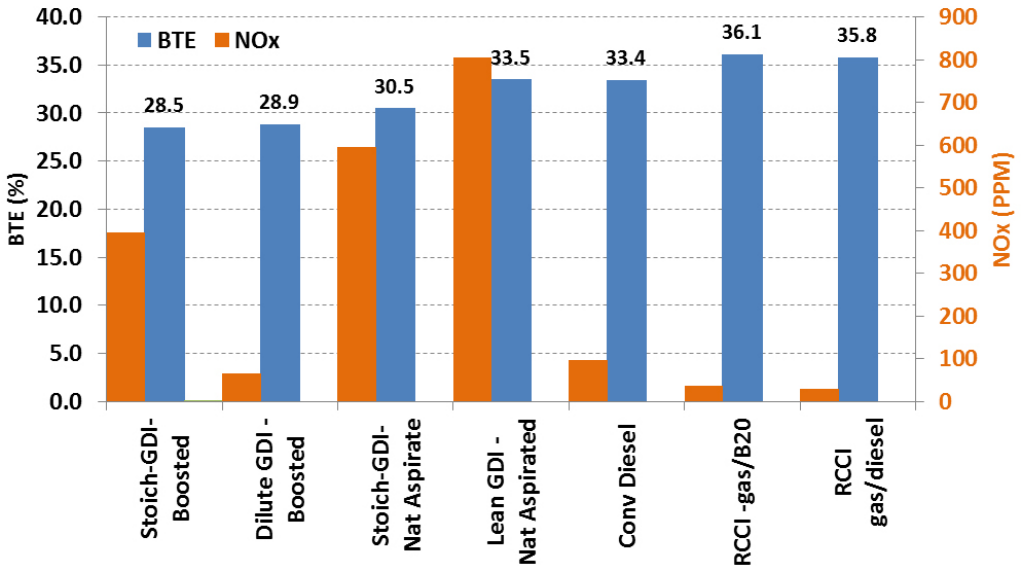
Advanced Fuels Enabling Advanced Combustion in Multi-Cylinder Engines

The second quarter milestone to demonstrate the synergies of fuel properties and ACI combustion to meet the U.S. DRIVE ACEC 2020 stretch goal of 36% BTE at 2,000 rpm and 20% peak load was met. Engine experiments were performed on a General Motors 1.9 L multi-cylinder diesel engine modified to allow for port fuel injection for dual-fuel operation while maintaining the stock common rail direct injection fuel system, variable geometry turbocharger, and high pressure EGR. The effects of fuel properties on both single- and dual-fuel combustion strategies on the same engine platform was considered in being able to demonstrate the ACEC 2020 stretch goal. The 2,000 rpm, 20% load (4.0 bar brake mean effective pressure) point represents a very common condition seen during real-world driving. The 36.1% BTE achieved with this goal using biodiesel and gasoline as the high- and low-reactivity fuels, respectively, for RCCI represents a 6% improvement over the ACEC conventional diesel combustion (CDC) baseline diesel fuel as shown in Figure 1.

In addition, GCI fuel effects experiments using the gasoline range fuels supplied by Chevron Energy Technologies in partial fuel stratification (PFS) and heavy fuel stratification (HFS) modes were completed as shown in Figure 2. This is part of the larger GCI/RCCI comparison in collaboration with Chevron who is supplying the gasoline range fuels of interest for GCI operation as shown in Figure 3. The experiments investigated the role RON ranging from <40 to 87 both the PFS and HFS low temperature GCI modes. Each of the seven gasoline range fuels was run at 2,000 rpm, 4.0 bar brake mean effective pressure in an HFS mode sweeping the amount of EGR and other key parameters.

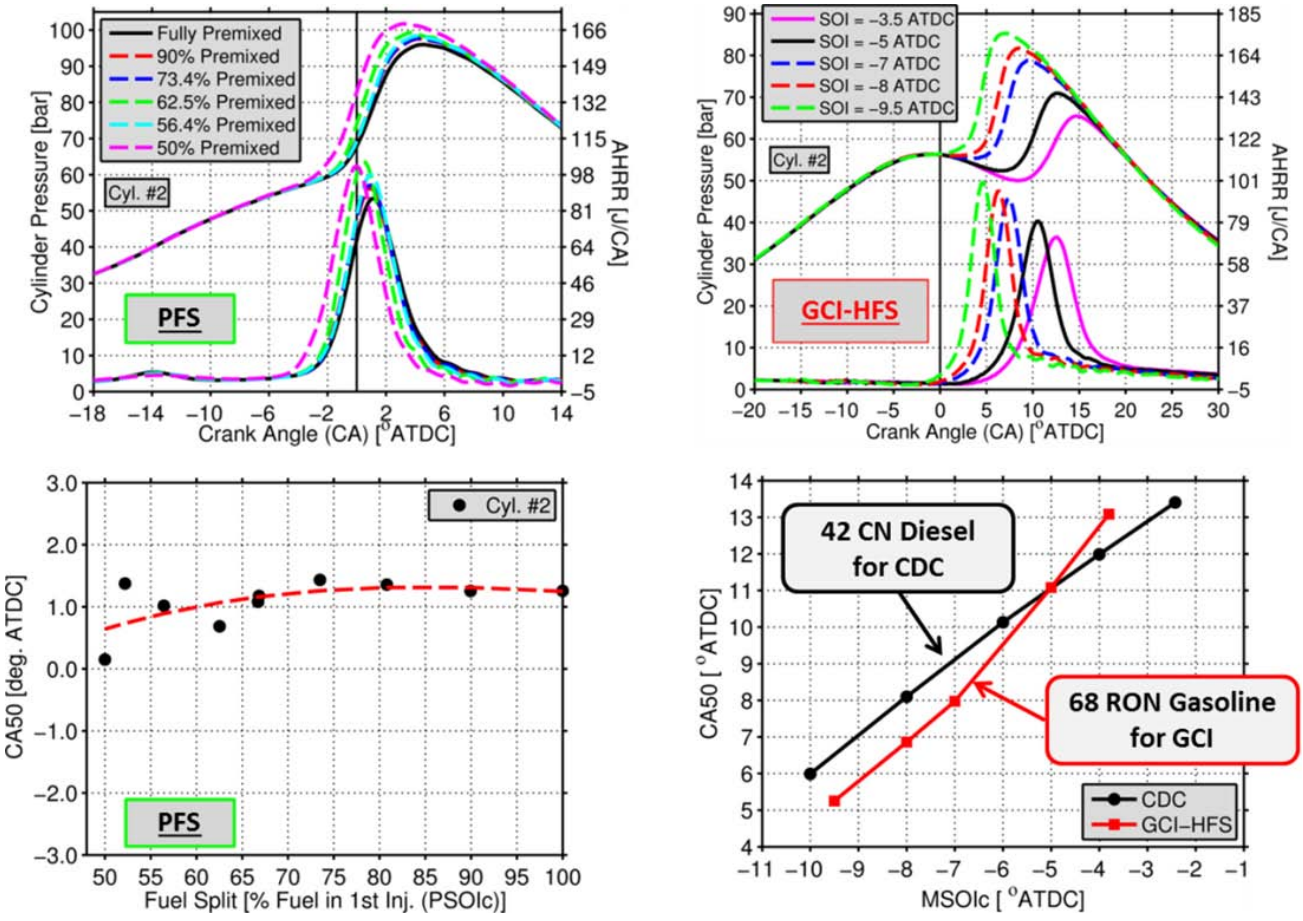
Gasoline-Like Fuel Effects in Advanced Combustion Regimes

Fuel-specific differences in EGR dilution tolerance were investigated in a modern, direct injection single-cylinder research SI engine. A total of six model fuel blends were examined at a constant RON of 95 using n-heptane, iso-octane, toluene, and ethanol, with the composition of each blend shown in Figure 4. Laminar flame speeds for these mixtures, which were calculated by two different methods (an energy fraction mixing rule and a detailed kinetic simulation), spanned a range of about 6 cm/s, as shown in Figure 5. A constant fueling nominal load of 350 kPa gross indicated mean effective pressure (IMEP) at 2,000 rpm was operated with varying CA50 from 8–20 crank angle degrees after top dead center firing, and with EGR increasing until a coefficient of variation (COV) of IMEP of 5% is reached. The results illustrate that flame speed affects EGR dilution tolerance; fuels with increased flame speeds increase EGR tolerance, as shown in Figure 6. Since ethanol is the highest flame speed component used in this investigation, the fuel blends with the highest ethanol content were the most tolerant to dilution. Specifically, flame speed correlates most closely



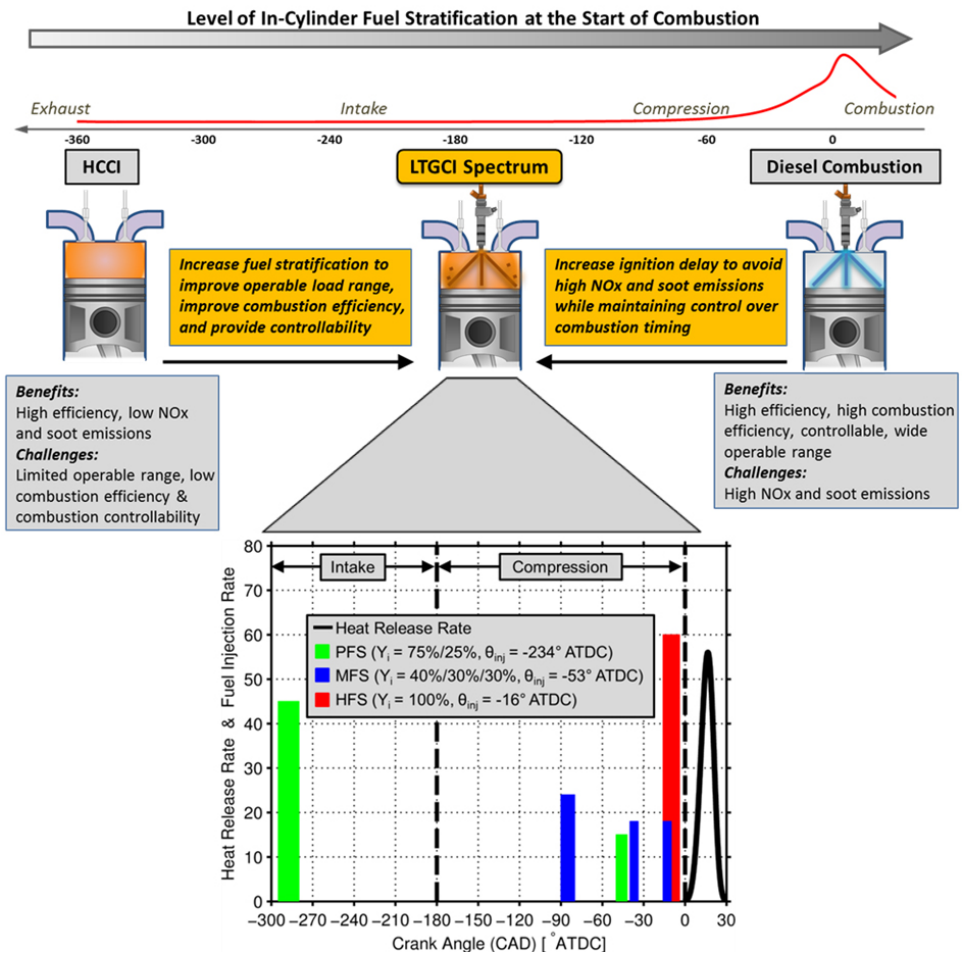
GDI – gasoline direct injection

Figure 1. Comparison of Joule millstone accomplishment to other combustion technologies



ATDC – after top dead center; AHRR – apparent heat release rate; CA – crank angle; CN – cetane number; SOI – start of injection; PSOIc – pilot start of injection; MSOIc – main start of injection

Figure 2. Comparison of controllability of PFS (left) and HFS (right) with a 68 RON gasoline range fuel



HCCI – homogeneous charge compression ignition; CAD – crank angle degree; MFS – moderate fuel stratification

Figure 3. Low temperature GCI (LTGCI) space being investigated

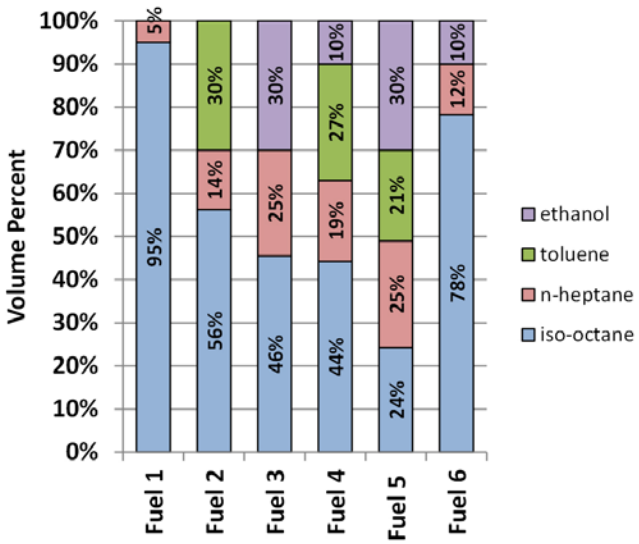


Figure 4. Compositions of the six surrogate blends used to investigate EGR dilution tolerance in SI engines, each with RON = 95

to the initial flame kernel growth, measured as the time of ignition to 5% mass fraction burned. The effect of the latent heat of vaporization on the flame speed is taken into account for the ethanol-containing fuels. At a 30 vol% blend level, the increased enthalpy of vaporization of ethanol compared to conventional hydrocarbons can decrease the temperature at the time of ignition by a maximum of 15°C, which can account for up to a 3.5 cm/s decrease in flame speed. The ethanol-containing fuels, however, still exhibit a flame speed advantage, and a dilution tolerance advantage over the slower flame-speed fuels. The fuel-specific differences in dilution tolerance are significant at the condition examined, allowing for a 50% relative increase in EGR (4% absolute difference in EGR) at a constant COV of IMEP of 3%.

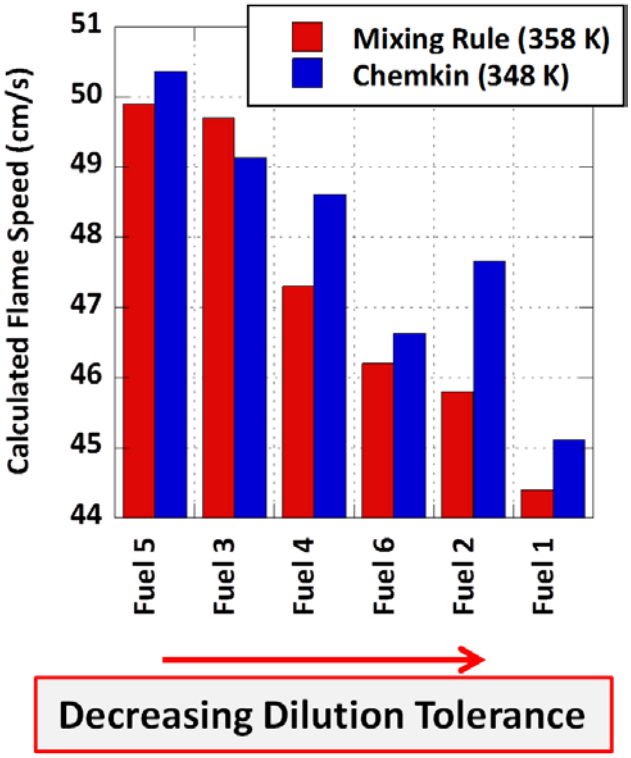
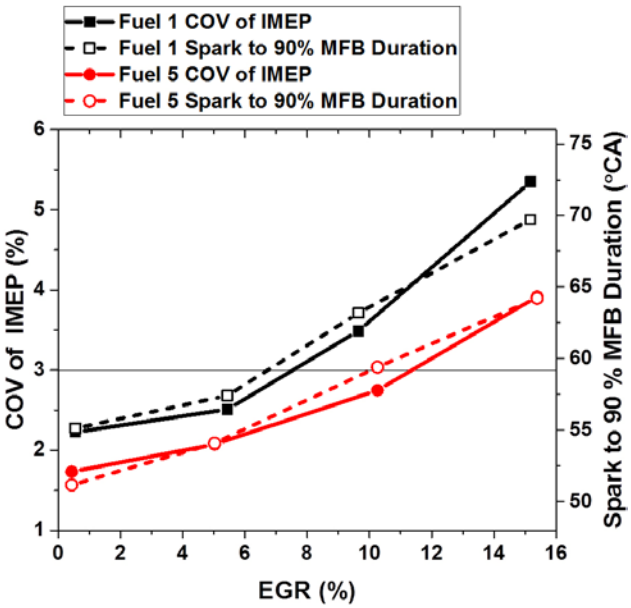


Figure 5. The laminar flame speed of the six fuels used to investigate EGR dilution tolerance in SI engines calculted using two different methods, an engine fraction mixing rule and through a detailed chemical kinetic calculation



MFB – mass fraction burned; °CA – degrees crank angle

Figure 6. The COV of IMEP and the combustion duration for two fuels as a function of EGR. The fuel with the shorter combustion duration produced a lower COV of IMEP at every EGR level, thus allowing it to be more tolerant to EGR dilution

Conclusions

- Many renewable and advanced fuels have unique properties which can enable increased efficiency for both ACI modes as well as high efficiency SI combustion modes.
- Fuel properties can enable expanded operation of ACI methods and improve performance as compared to conventional fuels as methods and improve performance as compared to conventional fuels. The role of alternative and advanced fuels to enable advanced combustion operation has been demonstrated.
- Fuel-specific effects on dilution tolerance in SI engines are primarily due to differences in the flame speed. The initial flame kernel development for slow flame speed fuels is prone to stochastic turbulent events, causing the combustion stability to decline. In contrast, when the flame speed is fast, the early flame kernel development takes less time, making it more resilient to stochastic turbulent events, thereby enhancing combustion stability and making it more tolerant to dilution.

FY 2015 Publications/Presentations

1. 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 Multicylinder Compression Ignition Engine," *J. Engineering for Gas Turbines and Power*, Vol 137, No 11, 111506.

2. Curran, S.J., Gao, A., and Wagner, R.M., "Reactivity-controlled compression ignition drive cycle emissions and fuel economy estimations using vehicle system simulations," *Int. J.Engine Research*" 2015 16: 1014–1024.

3. Splitter. D.A., Wagner, R.M., Dempsey, A.B., and Curran, S.J., "The Landscape of GCI combustion "Fuel Properties and Stratification," SAE 2015 Gasoline Compression Ignition Engine Symposium, September 17, 2015, Capri, Italy [Invited].

4. Curran, S.J., Wagner, R.M., and Dempsey, A.B., "Next Generation Compression Ignition Engines and Future Fuel Opportunities," 2015 SAE/JSAE Powertrain Fuels and Lubricants International Meeting, September 1–4, 2015, Kyoto, Japan [Invited].

5. Wagner, R.M., Dempsey, A.B., and Curran, S.J., "Directions in High Efficiency Engine Research and Future Fuel Opportunities," 13th International Conference on Engines for Vehicles, Port Jefferson, NY, June 22, 2015 [Invited].

6. Szybist, J.P., Curran, S.J., Sluder, C.S., Splitter, D.A., Dempsey, A., and Wagner, R.M., "Gasoline-Like Fuel Effects on Advanced Combustion Regimes," DOE Vehicle Technologies Office Annual Merit Review, June 2015, Arlington, VA.

7. Wagner, R., et al., "FUTURE ENGINES: Incremental Advances Driving Disruptive Opportunities," SAE 2015 High Efficiency Engine Symposium, Detroit, MI: April 19, 2015 [Invited].

8. Splitter, D.A. and Szybist, J.P., "Fuel Effects and EGR Dilution Limits with SI Combustion," Advanced Engine Combustion Program Review, February 2015, Livermore, CA.

9. Curran, S.J., et al., "Opportunities and Challenges Associated with Multi-mode Diesel/ RCCI Combustion: An Aftertreatment Perspective," Presentation, SAE LD Emissions Control Symposium Troy, MI: December 2014) [Invited].

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

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

12. 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.

13. Curran, S.J., et al., "Opportunities and Challenges Associated with Multi-mode Diesel/ RCCI Combustion: An Aftertreatment Perspective," Presentation, SAE LD Emissions Control Symposium Troy, MI: December 2014) [Invited].

Special Recognitions and Awards/ Patents Issued

1. Jim Szybist was awarded SAE Horning Award at the 2015 SAE World Congress in April in Detroit, MI for best paper demonstrating optimization of fuels and efficiency.

2. Scott Curran was awarded the SAE 2015 Stefan Pischinger Young Industry Leadership Award at the SAE Foundation Annual Celebration in March in Detroit, MI.

V.2 Fuel Ignition Characterization for Advanced Combustion Regimes and Biofuels

Overall Objectives

- Address technical barriers of inadequate data and predictive tools for fuel, especially biofuel, effects on combustion, engine optimization, and emissions
- Develop understanding of fuel chemical and physical properties that enable furtherance of the DOE Vehicle Technologies Office Advanced Combustion Engines research and development program for high-efficiency engines with cost-effective emission controls

Fiscal Year (FY) 2015 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, surrogates, and blends, and related reduced kinetic mechanisms to further enable advanced combustion engine development and increased utilization of renewable fuels

FY 2015 Accomplishments

- Continued development of Ignition Quality Tester (IQT)-based experimental and simulation research platform to characterize fuel ignition performance, including IQT cooling and injection system upgrades to enable higher temperature operation while avoiding boiling of low-end fractions within the injection system for gasoline-range blends
- Measured and distributed critical ignition characterization data for alternative and renewable fuels; these data support continual updates to the frequently cited NREL report, *Compendium of Experimental Cetane Numbers*
- Characterized ignition performance of fuel compounds and simple blends to support development of kinetic mechanisms, including blend mechanisms and reduced mechanisms; focus in FY 2015 included ethanol/iso-octane blends, primary reference fuel (PRF) blends, toluene standardization fuel (TSF) blends, and blends of ethanol into PRFs and TSFs
- Evaluated and validated reduced kinetic mechanisms for key fuel surrogates

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- Continued development of KIVA-based computational fluid dynamics linked to CHEMKIN simulation for the IQT

Future Directions

NREL's fuel ignition research will continue in FY 2016, but fuel components and blends studied will be coordinated and aligned with the New Fuels-Vehicle Systems Optima Program. NREL will continue expanding IQT-based experimental and simulation research to:

- Develop broader understanding of fuel chemistry impacts on ignition, covering wider parametric space and providing more information that traditional Research Octane Number (RON), Motor Octane Number (MON) or derived cetane number measurements.
- Develop and validate improved kinetic mechanism reductions.
- Assist in rapid development of simple chemical kinetic models for screening of advanced biofuel compounds.
- 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 research fuels used in engine studies, providing more insight than RON or MON.

- Explore oil droplet contamination of fuel/air charge on ignition kinetics, to mitigate low speed pre-ignition in gasoline direct injection (GDI) engines

Introduction

Advances in engine combustion increasingly rely on a thorough understanding of the physicochemical properties of fuel, especially ignition kinetics behavior. In addition, the ignition properties of advanced alternative and renewable fuels may significantly differ from traditional petroleum-based fuels. NREL has developed a flexible, constant-volume combustion chamber research platform using the IQT to understand the relationship between fuel composition, reaction kinetics, and ignition properties to support development of kinetics-dominated advanced engine combustion strategies.

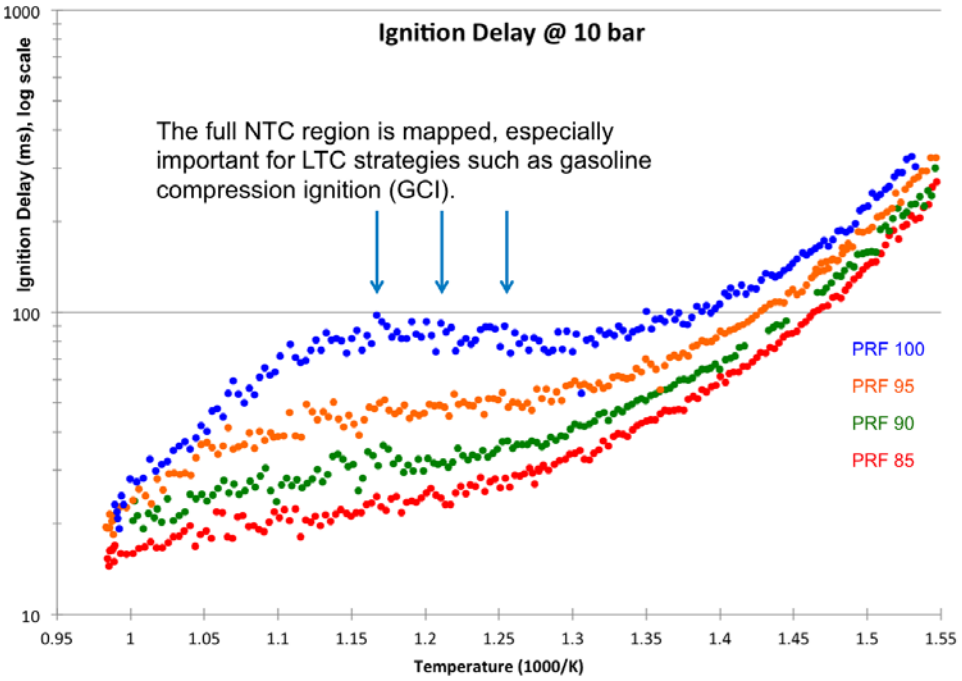
The IQT-based studies allow fuel ignition performance measurements such as ignition delay (ID) and low temperature heat release (LTHR) over engine relevant parametric space. The IQT measurements complement those from other fundamental devices such as shock tubes and rapid compression machines (RCMs), while offering flexibility to work with complex blends and ability to map the critical negative temperature coefficient (NTC) region important to advanced combustion strategies. The IQT measurements also provide broader ignition performance characterization than traditional single-condition RON, MON, or derived cetane number measurements. This research supports the simultaneous development of advanced fuel chemistries and advanced combustion engines by providing bridging experiments and simulation between fundamental chemical kinetics and engine studies.

Approach

NREL's ignition kinetics research builds on continual development and modification of the IQT as a flexible research platform. The development of techniques to conduct ID studies over temperature sweeps at various fixed pressures was a significant achievement. Extending that work to gasoline-range fuels with inherently longer ID times allowed better mixing and reduced spray physics to affect only a small portion of the overall ID. As a result, NREL's modified IQT produces high-value ignition kinetic data for gasoline-range compounds. NREL initially focused on PRF and TSF blends, before moving onto more complex gasoline blends. Valuable industry feedback via the Advanced Engine Combustion Memorandum of Understanding and presentations at individual companies established great interest, with the acknowledgement that these techniques require significant development before their full value is known. NREL has included two faculty joint appointments from Colorado School of Mines with this research, in addition to hosting a doctoral candidate from the University of Michigan in a collaborative appointment to tie IQT studies with RCM studies. NREL is sharing ID data with other researchers, and has begun applying these techniques to fuel samples shared from other DOE laboratory and industry partners. These collaborations are critical to correlating the IQT-based ID temperature sweeps to engine studies, and developing the potential for IQT based techniques to provide faster screening and ignition performance insight for biofuel candidate blends.

Results

NREL built on exploratory studies in FY 2014 with gasoline-range fuel blends, expanding temperature sweeps to higher temperatures and pressures to more closely reach conditions relevant to modern GDI engines. The hypothesis was IQT-based temperature sweep ID data over various fixed pressures could provide greater understanding of fuel knock resistance than octane numbers derived from single-point engine test conditions alone. Initial focus included PRF blends, as these fuels define octane rating numbers, and similar TSF fuels primarily used to extend octane rating beyond 100 (iso-octane). As shown in Figure 1 for PRF blends defining 85, 90, 95, and 100 octane (both RON and MON), the IQT maps ID over a broad temperature range. NREL has conducted similar experiments with gasoline-range fuels up to ~20 bar. While prior NREL work has shown ID is significantly influenced by spray physics up to ~40 ms, the long IDs typical of gasoline-range fuels allow the IQT to produce useful ignition kinetics data. Mapping the NTC region is especially important for low temperature combustion strategies such as gasoline compression ignition. Strong NTC behavior is typical of paraffinic fuels, and significantly less likely for commercial fuels containing olefins, aromatics, and ethanol. However, because the reference fuels used to define octane ratings exhibit NTC, mapping that region and contrasting deviations from the reference NTC behavior provide significantly more insight than octane numbers alone. Figure 2 illustrates additional value of the IQT-based ignition experiments. For each of the individual ID points illustrated in temperature sweeps (such as Figure 1), pressure data are also captured which include details such as LTHR. These pressure data can be mined to provide



LTC – low temperature combustion

Figure 1. Plot of ignition delay versus temperature for PRFs at 10 bar. Note the full NTC region is mapped.

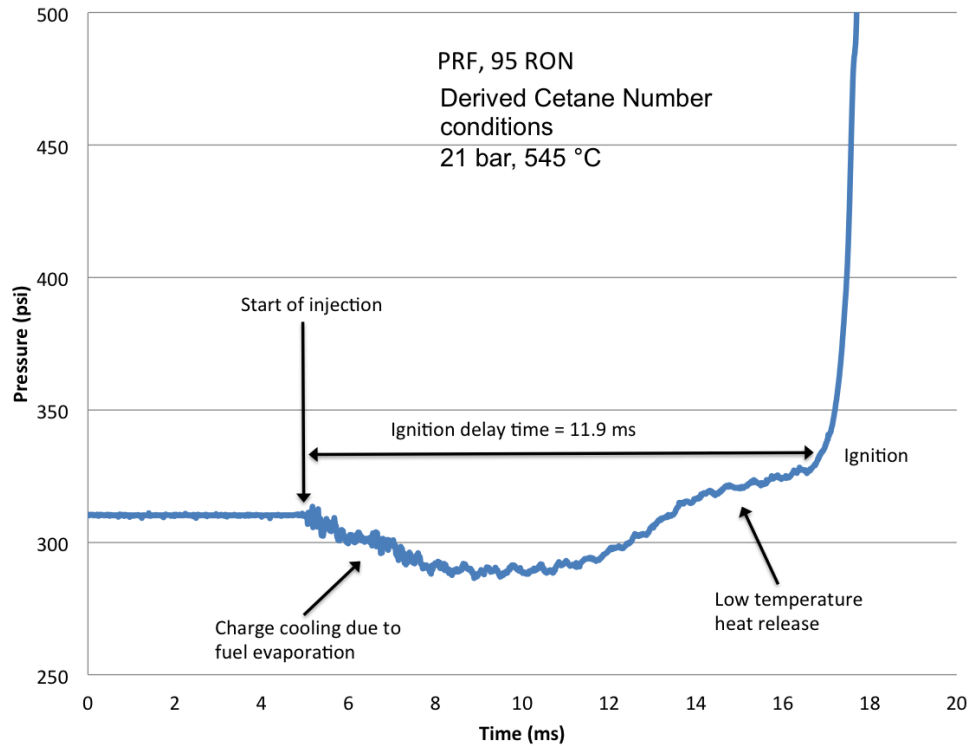


Figure 2. Pressure trace for a single IQT injection event. Ignition delay is measured from start of injection to rapid pressure rise (a non-trivial calculation). The pressure trace data also include other important features, such as LTHR.

additional technical understanding of the fuel ignition performance over broad, engine-relevant parametric space.

NREL subsequently expanded the gasoline-range studies to include ethanol blends into PRFs and TSFs, in progress toward testing more realistic fuel blends and correlating the ID trends to octane ratings and engine studies. Figure 3 illustrates these types of studies, in which fuels used in other single-cylinder GDI engine knock limit studies at NREL were mapped. As Figure 3 shows, three fuels with nominally the same RON but different octane sensitivity (S) exhibit significantly increased ID at lower temperatures characteristic with increased S. These data offer insight to explain why increasing S enables higher boost and load with retarded combustion phasing, taking advantage of longer ID with reduced temperature (even though RON is fairly high to begin with). In FY 2016, NREL will focus on correlating IQT-based data with engine data, both internally and in collaboration with other DOE labs and industry partners (likely via the Coordinating Research Council).

NREL also performed a series of IQT studies of ethanol/iso-octane binary blends, including extension of some experiments to correlate to similar RCM studies at the University of Michigan. Figure 4 highlights a portion of that work, with interesting results. A 10% blend of ethanol into iso-octane increased ID while maintaining iso-octane's NTC behavior, with little effect to high temperature ID. But increasing ethanol to 20% eliminated NTC behavior while increasing ID over even neat ethanol in that same region. These experiments support further development of reduced mechanisms to accurately incorporate ethanol as a blend, a necessary tool for GDI and low temperature combustion engine development.

Conclusions

- IQT experiments quantify fuel ignition performance over engine-relevant parametric space.
- Unique IQT data complement data from other devices such as shock tubes and rapid compression machines, and offer additional insight than RON or MON values alone.
- The PRF, TSF, and simple ethanol blend work sets the stage to expand to real fuel blends.
- While IQT experiments are not ideal, they demonstrate the potential for bench-scale fuel ignition performance "metric" complementing octane ratings while providing multi-dimensional information (a curve or surface instead of a number).
- Numerical simulation permits IQT experiments to be part of the feedback loop for development of reduced kinetic mechanisms.

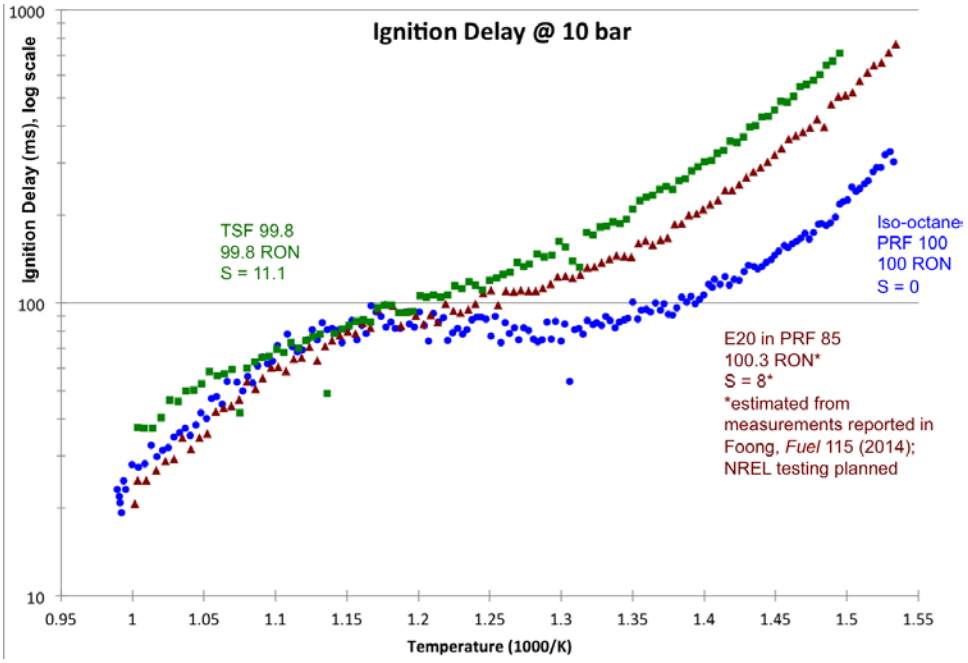


Figure 3. Plot of ignition delay versus temperature for three ~100 RON fuels at 10 bar. Note the increased ignition delay at lower temperatures characteristic with increased octane sensitivity.

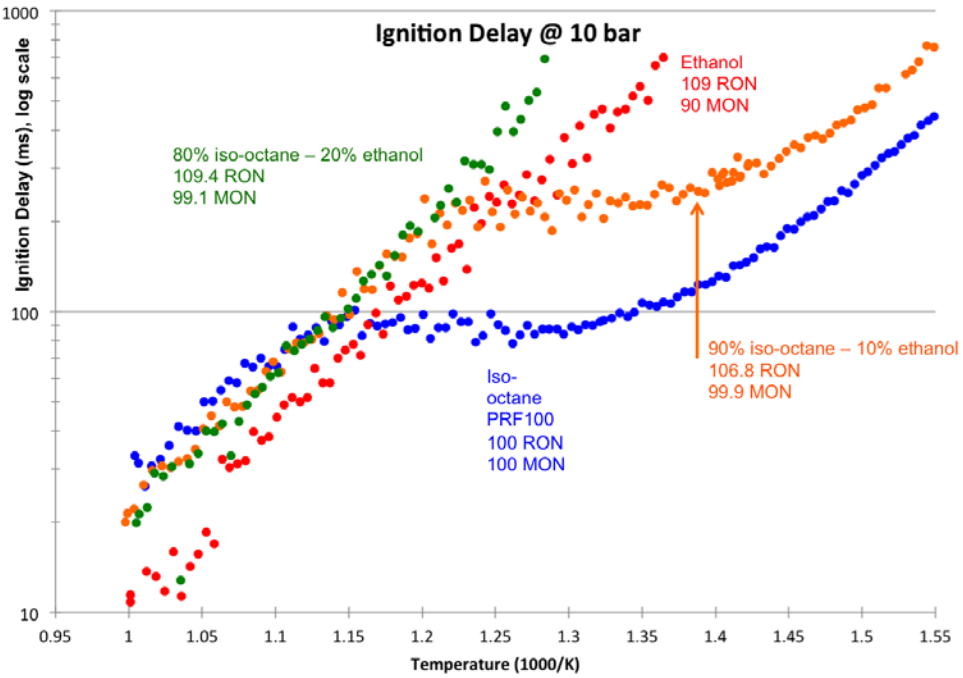


Figure 4. Plot of ignition delay versus temperature for ethanol blends into iso-octane at 10 bar. Note a 10% ethanol blend increases ignition delay over iso-octane, but maintains NTC behavior. A 20% blend exhibits much higher ignition delay, beyond even neat ethanol, and appears to eliminate NTC behavior.

- FY 2015 collaborations included:
  - Lawrence Livermore National Laboratory – data for kinetic mechanism development feedback.
  - Argonne National Laboratory – fuel ignition behavior impacts on gasoline compression ignition; kinetic mechanism reductions.
  - University of Michigan – ignition kinetics experiments for ethanol blends.
- The FY 2015 research feeds directly into Optima FY 2016 research.

References

1. J. Yanowitz, M.A. Ratcliff, R.L. McCormick, J.D. Taylor, and M.J. Murphy, "Compendium of Experimental Cetane Numbers," Technical Report NREL/TP-5400-61693, August 2014.
2. G.E. Bogin Jr., E. Osecky, M.A. Ratcliff, J. Luecke, X. He, B.T. Zigler, and A.M. Dean, "Ignition Quality Tester (IQT) Investigation of the Negative Temperature Coefficient Region of Alkane Autoignition," *Energy Fuels*, **27** 1632–1642, 2013. DOI: 10.1021/ef301738b.
3. G.E. Bogin Jr., A. DeFilippo, J.Y. Chen, G. Chin, J. Luecke, M.A. Ratcliff, B.T. Zigler, and A.M. Dean, "Experimental Investigation of n-Heptane Autoignition in the Ignition Quality Tester (IQT)," *Energy Fuels*, **25** 5562–5572, 2011. doi:10.1021/ef201079g.
4. G. Bogin, A.M. Dean, M.A. Ratcliff, J. Luecke, and B.T. Zigler, "Expanding the Experimental Capabilities of the Ignition Quality Tester for Autoigniting Fuels," *SAE International Journal of Fuels and Lubricants*, Vol. 3, Issue 1, 353–367, 2010.
5. T.M. Foong, K.J. Morganti, M.J. Brear, G. da Silva, Y. Yang, F.L. Dryer, "The Octane Numbers of Ethanol Blended with Gasoline and its Surrogates," *Fuel*, **115** 727–739, 2014. http://dx.doi.org/10.1016/j.fuel.2013.07.105

FY 2015 Publications/Presentations

1. G.E. Bogin Jr., E. Osecky, J.Y. Chen, M.A. Ratcliff, J. Luecke, B.T. Zigler, and A.M. Dean, "Experiments and Computational Fluid Dynamics Modeling Analysis of Large *n*-Alkane Ignition Kinetics in the Ignition Quality Tester," *Energy Fuels*, **28** 4781–4794, 2014. DOI: 10.1021/ef500769j.
2. B.T. Zigler, "Advanced Combustion and Fuels," Fuels and Lubricants Technologies, Project FT002, 2015 DOE Vehicle Technologies Program Annual Merit Review, Arlington, VA, June 8–12, 2015.

3. B. Zigler, J. Luecke, G. Bogin, M. Ratcliff, D. Cameron, and R. McCormick, “Fuel Ignition Studies of Octane References and Ethanol Blends,” Advanced Engine Combustion MOU Meeting, USCAR, Southfield, MI, August 18, 2015.

V.3 New Fuel Quality Metrics for GCI

Overall Objectives

- Utilize rapid compression machine (RCM) experiments and modeling to develop new fuel quality metrics that are capable of characterizing fuels for low temperature combustion (LTC) applications
- Quantify the impacts of fuel properties (i.e., composition, distillation) on combustion performance in a prototype gasoline compression ignition (GCI) engine, extending the database available under LTC operation in order to validate the new metrics

Fiscal Year (FY) 2015 Objectives

- Procure a full boiling-range gasoline to be used as the baseline fuel, and characterize its properties
- Acquire autoignition delay and heat release measurements for the baseline gasoline in ANL's twin-piston RCM
- Acquire performance and emissions data for the baseline gasoline using ANL's prototype GCI engine
- Initiate development of a correlation for the fundamental measurements that indicates operational performance within the GCI engine

FY 2015 Accomplishments

- Procured and fully characterized the chemico-physical properties of the baseline gasoline using ASTM standardized testing protocol
- Acquired autoignition delay and heat release measurements for the baseline gasoline over a range of engine-relevant conditions
- Acquired engine performance and emissions data for the baseline gasoline, covering a wide range of speed and load conditions
- Initiated development of correlations capable of comparing the RCM results with the engine measurements

Future Directions

- Blend and characterize the chemico-physical properties of a matrix of fuels containing the baseline gasoline and single-component surrogates representing various chemical classes found in conventional and non-conventional gasolines

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- Acquire autoignition delay and heat release measurements for the blended gasolines using ANL's twin-piston RCM covering a range of engine-relevant conditions
- Acquire engine performance and emissions data for the blended gasolines, covering a range of operating conditions selected to highlight fuel differences
- Extend the correlations in order to account for fuel compositional effects ■

Introduction

There is substantial potential to utilize advanced LTC schemes to achieve improved fuel economy and engine-out emissions relative to conventional approaches to internal combustion engine combustion, i.e., spark-ignition and direct injection. LTC modes such as GCI [1-7] and reactivity controlled compression ignition [8-10] employ precise modulations of physical processes (e.g., spray, evaporation and mixing) and fuel chemical reactivity within the combustion chamber to control the combustion process, including the rates of heat release and pollutant formation. In particular, GCI seeks to create zones of varying mixed-ness, temperature and stoichiometry, and thus reactivity via multiple injections of fairly volatile, low cetane fuel, i.e., gasoline. Like

most LTC approaches however, there are challenges for implementation across the entire engine operating map, and this inhibits wide-scale LTC deployment. At mid and high loads, where conditions favor the relatively long ignition delay characteristics typical of gasoline, multiple injection strategies must be employed in order to achieve proper combustion phasing and ensure that pollutant production is minimized. At low load, the fuel's low ignition propensity hinders adequate ignition and phasing, so that various techniques such as hot exhaust gas recirculation (i.e., exhaust rebreathing), negative valve overlap or supercharging must be employed for stable operation. These different fuel requirements at different load conditions are conflicting, particularly when fuels are characterized based on conventional metrics like Research and Motor Octane Number (RON and MON, respectively) and Cetane Number. Alternative fuel quality metrics are needed which can account for the physical-chemical variations that exist across the combustion chamber, and within different LTC modes of operation.

Approach

The work pursued for this project seeks to address existing challenges where new fuel quality metrics are to be developed which will overcome the limitations of RON and MON as indicators of performance in LTC regimes. Experimental data will be acquired using an RCM and a prototype GCI engine, while reduced-order and detailed modeling will be conducted to better understand fuel property impacts. The unique combination of the RCM and GCI engine datasets provide an excellent avenue to fundamentally understand and characterize fuel effects for LTC operation.

RCMs are sophisticated experimental tools that can be employed to fundamentally understand and quantify the autoignition behavior of single-component fuels, multi-component surrogate blends and full boiling-range fuels, especially at conditions relevant to advanced, LTC concepts [11-12]. They are capable of creating and maintaining well-controlled, elevated temperature and pressure environments (e.g., T = 600 K to 1,100 K, P = 5 bar to 80 bar) where the chemically active period preceding autoignition can be decoupled from physical interactions that occur in an engine, e.g., spray breakup, turbulent fuel/air mixing, thermal/compositional stratification, and thus monitored/probed via advanced in situ and ex situ diagnostics. The ability to utilize wide ranges of fuel and oxygen concentrations within RCMs, from ultra-lean to over-rich (e.g., ϕ = 0.2 to 2.0+), and spanning dilute to oxy-rich regimes (e.g., O_2 = 5% to >21%), offers specific advantages relative to other laboratory apparatuses such as shock tubes and flow reactors, where complications can arise under such conditions. ANL's twin-piston RCM is utilized in this project.

Various GCI approaches have demonstrated the capability to achieve the same power density as modern, state-of-the-art boosted, direct injection gasoline spark-ignition engines with variable valve actuation (up to 20 bar brake mean effective pressure [BMEP]), but also operate with reduced levels of brake specific fuel consumption (BSFC), especially at low- and mid-loads. Even compared to reduced power density, Atkinson cycle engines, GCI engines have comparable or superior minimum BSFC. Recent improvements to the hardware at ANL, including reduced compression ratio pistons (15:1 rather than stock 17.5:1) and a new Eaton supercharger, allow for additional opportunity to reduce combustion noise and NO_x, and the flexibility to adjust to variations in fuel properties, as well as the possibility to take advantage of intermediate temperature heat release (ITHR) at highly boosted conditions under low speed operation [13].

Results

A baseline (California Reformulated Gasoline Blendstock for Oxygenate Blending, regular grade) gasoline fuel was procured from Chevron's Richmond refinery by Chevron Energy Technology Company and transported to their Richmond Technology Center. Samples of this 2,000-gallon feedstock were submitted to Chevron Energy Technology Company's analytical lab for analysis. The fuel's chemico-physical properties, including RON/MON, ASTM D86 distillation, net heat of combustion, and carbon/hydrogen content were determined using ASTM standardized testing protocol, while detailed hydrocarbon analysis was also conducted. The detailed hydrocarbon analysis identified in particular the fraction of the fuel composed of its primary hydrocarbon classes, including n-paraffin, iso-paraffin, olefin, naphthene, aromatic, and oxygenate. Furthermore, the carbon sizes of the molecules in each class were also identified. There is no standard test protocol to ascertain the heat of vaporization for full boiling-range fuels, so this was not undertaken. However, this may be an important fuel property affecting some LTC operating conditions, so attempts will be made to estimate this for the different fuels utilized in this project.

The baseline fuel was tested in ANL's twin-piston RCM. Data were acquired with a stoichiometric fuel–oxygen ratio mixture that was diluted to 11% O_2. The balance of the diluent gas was either nitrogen, or a blend of nitrogen and argon. The measurements covered compressed temperatures ranging from 700 K to 1,000 K, and compressed pressures from 20 bar to 70 bar, which revealed the negative temperature coefficient behavior

of the fuel. The ignition delay times and rates of heat release were derived from the pressure records. The ignition times ranged from less than 1 ms to 60 ms. The low temperature heat release (LTHR) and ITHR were quantified at each of the test points using definitions described in Vuilleumier et al [14]. These parameters were the primary characteristics used in the initial correlation between the RCM data and the GCI engine data.

The baseline fuel was tested in ANL's GCI engine. Data were acquired at five operating points, including 850 rpm/idle; 1,500 rpm/2 bar BMEP; 2,000 rpm/5 bar BMEP; 2,500 rpm/8 bar BMEP; and 2,750 rpm/12 bar BMEP. Injection timing sweeps were conducted over a range of intake pressures from 1.0 bar to 1.2 bar, while the injection pressure and exhaust gas recirculation were adjusted under the high load operating conditions. For all points the coefficient of variance was maintained to less than 3%, while the noise of limited to around 90 dB. Measurements included dynamic pressure as a function of crank angle degree and emissions profiles (NO_x, CO, hydrocarbons, and Filter Smoke Number). The data were post-processed to derive BSFC, indicated mean effective pressure, indicated efficiency, and crank angle resolved heat release rates.

The trends observed in the autoignition characteristics of the full boiling-range baseline fuel within the RCM platform were correlated based on temperature and pressure in order to fundamentally understand the operational characteristics of the fuel in the GCI engine. These correlations were not able to capture influences of reactivity gradients within the combustion chamber of the engine due to compositional stratification, because the equivalence ratio and dilution of the mixtures used in the RCM were not varied. This deficiency will be addressed in FY 2016.

Work in FY 2016 will expand the RCM measurements for the baseline gasoline covering a wider range of stoichiometry and dilution which will provide insight into the influence of reactivity gradients within the GCI engine under some operating conditions. These features will be incorporated into the correlation, while a test protocol will be formulated so that this autoignition property information can easily be determined for the various fuels included in the test matrix. The fuels in the test matrix will then be used in the RCM, and also be used in the GCI engine covering a range of operating conditions.

Conclusions

- ANL's RCM has been used to acquire autoignition data for the full boiling-range, baseline gasoline over a range of engine-relevant conditions, while the baseline gasoline was utilized over a range of conditions in ANL's prototype GCI engine.
- Autoignition features of the baseline gasoline, including ignition delay time and extent of LTHR/ITHR were correlated to conditions utilized in the engine.

References

1. S. Ciatti and S.N. Subramanian, "An experimental investigation of low-octane gasoline in diesel engines," J. Eng. Gas Turb. Power (133) 092802-1, 2011.
2. S. Ciatti, S.N. Subramanian, A. Ferris, "Effect of EGR in a gasoline operated diesel engine in LTC mode," Proc. ASME 44663, ICES2012-81010, 2012.
3. B.D. Adhikary, Y. Ra, R. Reitz, S. Ciatti, "Numerical optimization of a light-duty compression ignition engine fuelled with low-octane gasoline," SAE Paper 2012-01-1336, 2012.
4. B.D. Adhikary, R. Reitz, S. Ciatti, "Study of in-cylinder combustion and multi-cylinder light duty compression ignition engine performance using different RON fuels at light load conditions," SAE Paper 2013-01-0900, 2013.
5. S. Ciatti, M. Johnson, B.D. Adhikary, R. Reitz and A. Knock, "Efficiency and emissions performance of multizone stratified compression ignition using different octane fuels," SAE 2013-01-0263, 2013.
6. C. Kolodziej, S. Ciatti D. Vuilleumier, B. D. Adhikary, R. Reitz, "Extension of the lower load limit of gasoline compression ignition with 87 AKI gasoline by injection timing and pressure," SAE 2014-01-1302, 2014.
7. B.D. Adhikary, R. Reitz, S. Ciatti, C. Kolodziej, "Computational investigation of low load operation in a light-duty gasoline direct injection compression ignition (GDICI) engine using single-injection strategy," SAE Paper 2014-01-1297, 2014.
8. S.L. Kokjohn, R.M. Hanson, D.A. Splitter, R.D. Reitz, "Fuel reactivity controlled compression ignition (RCCI): a pathway to controlled high-efficiency clean combustion," Int. J. Eng. Res. (12) 209–226, 2011.
9. D.A. Splitter, R.D. Reitz, "Fuel reactivity effects on the efficiency and operational window of dual-fuel compression ignition engines," Fuel (118) 163–175, 2014.
10. V. Fraioli, E. Mancaruso, M. Migliaccio, B.M. Vaglieco, "Ethanol effect as premixed fuel in dual-fuel CI engines: Experimental and numerical investigations," Applied Energy (119) 394–404, 2014.

11. C.-J. Sung and H.J. Curran, “Using rapid compression machines for chemical kinetics studies,” Prog. Energy Comb. Sci. (44) 1–18, 2014.

12. S.S. Goldsborough, D. Longman, M.S. Wooldridge, R.S. Tranter and S. Pratt, “1st International RCM Workshop Meeting Report,” August 28–29, 2012. (http://www.transportation.anl.gov/rcmworkshop)

13. Y. Yang, J. Dec, N. Dronniou, W. Cannella, “Boosted HCCI combustion using low-octane gasoline with fully premixed and partially stratified charges,” SAE Paper 2012-01-1120, 2012.

14. D. Vuilleumier, D. Kozarac, M. Mehl, S. Saxena, W.J. Pitz, R.W. Dibble, J.Y. Chen, S.M. Sarathy, “Intermediate temperature heat release in an HCCI engine fueled by ethanol/n-heptane mixtures: An experimental and modeling study,” Comb. Flame (161) 680–695, 2014.

V.4 Utilizing Alternative Fuel Ignition Properties to Improve SI and CI Engine Efficiency

Overall Objectives

- Demonstrate a combination of fuel selection, fuel injection strategy, and mixture preparation that enables meeting the DOE targets for brake thermal efficiency (BTE) of greater than 40% for spark-ignited engines and greater than 50% for compression-ignited engines

Fiscal Year (FY) 2015 Objectives

- Demonstrate upgraded operation of two single-cylinder and one multi-cylinder engine facilities

FY 2015 Accomplishments

- Single-cylinder Ford Fox engine installed and baseline knock limits determined using dual fuels of ethanol and gasoline
- Single-cylinder Ricardo Hydra engine installed and baseline knock limits determined using gasoline
- Multi-cylinder Daimler M274 2.0 L installed
- Multi-cylinder General Motors 1.9 L turbodiesel configured for dimethyl ether (DME)/propane dual fuel combustion studies, dual fuel combustion studies completed, go/no-go decision point reached

Future Directions

- Develop ignition and fuel spray correlations that can be used to guide injection and spark timing strategies and can be used in engine simulations
- Continue to develop fuel injection strategies to achieve target efficiencies using the Fox and Hydra single-cylinder engines
- Demonstrate fuel injection strategies developed using the single-cylinder engine studies on the multi-cylinder engine ■

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Introduction

Downsized boosted spark-ignition (SI) engines offer considerable thermal efficiency benefits compared to naturally aspirated gasoline SI engines [1,2], and ethanol offers even further fuel economy benefits [3]. However, turbocharging SI engines increases the risk of knock (normal pre-ignition) and super-knock (more infrequent, more intense and particularly damaging ignition) in these engines. Ethanol is well known to have knock-suppressing properties compared to gasoline, including high heat of vaporization (which is not fully captured in current octane rating methods). What is currently missing is an engineering-based recommendation for the optimal blend ratio of ethanol to gasoline and strategies which leverage the intrinsic properties of ethanol to improve engine fuel economy, and a comprehensive means of mitigating (rather than simply avoiding) spark knock. In addition, ad hoc levels of 10% and 85% ethanol have not leveraged the valuable characteristics of ethanol. Achieving the DOE Vehicle Technologies Office goal of 45% peak thermal efficiency for light-duty engines will require additional boosting and higher compression ratios, as well as strategies to mitigate knock at these high compression ratios, including stratification and the use of exhaust gas recirculation. The objective of this work is to develop fuel injection and spark strategies which leverage the thermophysical properties of ethanol to maximize engine efficiencies.

Dual fuel combustion has shown significant potential for increased thermal efficiency in compression-ignition (CI) engines. An additional goal of this project is to utilize the unique properties of DME and its synergy with propane to enable meeting the DOE target for BTE of >50% for CI engines.

Approach

This work focuses on building the combustion science necessary to advance SI engines to >40% BTE and CI engines to >50% BTE. The project leverages shared experimental diagnostics, methods, and platforms. Further, the work is based on extensive experience with the well-studied alternative fuel ethanol. For SI engines, achieving the DOE goal of 45% peak thermal efficiency will require additional boosting and higher compression ratios, as well as strategies to mitigate knock at these high compression ratios, including stratification and the use of exhaust gas recirculation.

This work leverages the experimental facilities and modeling tools developed at the University of Michigan to generate realistic burn rates and the integration of appropriate burn rates and limiting behavior (including flammability limits and knock limits) to create realistic engine maps to quantify fuel economy benefits [2,3]. The scope of work includes studies to improve our understanding of the fundamental combustion science of SI, to demonstrate high thermal efficiency engine operating strategies, and to model the impact of the fuels and operating strategies on vehicle fuel economy. The modeling work will guide the engine studies in terms of identifying the optimal ethanol/gasoline blend ratios, exhaust gas recirculation levels, boost pressures, and target burn rates (which will guide stratification levels). The CI work leverages an existing General Motors 1.9 L turbodiesel engine facility, which has been augmented with hardware for studies of dual fuel combustion.

The results of the ignition studies provide information to the model simulation of engine cycles to help predict efficiency limits. Together the ignition and simulation studies guide single-cylinder engine work that seeks to extend knock limits and control particulate matter (PM) emissions while operating under lean spray-guided combustion strategies. The results of the single-cylinder engine studies guide the multi-cylinder engine studies. In-kind support by Bosch is directed toward the single-cylinder and multi-cylinder engine work.

Results

Fundamental Combustion Studies

During this past year, we completed the ignition and speciation studies of 100% ethanol using the University of Michigan rapid compression facility (RCF) [4]. These ignition studies leverage support from our DOE Basic Energy Sciences sponsored project [5]. The results show generally good agreement with predictions from ethanol reaction mechanisms used in the literature. The RCF data are the baseline for speciation studies of ethanol and iso-octane blends. The initial results of ignition delay times of ethanol and iso-octane show the model predictions are accurate at reproducing the experimental data for blends at some state conditions, but as seen in Figure 1, there are discrepancies between the model predictions and experimental observations at lower temperatures. The speciation data of the blends will provide insight into the source of the discrepancies between the experimental results and the model predictions, and will provide additional data for reaction mechanism development.

During this past year, we have also partnered with Dr. Bradley Zigler at the National Renewable Energy Laboratory (NREL) to conduct complementary ethanol

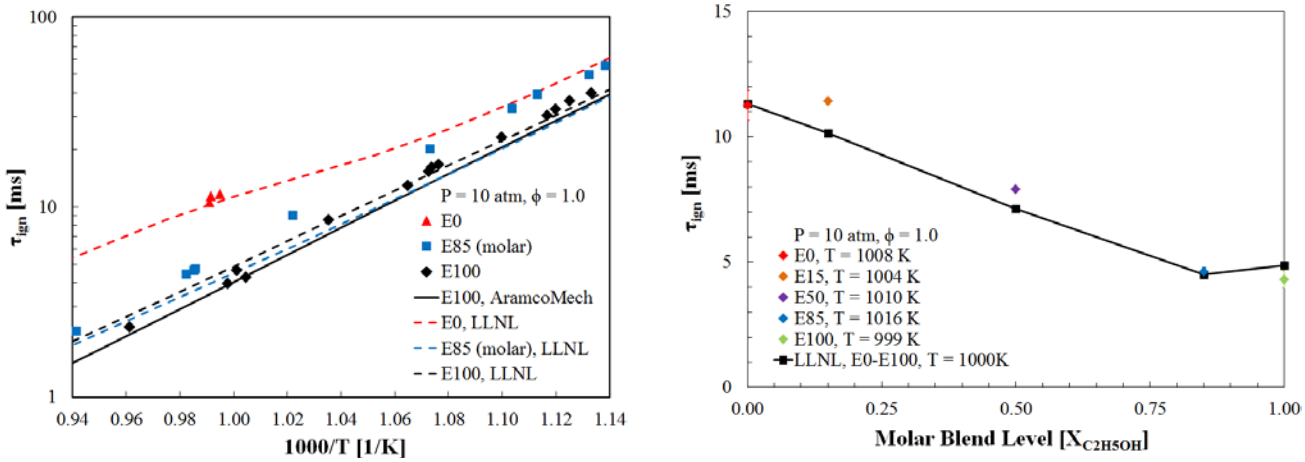

Figure 1. Experimental results for ignition delay time from University of Michigan RCF studies of ethanol and iso-octane blends (solid symbols) as a function of inverse temperature (left panel) and blend volume fraction (right panel). Solid and dashed lines correspond to simulations based on the reaction mechanisms from Lawrence Livermore National Laboratory (LLNL) [6] and Aramco [7,8]. Experimental UM RCF data are from Barraza-Botet et al. 2015 [9]

blend studies using the NREL ignition quality tester facility. This effort leverages the strong foundation on ignition quality tester spray studies previously developed at NREL and the foundation in fundamental ignition studies using The University of Michigan RCF. We are focusing on conditions which allow validation of overlapping regimes between the experimental facilities. The results build confidence in extending the results from each facility to conditions that are important to current engines.

In the 2014–2015 project period, we also completed fuel spray imaging studies of the Spray G injector from the Engine Combustion Network. We are currently analyzing the results and developing methods to quantify the spray characteristics of this important reference fuel injector.

Simulations of Engine Efficiency Enhancement and Limitations

Simple GT-POWER models are now available for the partially premixed charge combustion engines: the Fox, and the Daimler M274 engines which are being used for this project. The model for the Ricardo Hydra boosted single-cylinder engine is under development. Work is focused on realistically modeling the fueling process in these engines particularly on the manner in which evaporation influences thermal efficiency. This will be needed for ethanol blends and other fuels with high heats of evaporation as well as for the planned port fuel injection plus direct injection experiments. At the same time, progress is being made toward developing a simple method to estimate vehicle fuel economy benefits from engine efficiency changes. The approach will optimally select mapping points and weighting factors to best represent the engine–vehicle interaction.

Single- and Multi-Cylinder Engine Studies of Extending Knock Limits

Two single-cylinder engines have been installed and instrumented at the University of Michigan in the past year. In one test cell, a Ricardo Hydra 0.5 L single-cylinder engine with a dual overhead cam, pent-roof cylinder head, central mount spark plug and port fuel injection has been mounted in a test stand that provides hydraulic dynamometer-based control of engine operation, boosted intake and exhaust flows (up to 3 bar intake boost) and real time engine control. This test engine has provided baseline data against which the lean spray-guided engine studies will be compared. The engine will be converted to direct injection spray-guided operation by installing a direct injection fuel injector (HDEV-4) in the engine and moving the spark plug to an off-center location. Our partner company on the project, Robert Bosch LLC, is providing an engine control unit to operate the injector via the real time interface of the test cell. A Bosch gasoline direct injection injector (central mount, spray-guided) has been acquired for the engine and installation in a cylinder head is in progress.

Baseline experiments of the Hydra engine were conducted with reference gasoline fuel and port fuel injection to establish thermal efficiency and knock limit baselines at 1,200 rpm. The intake pressure was varied from 0.4 bar to 1.4 bar, and spark timing was varied to identify the maximum brake torque (MBT) at each pressure point. Emissions data were collected using a Horiba emissions bench at each test point. The baseline tests included iso-octane and will be extended to oxygenated fuel blends in the next quarter. The port fuel injection system will remain on the engine stand to permit the potential for combined gasoline direct injection plus port fuel injection operation of the Hydra engine, as one of several schemes that will be explored for knock mitigation.

In the second test cell, a three-cylinder Ford Fox engine was installed and two of the cylinders were deactivated to allow single-cylinder operation of the engine. Baseline experiments have been conducted using reference grade gasoline (octane number of 87) and using blends of ethanol and gasoline. Engine load was increased by boosting the engine from 1 bar (naturally aspirated at wide open throttle) to 1.5 bar absolute pressure. As the operation was limited by knock even at the ambient (1 bar) intake pressures for gasoline, operation at boosted conditions required spark retard which resulted in lower thermal efficiencies as we moved further away from the MBT timing. The studies included effects of changing the start of injection from 300° to 50° before top dead center (BTDC) in intervals of 50° crank angle. Advancing the injection earlier than 300° BTDC resulted in high PM emissions which was attributed to fuel impingement on the piston. Similar observations of high PM emissions were observed for retarded start of injection of 50° BTDC and beyond of more stratified sprays. For single injection strategies, the highest indicated thermal efficiencies were observed for earlier injection timing of 300° BTDC and retarding the timing beyond 200° BTDC resulted in noticeable decrease in the efficiency.

Ethanol was splash blended with gasoline to investigate its effects on the knock limit. Results of two blends E30 (30% ethanol, 70% gasoline by volume) and E50 (50% ethanol, 50% gasoline by volume) are presented here. As percentage of ethanol was increased in the fuel blend, the amount of fuel required increased due to ethanol's lower heating value than gasoline. This resulted in piston impingement indicated by PM emissions with E30 when injecting fuel at 300° BTDC. Thus, the injection timing

for E30 was retarded to 270° BTDC and for E50 to 240° BTDC to avoid spray impingement on the piston. Both of the blends were used to achieve the same loads as the baseline gasoline with intake pressure varying from 1 bar to 1.5 bar absolute. No knock was observed for E30 or E50 even at the 1.5 bar boosted condition which enabled the engine to be operated at MBT corresponding higher thermal efficiencies compared with gasoline. At 1.5 bar boost condition the peak in-cylinder pressures (approximately 90 bar) reached the rated limits for the engine, and further boosting was limited by the peak pressure and not the knock limit. The results are plotted in Figure 2, which presents the net indicated thermal efficiency for E0, E30, and E50 as a function of net indicated mean effective pressure. The figure shows the efficiency improvement and load extension obtained by using ethanol blends. The data show ~2% improvement in net indicated mean effective pressure with the use of boosted E50 compared to the gasoline baseline. Gasoline load extension could only be achieved by spark retard at the boosted conditions to mitigate knocking, but ethanol blends could be operated at MBT and load extension was accompanied with improved efficiency.

Higher combustion and thermal efficiencies were limited for higher blends of ethanol, because the start of injection needed to be retarded to mitigate spray impingement on the piston and resulting PM emissions. Split injection strategies were implemented to resolve these issues, and initial results show further improvement of ~0.5% in efficiency. Work for the year includes exploring the effects of split injection at boosted intake pressure conditions as well as lean high compression ratio operation of this engine using ethanol blends.

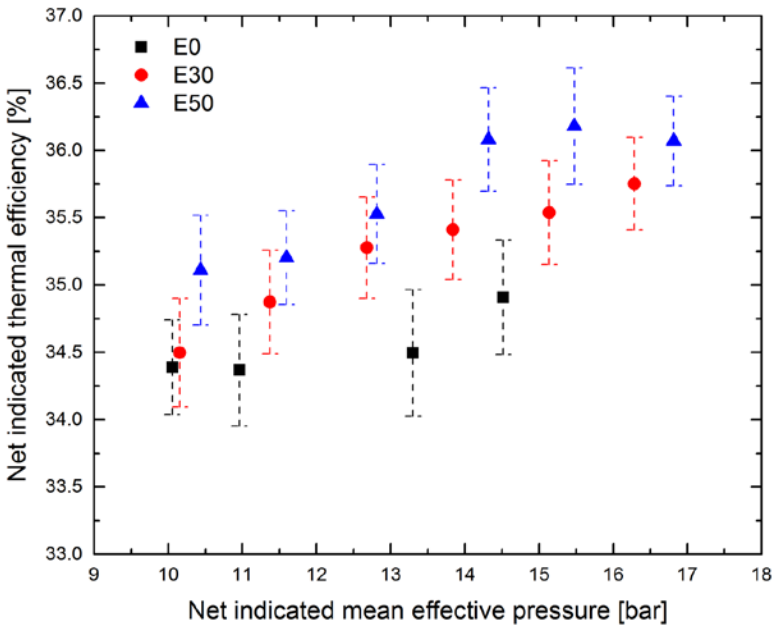

Figure 2. Net indicated thermal efficiency in the Fox single-cylinder engine as a function of net indicated mean effective pressure for E0, E30, and E50.

In the past year, our partner Robert Bosch LLC provided a Daimler M274 2.0L engine with a piezo fuel injection system which has been mounted on an engine dynamometer cart and has been fully instrumented. The engine and cart were delivered to the University of Michigan and installed in the transient dynamometer facility. The engine control unit and controller area network of the Daimler engine have been modified to allow open access to the software and calibration via an ETK interface. The engine has been commissioned in the test cell and achieved first fire along with some preliminary investigations. Additionally, a secondary cylinder head has been produced which allows for optical access via an endoscope and light source.

Dual Fuel Combustion for High CI Engine Efficiency

This task was meant to demonstrate 50% peak thermal efficiency at one speed–load condition in a new 1.9 L turbodiesel test engine and pursue extension of the operating range and optimization of the combustion strategy. Much of the first year of the project was devoted to configuration of the dual fuel delivery system, using an intake fumigator developed prior to DOE-sponsored work and a DME and propane delivery system to provide high accuracy control and delivery of the liquefied gaseous fuels. The last quarter of Year 1 was devoted to the dual fuel combustion research activity. In Figure 3, we present a sample of the matrix of test results. Unfortunately, the results from the completed test facility demonstrated little to no improvement in thermal efficiency over the baseline of conventional diesel combustion. As we could not meet the go/no-go decision point, this task will be discontinued.

We have explored the dual fueling strategy using liquefied gas mixtures of DME and propane over a broad range of compositions and engine operating conditions. We have extended previous test conditions to high speed and load and evaluated substitution of diesel by the fumigated gas mixtures up to 70% on an energy basis. We evaluated the resulting engine behavior through heat release analysis, brake specific fuel consumption, and emissions measurements. We are in the process of performing a statistically-based optimization of the

fueling strategy over the range of engine conditions tested, working with two master of science students for their capstone design project. That work will continue, despite our official end of work on this task for the present DOE project.

Under this subtask, we have conducted testing to look for an optimal level of diesel substitution (including variation of the injection strategy for the diesel fuel itself), using lessons learned in the studies of reactivity controlled compression ignition and combustion and DME/propane ratios to attempt to optimize the dual fuel combustion.

Overall, we were not able to reproduce the extent of thermal efficiency improvement that we observed previously, and never got close to 50% BTE.

Conclusions

- Well-validated reaction mechanisms for ethanol and iso-octane accurately predict autoignition behavior of neat (100%) ethanol and iso-octane fuels, but model simulations do not reproduce the experimentally observed trends for blends of ethanol and iso-octane.

	Conv.	20% Premixed			40% Premixed			60% Premixed			
BTE	37.3%	36.2%	36.6%	36.7%	35.7%	36.2%	36.1%	36.5%	36.4%	36.9%	50% DME
		36.3%	36.3%	36.5%	34.9%	35.5%	35.7%	33.2%	34.9%	35.5%	33% DME
		35.9%	36.2%	36.5%	34.5%	35.5%	35.5%	29.9%	33.4%	34.8%	17% DME
CO, ppm	285	1605	1444	1290	3344	2775	2390	3040	3085	2779	50% DME
		1416	1293	1184	2719	2407	2078	4593	3414	2782	33% DME
		1295	1223	1113	2387	2121	1895	3732	3123	2581	17% DME
THC, ppm	216	856	804	717	1220	1146	1063	1329	1187	1116	50% DME
		1154	980	912	2008	1793	1567	3056	2356	1939	33% DME
		1389	1233	1065	2659	2272	1911	5264	3548	2704	17% DME
Comb. Eff.	99.1%	95.7%	96.1%	96.5%	91.8%	93.0%	93.8%	92.0%	92.4%	93.1%	50% DME
		95.5%	96.0%	96.3%	91.5%	92.5%	93.5%	85.7%	89.5%	91.5%	33% DME
		95.3%	95.7%	96.2%	90.9%	92.2%	93.2%	83.1%	87.8%	90.4%	17% DME
FSN	0.487	0.413	0.503	0.502	0.401	0.532	0.559	0.377	0.497	0.593	50% DME
		0.290	0.367	0.389	0.120	0.274	0.371	0.048	0.225	0.419	33% DME
		0.203	0.280	0.325	0.071	0.144	0.218	0.018	0.056	0.174	17% DME
NO_x, ppm	612	510	527	525	387	409	407	317	356	366	50% DME
		528	556	534	458	439	426	335	352	341	33% DME
		543	560	554	450	479	465	259	370	376	17% DME
Peak Pressure, kPa	6949	6984	7092	7070	7010	7074	6998	7530	7587	7495	50% DME
		6921	7101	7065	6590	6921	6909	6041	6880	7050	33% DME
		6912	7101	7067	6415	6734	6841	5462	6032	6612	17% DME
SD Peak Pres., kPa	54	42	43	44	43	38	39	164	83	55	50% DME
		43	51	48	50	56	52	98	67	55	33% DME
		44	51	53	44	63	64	55	68	84	17% DME
Max. PRR, kPa/CAD	835	819	717	696	722	440	412	509	432	369	50% DME
		940	836	803	867	759	650	623	583	437	33% DME
		1023	930	865	881	855	805	492	592	605	17% DME
		0%	10%	20%	0%	10%	20%	0%	10%	20%	

% of premixed fuel energy from DI diesel squish conditioning pulse

THC – total hydrocarbon, FSN – filter smoke number, SD – standard deviation; PRR – pressure rise rate; CAD – crank angle degrees; DI – direct injection

Figure 3. Table of combustion and emissions results from the dual fuel combustion process. Variation in pilot and main diesel fuel injection, over range of pilot injection from 0–60% of diesel fuel injection on an energy basis, with variation in the DME content (up to 50% on energy basis) and propane content (up to 20% on energy basis). Compared to the conventional combustion condition, coloring in the table indicates whether the measured variable was better (green), similar (yellow) or worse (orange to red).

- We have demonstrated knock limit extension using ethanol blended with gasoline at normally aspirated and boosted conditions using single fuel injection events.
- Results from the single-cylinder study indicate additional gains can be made using multiple fuel injection events at boosted conditions.
- The previous work on DME/propane dual fuel combustion in a 2.5 L VM Motori turbodiesel engine could not be reproduced in the General Motors 1.9 L turbodiesel engine in terms of thermal efficiency increases. As a consequence, on the go/no-go decision point on Task 1.5, the decision is no-go and work under this task will be discontinued. The 50% BTE target was not achieved so work will focus on Tasks 1.1–1.4 for the duration of the program.

References

1. Richard, S., Font, G., Le Berr, F., Grasset, O., Fremovici, M. (2011) "On the use of system simulation to explore the potential of innovative combustion systems: methodology and application to highly downsized SI engines running with ethanol-gasoline blends," SAE Technical Paper No. 2011-01-04.
2. Lavoie, G., Ortiz-Soto, E., Babajimopoulos, A., Martz, J. B., Assanis, D.N. (2012) "Thermodynamic sweet spot of high-efficiency, dilute, boosted gasoline engines," Int. J. Engine Res. pp. 1–19.
3. Lewis, A.M., Ortiz-Soto, E., Lavoie, G., Assanis, D.N. "Scaling and dimensional methods to incorporate knock and flammability limits in models of high efficiency gasoline and ethanol engines," in preparation (2015).
4. Donovan, M.T., He, X., Zigler, B.T., Palmer, T.R., Wooldridge, M. S., Atreya, A. (2004) "Demonstration of a free-piston rapid compression facility for the study of high temperature combustion phenomena," Combust. Flame, 137, pp. 351–365
5. Wooldridge, M.S. (2013) "The effects of oxygenated fuel compound structure on combustion and pollutant reaction chemistry," Department of Energy, Basic Energy Sciences, Contract No. DE-FG02-09ER16102.
6. Mehl M., Pitz W.J., Westbrook C.K., Curran H.J. (2011) "Kinetic modeling of gasoline surrogate components and mixtures under engine conditions," Proc. Combust. Inst. 33 pp. 193–200.
7. Metcalfe W.K., Burke S.M., Ahmed S.S.,Curran H.J. (2013) "A Hierarchical and Comparative Kinetic Modeling Study of C1−C2 Hydrocarbon and Oxygenated Fuels", Int. J. Chem. Kinet. 45, pp. 639-673.
8. Mittal, G., Burke, S.M., Davies V., Parajuli, B., Metcalfe, W.K., Curran H.J. (2014) "Autoignition of ethanol in a rapid compression machine," Combust. Flame, 161, pp. 1164–1171.
9. Barraza-Botet, C., Wagnon, S., Wooldridge, M.S., "Ignition Measurements of Ethanol-Air Mixtures in a Rapid Compression Facility," 9th U. S. National Combustion Meeting of the Combustion Institute, May 17–20, 2015, Cincinnati, Ohio.

V.5 Development of Kinetic Mechanisms for Next-Generation Fuels and CFD Simulation of Advanced Combustion Engines

Overall Objectives

- Develop predictive chemical kinetic models for surrogate components and surrogate mixtures to represent next-generation fuels
- Use these models in computational fluid dynamics (CFD) simulations to optimize alternative fuel formulations and advanced engine combustion for maximum engine efficiency and very low pollutant emissions, thereby allowing the utmost petroleum displacement

Fiscal Year (FY) 2015 Objectives

- Design and build a prototype microliter fuel tester, and perform initial modeling effort
- Develop an accelerated, rapid compression machine model
- Use detailed chemical kinetic modeling to interpret direct injection spark-ignition (DISI) experiments on intermediate blends of gasoline–ethanol
- Develop mechanism for biofuel cyclopentanone

FY 2015 Accomplishments

- Octane Number correlations for gasoline surrogate fuels, including ethanol
- Computed flame speed correlations to help interpret dilute DISI engine experiments using gasoline–ethanol mixtures
- Preliminary simulations of leaner lifted-flame engine combustion of methyl decanoate
- Preliminary fired simulations of lean/dilute DISI engine experiments at Sandia National Laboratories

Future Directions

- Develop chemical kinetic models for biofuel components and biofuel mixtures that enhance fuel octane ■

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Introduction

Predictive chemical kinetic models are needed to represent next-generation fuel components and their mixtures with conventional gasoline and diesel fuels. These kinetic models will allow the prediction of the effect of alternative fuel blends in CFD simulations of advanced spark-ignition and compression-ignition engines. Enabled by kinetic models, CFD simulations can be used to optimize fuel formulations for advanced combustion engines so that maximum engine efficiency, fossil fuel displacement goals, and low pollutant emissions goals can be achieved.

Approach

Chemical kinetic models for each next-generation fuel component of interest for blending with gasoline and diesel are developed. Next, models for next-generation fuel components and for conventional fuel components are combined to make models for surrogates (or mixtures) used to represent next-generation ground transportation fuels. The mechanisms are used in a multidimensional code using multi-zone method with parallel CFD solvers for simulating advanced combustion engines. These chemistry-enabled CFD engine codes can be used to simulate combustion processes in advanced spark-ignition and compression-ignition engines to assess fuel property effects and to optimize fuel and engine design for the best performance and engine efficiency, and for minimum pollutants.

Results

Cyclopentanone is a bio-derived fuel component with a high autoignition resistance [1] that is potentially

attractive for blending with gasoline. The overall performance of cyclopentanone in a homogeneous combustion compression ignition engine engine is similar to that of ethanol [1]. In collaboration with the National University of Ireland, Galway, rates of abstraction of H atoms from cyclopentanone by OH and HO_2 radicals have been calculated using fundamental chemistry methods. These rate constants are important in controlling the rate of autoignition of cyclopentanone under engine conditions. Also, decomposition rates of cyclopentanone radicals have been computed. These rates are difficult to estimate because of the cyclic nature of cyclopentanone and the presence of a ketone group in the ring. These new rate constants are valuable towards the development of a predictive chemical kinetic model for cyclopentanone.

The ability of mimicking the chemical behavior of real fuel through simpler surrogate mixture models is a fundamental prerequisite for the simulation of engine combustion. In the past years LLNL has developed a methodology based on simple ignition delay calculations to match surrogate mixtures to real gasolines. The numerical procedure developed by LLNL is based on correlations between calculated ignition delay times and measured octane numbers (expressed as Anti-Knock Index [AKI] and sensitivity: Research Octane Number - Motor Octane Number [RON - MON]) of a large database of gasoline components and their mixtures. Previous versions of these correlations were based exclusively on fuels that did not contain oxygenates. More recently, the octane number database of fuel component mixtures used to extrapolate the correlation has been revised to include mixtures containing increasing fractions of ethanol and excluding fuels containing aromatic concentrations in excess of the existing legal limits. The result is a new set of correlations that can be applied to fuels relevant to commercial gasoline with an arbitrary amount of ethanol mixed in (Figure 1).

LLNL gasoline–ethanol models have been used to make simulations to guide DISI operation. One way to increase efficiency of ethanol–gasoline fueled engines is to operate under more dilute conditions. However, under dilute operation, the flame speeds are reduced and misfire may result. To assess this effect, the flame speeds of ethanol–gasoline fuel mixtures under dilute conditions in the engine have been simulated and the functional dependence of the burning velocity on in-cylinder temperature and pressure has been evaluated at different stoichiometries relevant to engine operations. The flame speed expressions for different fuels (e.g., RD387 gasoline, E30 [blend of 30% ethanol, 70% gasoline], and E85 [blend of 85% ethanol, 15% gasoline]) have been shared with Magnus Sjöberg at Sandia National

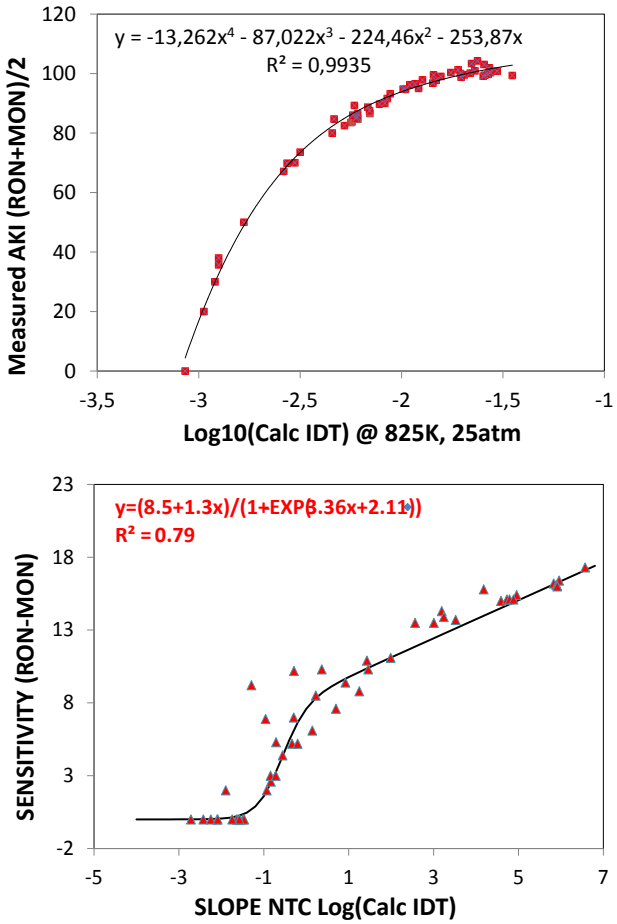

Figure 1. Correlation between computed ignition delay (at 850 K and 25 atm) of a gasoline–ethanol surrogate and measured AKI of gasoline components and their mixtures (upper plot). Correlation between computed slope in the negative temperature coefficient (NTC) region of a gasoline–ethanol surrogate and measured sensitivity of gasoline components and their mixtures (lower plot).

Laboratories to assist the interpretation of his experiments and to provide insight into the behavior of his DISI engine operating with gasoline–ethanol mixtures (Figure 2).

LLNL and Louisiana State University are developing the microliter Fuel Ignition Tester (μ–FIT, pronounced micro-fit). μ–FIT offers the potential to provide high-throughput, low volume fuel testing to provide rapid evaluation of promising new fuel blends, bio-derived components, and additives. During this performance period, Prof. Schoegl (Louisiana State University), built the first prototype of μ–FIT (see Figure 3) to measure the autoignition and extinction behavior of flames with repetitive extinction and ignition (FREI) in a millimeter-scale quartz tube. The prototype is based on an earlier design of Maruta et al. [2–3]. Prof. Schoegl demonstrated the ability to measure quantitatively the flame dynamics using an inexpensive

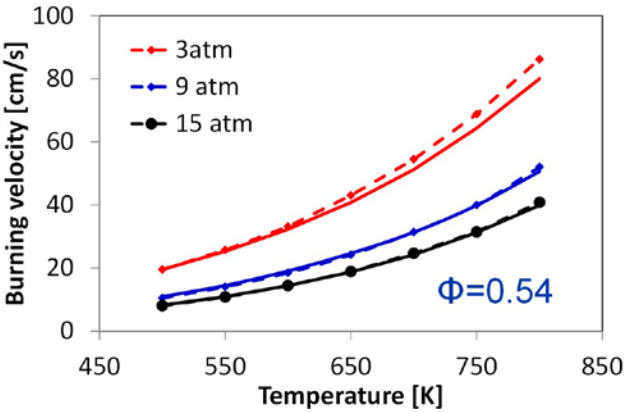

Figure 2. Burning velocity of E85 (dashed lines) and RD587 (solid lines) as a function of unburned gas temperature and pressure. For E85, burning velocity = $2.49P^{-0.515}e^{(0.00522*T)}$. For RD387, burning velocity = $2.63P^{-0.479}e^{(0.005011*T)}$.

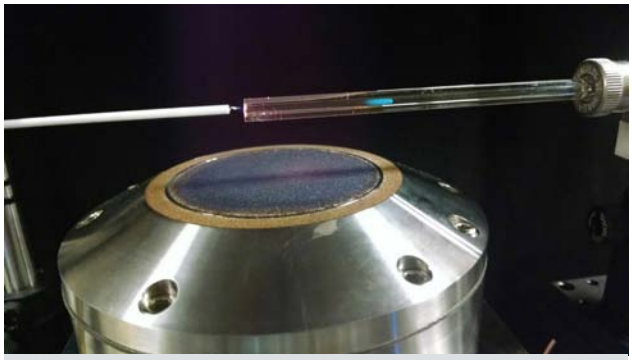

Figure 3. μ–FIT prototype developed at Louisiana State University by Prof. Schoegl. A McKenna burner (H_2/air) is used to externally heat the quartz tube. A premixed fuel-air mixture flows from right to left inside the tube. The premixed flow velocity is slower than the flame speed so that the flame spontaneously ignites in the downstream (hotter) region and then propagates upstream (colder) until it is extinguished due to heat loss to the wall. The image exposure is sufficiently long that the thin propane flame is smeared out between the ignition and extinction points.

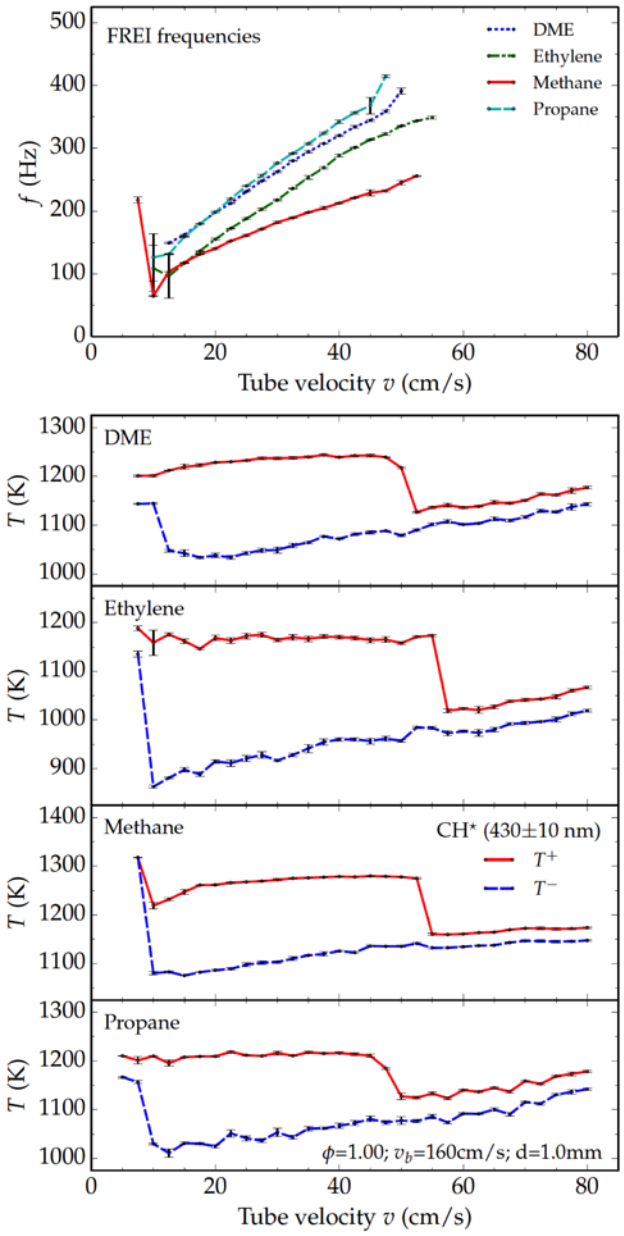

Figure 4. Comparison of the μ–FIT measurements for four gaseous fuels: (top) frequency of the flame repetitive ignition and extinction (FREI) events as a function of the pre-mixed flow velocity; and (bottom) the ignition T+ and extinction T- points as a function of flow velocity that show the transition from the high and low speed stable flames.

microphone, which the authors believe is the first published example. Thorough measurements were made to isolate and evaluate the impact of the external heat source and tube geometry on the flame dynamics. Finally, the kinetic behavior of the fuel–air mixture was related to the flame dynamics for four gaseous fuels (methane, ethane, ethylene, and dimethylether [DME]) as shown in Figure 4.

CFD simulations of alternative fuel research engine experiments were performed which leverage this project's kinetics efforts to improve understanding of the interaction of chemical kinetics with other engine physics including gas-exchange and fuel sprays. Despite advances in computationally efficient integration of large chemical mechanisms developed in this and related projects, it is still necessary to use reduced mechanisms for practical simulation time in detailed fluid dynamics calculations. Simulations of a diesel engine fueled by methyl-decanoate

were performed to study leaner lifted flame combustion which holds the promise of efficient and soot-free diesel combustion. The engine experiments were performed by C. Mueller of Sandia National Laboratories as part of the Fuel & Lubricant Technologies subprogram. Methyl-decanoate is a promising biodiesel methyl-ester because of its stability and volatility. The simulations showed good agreement with experimental heat release rates and timing. The intake and exhaust plenums where included which enable accurate simulation of the breathing process. Figure 5 shows iso-surfaces of fuel concentration and temperature during the injection, showing the lifted flame behavior at these conditions. These results were obtained with a 115 species chemical mechanism that was reduced from the 3,299 species mechanism developed in this project.

Simulations were also performed to analyze partial fuel stratification in a DISI engine fueled with E85. Partial fuel stratification enables control of the combustion timing at lean and dilute conditions, which enables cleaner and more efficient operation. The DISI experiments were performed by M. Sjöberg of Sandia National Laboratories as part of the Fuel & Lubricant Technologies subprogram. The simulations are able to capture the compression, intake swirling, and spark ignition and flame propagation in this configuration. The chemical kinetics model used a 312 species mechanism reduced from a 1,389 species mechanism developed in this project for ethanol–gasoline blends. Figure 6 shows the combustion chamber with iso-surfaces of fuel and temperature during the primary combustion event. These simulations employed the fast kinetic solver algorithms developed at LLNL for a 2x reduction in simulation time. Future work in these simulations will incorporate the full intake and exhaust geometry once the components have been measured by the experimenters.

Conclusions

- New correlation has been developed for matching surrogate gasolines containing ethanol with real gasoline containing ethanol
- Flames speed expressions as a function of temperature and pressure have been developed for RD587 reference gasoline, E30, and E85
- μ–FIT built and autoignition and extinction behaviors of four gaseous fuels have been measured
- CFD engine simulations performed using fast kinetic solver algorithms developed at LLNL:
  - Leaner, lifted-flame combustion in a diesel engine fueled with methyl decanoate
  - Lean, stratified DISI combustion fueled with E85

Acknowledgements

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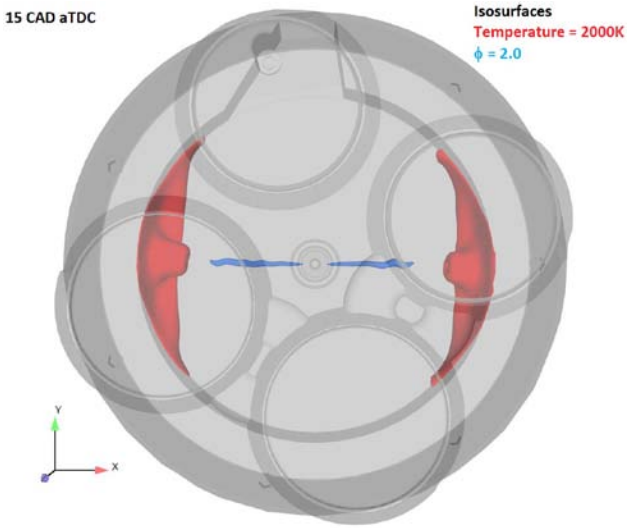

CAD – crank angle degree

Figure 5. Isosurfaces of the equivalence ratio equal to 2.0 (blue) and temperature equal to 2,000 K (red) during leaner lifted flame combustion of methyl-decanoate at 15 degrees after top dead center (aTDC).

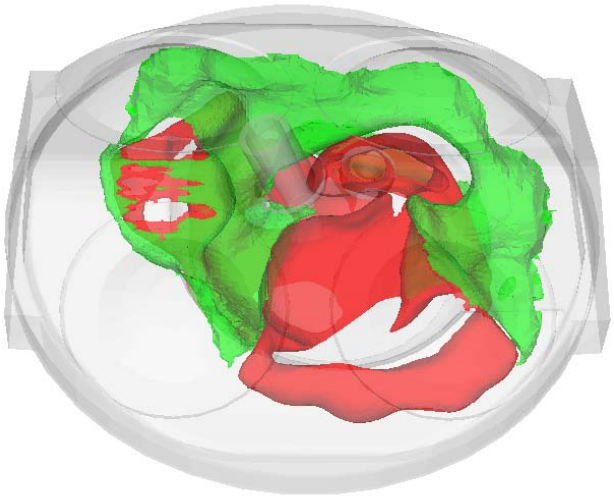

Figure 6. Iso-surfaces of fuel mass fraction equal to 0.05 (green) and temperature equal to 1,500 K (red) during stratified, DISI combustion of E85 at 4° aTDC.

References

1. Y. Yang and J. Dec, "Bio-Ketones: Autoignition Characteristics and Their Potential as Fuels for HCCI Engines," Society of Automotive Engineers, SAE 2013-01-2627, (2013).

2. K. Maruta, J.K. Parc, K.C. Oh, T. Fujimori, S.S. Minaev, R.V. Fursenko, Combust. Explos. Shock Waves 40 (5) (2004) 516–523.

3. K. Maruta, T. Kataoka, N.I. Kim, S. Minaev, R. Fursenko, Proc. Combust. Inst. 30 (2005) 2429– 2436.

FY 2015 Publications/Presentations

1. Burke, U., Pitz, W.J. and Curran, H.J., "Experimental and Kinetic Modeling Study of the Shock Tube Ignition of a Large Oxygenated Fuel: Tri-Propylene Glycol Mono-Methyl Ether," Combustion and Flame Propylene Glycol Mono-Methyl Ether," Combustion and Flame 162 (2015).

2. C.K. Westbrook, W.J. Pitz, M. Mehl, "A Chemical Kinetic Study of Octane Sensitivity", 9th U. S. National Combustion Meeting, Cincinnati, OH, May 17–20, 2015, paper # 2F12.

3. R.A. Whitesides and M.J. McNenly, "Practical Combustion Kinetics with CUDA," GPU Technology Conference, San Jose, CA, March 17–20, 2015.

4. E. Elmtoft, A.S. Cheng, N.J. Killingsworth, and R.A. Whitesides, "Injected Droplet Size Effects on Diesel Spray Results with RANS and LES Turbulence Models," SAE 2015 World Congress & Exhibition Paper 2015-01-0925.

5. G. Petitpas, M.J. McNenly, and R.A. Whitesides, "Accounting for experimental and model uncertainties in HCCI Simulation," AEC Working Meeting, Livermore, CA, February 9–12, 2015.

6. Nakamura, H., Curran, H., Córdoba, A.D.P., Pitz, W.J., Dagaut, P., Togbé, C., Sarathy, S.M., Mehl, M., Agudelo, J. and Bustamante, F., "An Experimental and Modeling Study of Diethyl Carbonate Oxidation," Combustion and Flame 162 (4) (2015) 1395–1405.

Special Recognitions & Awards/ Patents Issued

1. R&D 100 Award for Zero-order Reaction Kinetics software (Matt McNenly and Russell Whitesides).

V.6 Improved Fuels and Mixing-Controlled Combustion Strategies for High-Efficiency Compression-Ignition Engines

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Kevin Stork

Overall Objectives

Facilitate the introduction of renewable, bio-derived, 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 blending stocks as well as pure compounds.
- High-quality experimental data for computational fluid dynamics (CFD) model development to facilitate accurate, rapid, and cost-effective computational engine optimization for evolving fuels.
- New technologies to dramatically increase the performance per unit cost of future high-efficiency engine/fuel systems.

Fiscal Year (FY) 2015 Objectives

- Model and measure the physical and chemical properties of a set of diesel surrogate fuels exhibiting increasing levels of accuracy in matching the compositional characteristics of a single real-world target fuel, to facilitate testing in engine and combustion vessel experiments as well as CFD simulations
- Determine whether leaner lifted-flame combustion (LLFC, i.e., mixing-controlled combustion that does not form soot because it occurs at local equivalence ratios ≤ 2) can be sustained throughout an engine combustion event using a two-hole injector tip and a commercial #2 ultra-low sulfur diesel certification fuel (CF) vs. using a blend of CF with an oxygenate
- Determine whether the new ducted fuel injection technology (DFI, i.e., directly injecting fuel through a duct aligned with the fuel jet) can increase the degree of fuel/charge-gas premixing present in the autoignition zone, thereby facilitating the achievement of LLFC.

FY 2015 Accomplishments

- Co-led a United States–Canadian team of researchers under the auspices of the Coordinating Research Council (CRC) in modeling and measuring dozens of physical and chemical properties for a set of four ultra-low sulfur #2 diesel surrogate fuels with increasing compositional accuracies relative to a single target fuel
- Conducted optical engine experiments showing that LLFC could be sustained, i.e., in-cylinder soot formation could be prevented throughout the combustion event, with a two-hole injector tip and the CF–oxygenate blend, but not with neat CF
- Demonstrated that DFI can increase the degree of fuel/charge-gas premixing present in the autoignition zone, leading to the achievement of sustained LLFC over a range of conditions in constant-volume combustion vessel experiments.

Future Directions

- Conduct optical engine experiments on the CF target fuel and the set of corresponding diesel surrogate fuels described in this report to determine the level of surrogate fuel compositional accuracy required to adequately match the target fuel combustion performance
- Further assess the feasibility of LLFC achieved via oxygenated fuels and/or DFI as a means to mitigate

in-cylinder soot formation, to facilitate the deployment of renewable fuels and less expensive exhaust gas aftertreatment systems

- Collaborate with one or more CFD modeling groups to: (1) identify and overcome barriers to truly predictive computational engine simulations using the surrogate fuels described herein, and (2) better understand and optimize LLFC–DFI parameters for use in future engines ■

Introduction

Steady progress is required in the co-optimization of engines and fuels to meet Department of Energy, industry, and societal objectives of high-efficiency, emissions compliant, cost-effective, durable, high-performance engine/fuel systems that are sustainable and enhance domestic energy security, environmental quality, and customer value. Meeting these objectives is a challenging but achievable task. Two factors that are likely to play key roles are: (1) the ability to computationally optimize engine-system designs for evolving real-world fuels, and (2) the development and refinement of novel combustion strategies that are synergistic with emerging fuels. Regarding the first factor, the lack of adequate diesel surrogate fuels and experimental data to rigorously assess the CFD models used in these optimizations is a significant barrier to progress. The surrogate fuels research conducted in this project is directly focused on overcoming this barrier. Regarding the second factor, there is tremendous potential to develop improved combustion strategies that will take advantage of the unique properties of future renewable fuels. The research into LLFC and DFI conducted in this project are examples of novel combustion strategies that could be integrated into future engines synergistically with emerging renewable fuels.

Approach

Three different approaches were employed to achieve the three major FY 2015 accomplishments listed above. First, for the surrogate fuel property characterization research, the principal investigator co-led CRC Project AVFL-18a, which is a large collaborative effort among approximately a dozen research groups in the United States and Canada. Property modeling and measurement activities were conducted by the collaborators and selected contractors. Second, the LLFC research was conducted using the principal investigator's optical engine lab at Sandia. Two fuels were used: CF and a blend, denoted T50, containing 50 vol% CF and 50 vol% tri-propylene glycol methyl ether (TPGME, an oxygenate) [1,2]. Third, the DFI research was conducted in Sandia's constant-volume combustion vessel using a single-hole fuel injector and a steel duct aligned with the axis of the fuel jet.

Results

In the diesel surrogate fuels research, the surrogate fuel formulation methodology previously developed under this collaborative project with CRC was applied to determine four surrogate fuel formulations, denoted V0a, V0b, V1, and V2, in order of increasing compositional accuracy relative to the target fuel, and to explicitly emulate the target fuel ignition quality (see Figure 1), volatility (see Figure 2), and density (see Figure 3). The surrogate compositions were verified by the techniques that were initially employed to characterize the target fuel (see Figure 4). To assist in evaluating the soundness of the current surrogate formulation methodology as well as the suitability of the surrogate fuels for testing in engines and other experimental setups, many property measurements were made, including ignition quality, volatility, and liquid density as shown above, as well as net heat of combustion, lubricity, cloud point, final melting point, fuel solidification at elevated pressures, elemental analysis, smoke point, sulfur content, flash point, corrosivity,

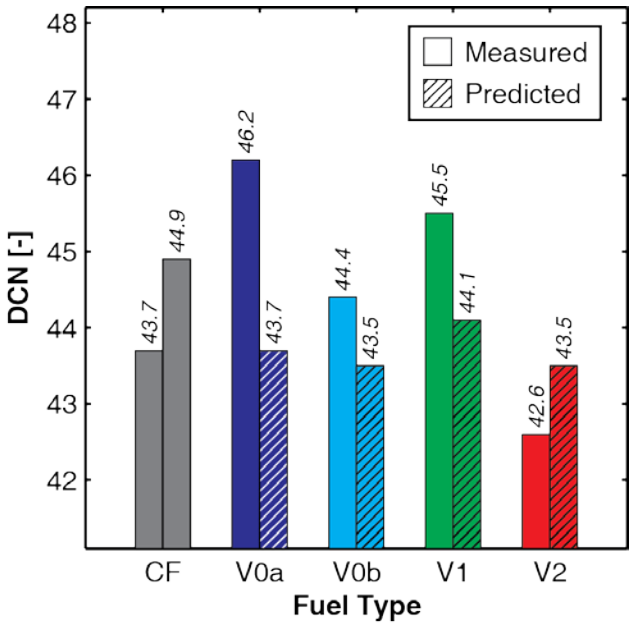


Figure 1. Target and surrogate fuel ignition qualities as quantified by derived cetane number (DCN) per ASTM D6890 [3] or estimated using a volume-fraction-weighted linear blending rule. For CF, both bars represent measured values, with the left-hand bar representing the average of measurements from 2009-2011 reported in previous work [4], and the right-hand bar representing the average value measured in October 2014.

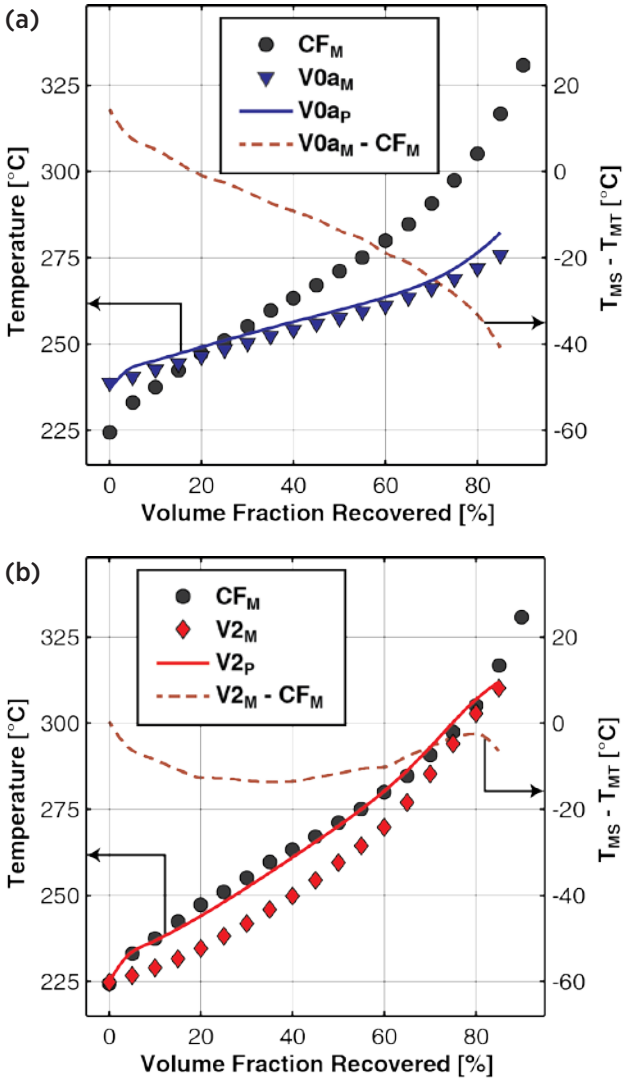


Figure 2. Fuel volatility as quantified by the advanced distillation curve technique [5]. (a) V0a surrogate. (b) V2 surrogate. Subscripts M, P, MS, and MT denote measured, predicted, measured surrogate fuel, and measured target fuel values, respectively.

kinematic viscosity, aromatic content, and surface tension. These measurements show that, in general, the more accurately a surrogate fuel embodies the compositional characteristics of its target fuel, the more accurately it also matches the target fuel properties. The surrogates are suitable for use in systems with modern fuel injection equipment and sulfur sensitive aftertreatment devices, although measures likely will be required to prevent fuel solidification at elevated pressures. Values of additional surrogate thermodynamic properties (critical properties and properties along the bubble point curve) also were estimated to assist researchers conducting numerical simulations with the surrogate fuels, for whom these data are required as input parameters. The increasing

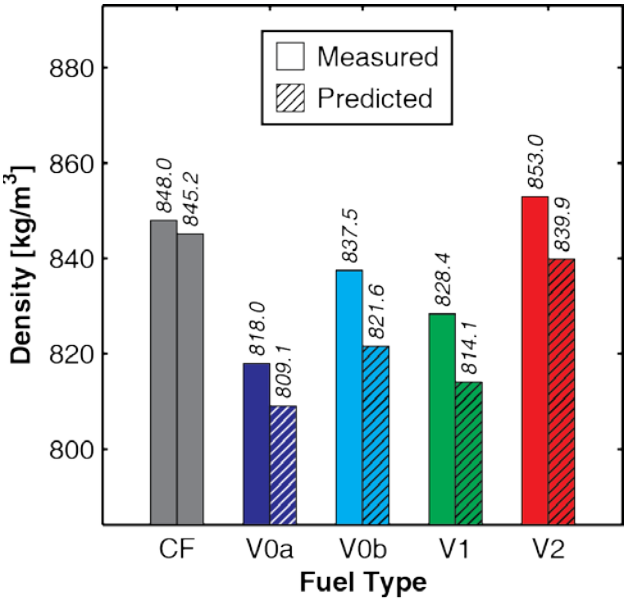
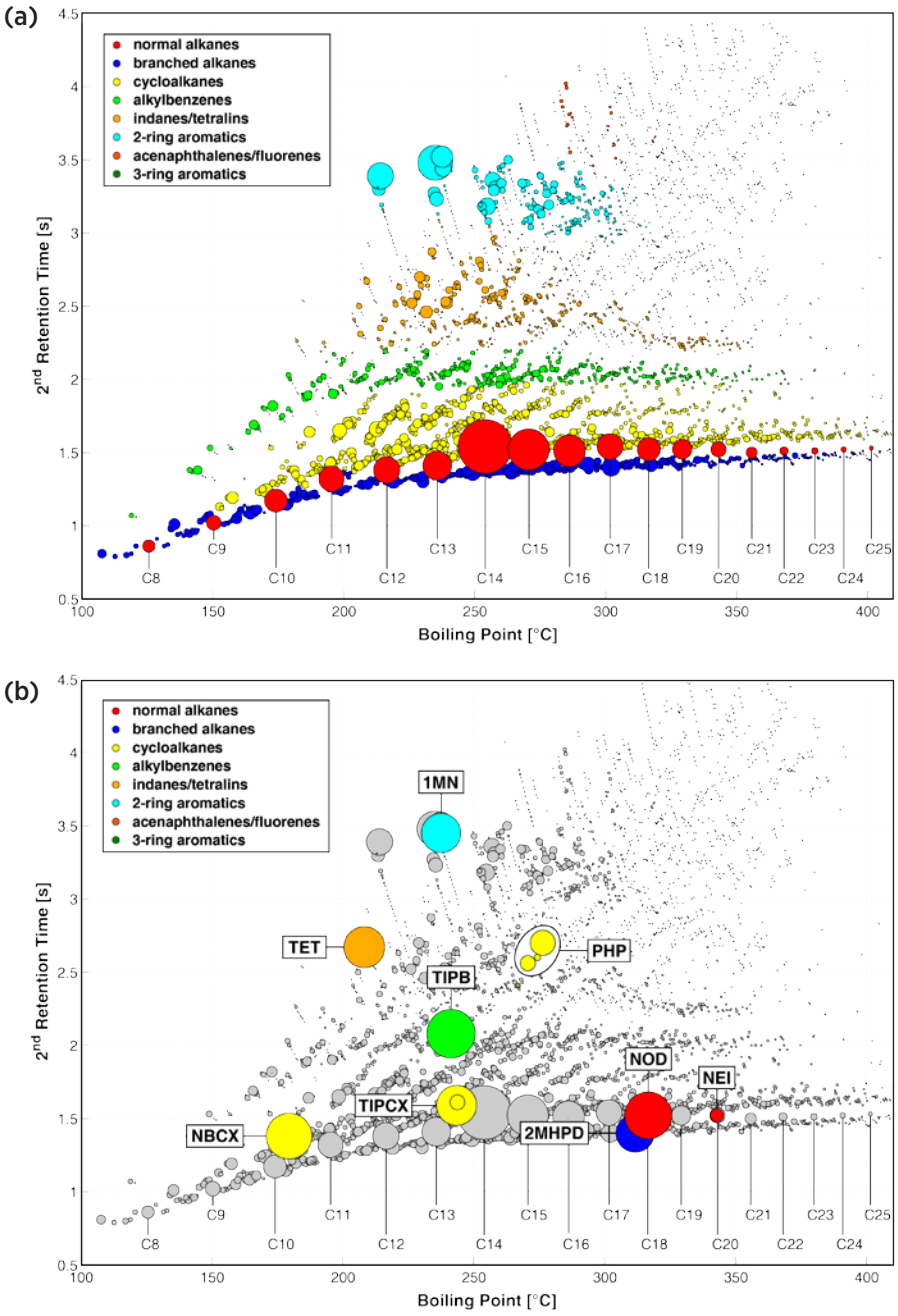


Figure 3. Measured target fuel densities, as well as measured and predicted surrogate fuel densities at 20°C and ~0.1 MPa ambient pressure. For CF, both bars represent measured values, with the left- and right-hand bars corresponding to measurements made by different testing labs in 2009 and 2014, respectively. Each non-cross-hatched bar represents a single measurement acquired per the ASTM D4052 test method [6].

levels of compositional accuracy relative to the target fuel embodied by the set of surrogate fuels are intended to assist researchers in determining the minimum level of surrogate fuel compositional accuracy required to adequately emulate the performance characteristics of the target fuel under different combustion modes. Further details are provided in Mueller et al. [8].

In the LLFC research, FY 2015 results include using a blend denoted T50 containing 50 vol% CF with TPGME to demonstrate mixing-controlled combustion in an engine that does not form any soot within the combustion chamber (i.e., LLFC was achieved) and that does not require charge-gas dilution. Optical engine experiments with a two-hole injector tip achieved LLFC at 2–3 bar gross indicated mean effective pressure with the T50 fuel at 240 MPa injection pressure, 50°C intake manifold temperature (IMT), 95°C coolant temperature, and +5 crank angle degree (CAD) after top dead center (ATDC) start of combustion timing. The achievement of LLFC was confirmed by independent soot measurements using a smoke meter, spatially integrated natural luminosity from high-speed imaging, equivalence ratio estimates from lift-off length imaging, and laser-induced incandescence measurements of soot volume fraction in the exhaust stream. In contrast to the results with T50, LLFC was not



NBCX – n-butylcyclohexane; TIPB – 1,3,5-triisopropylbenzene; 1MN – 1-methylnaphthalene; 2MHPD – 2-methylheptadecane; TET – tetralin; NEI – n-eicosane; NOD – n-octadecane

Figure 4. Fuel composition as quantified by two-dimensional gas chromatography with flame-ionization detection. Annotations showing the carbon numbers and boiling points of the individual n-alkanes are provided for reference. The 2nd retention time is proportional to polarity/polarizability. (a) Chromatogram of CF target fuel [7]. (b) Chromatogram of V2 surrogate, showing surrogate palette compounds (in color and labeled) overlaid on CF target-fuel composition (in gray). The area and color of the circle for each palette compound/isomer correspond to its mass fraction and hydrocarbon class, respectively. The individual isomers of 1,3,5-triisopropylcyclohexane (TIPCX) and perhydrophenanthrene (PHP) are evident in the chromatogram.

achieved under any of the test conditions with CF, showing that fuel oxygenation is an important facilitating element of the strategy. Selected results for T50 and CF are provided in Figure 5. LLFC was found to be tolerant of charge-gas dilution, which was used to lower engine-out emissions of nitrogen oxides (NO_x) by >90%. Combustion was stable under LLFC conditions, with a coefficient of variation of gross indicated mean effective pressure less than 1.5%. Combustion noise and ringing intensity were also lower for LLFC with T50, relative to using the same operating conditions with CF. Further details can be found in Gehmlich et al. [9].

In the DFI research, testing in a constant-volume combustion vessel showed that positioning a steel duct a short distance downstream of the injector tip can lower soot levels during combustion. In the best-case scenario at 950 K ambient temperature, a factor of 100 reduction in average soot incandescence was recorded from a photodiode, while achieving a combustion efficiency greater than or equal to that of a free jet at the same conditions, according to the pressure rise data. Natural luminosity (NL) images of free jet and DFI cases are provided for comparison in Figure 6 [10]. The relative importance of enhanced mixing, heat transfer, and/or other mechanisms in causing the decrease in soot production with DFI is unclear after this first round of experiments, highlighting the need for further research into this promising new combustion strategy.

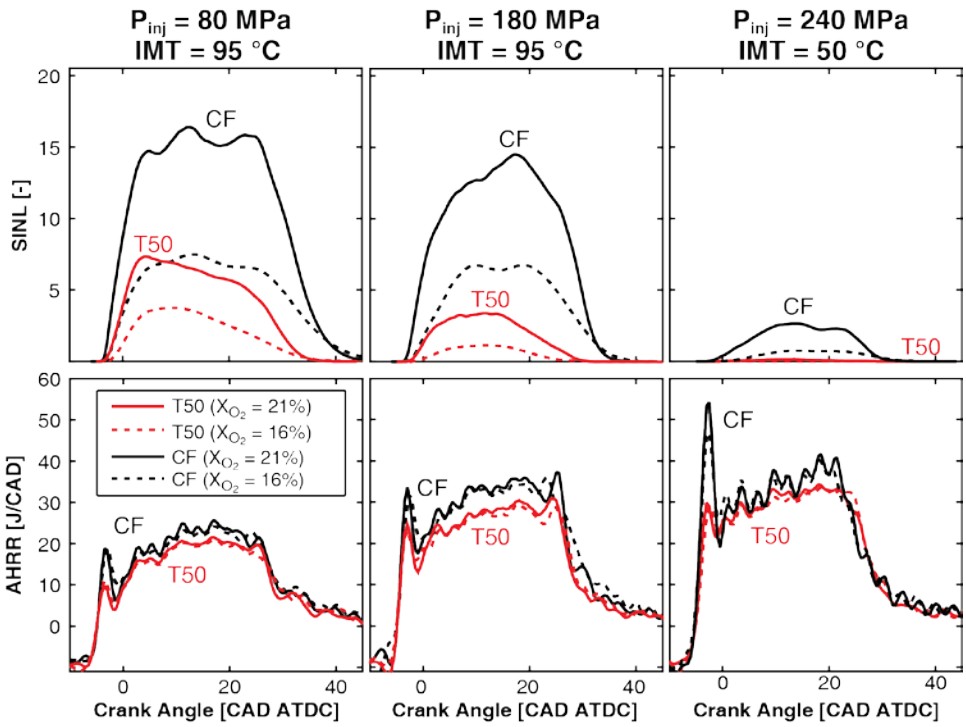


Figure 5. Spatially integrated natural luminosity (SINL, an indicator of the presence of hot soot) and apparent heat release rate (AHRR) as functions of crank angle for the two-hole tip experiments. X_{O2} is the mole fraction of oxygen in the intake charge.

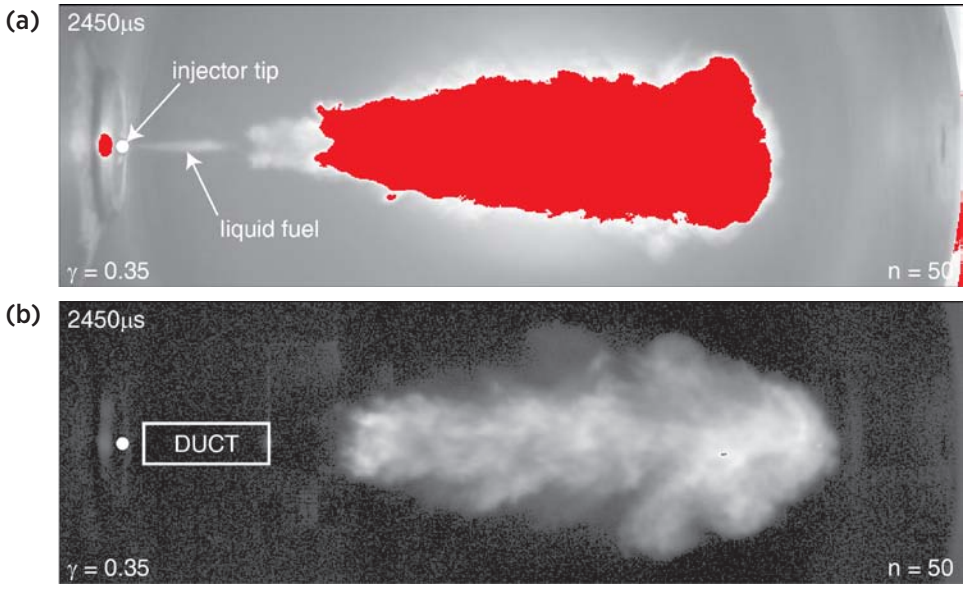


Figure 6. NL images acquired at ambient conditions of 900 K, 22.8 kg/m^3, and 21 mol% O_2, using 150 MPa injection pressure with a 90-μm orifice, n-dodecane fuel, and identical imaging parameters in both frames. (a) Free jet. Red areas in image indicate signal saturation due to radiation from hot soot. (b) DFI jet. NL signal is from chemiluminescence only, indicating the absence of hot soot.

Conclusions

- The diesel surrogate fuels that have been created are suitable for use in systems with modern fuel-injection equipment and sulfur-sensitive aftertreatment devices, although measures likely will be required to prevent fuel solidification at elevated pressures.
- The hypothesis has been generally confirmed that the more accurately a surrogate fuel embodies the compositional characteristics of its target fuel, the more accurately it also matches the target fuel properties.
- Mixing-controlled combustion that does not form any soot within the combustion chamber and does not require charge-gas dilution was demonstrated using a blend containing 50 vol% diesel fuel with an oxygenate. In addition to eliminating soot emissions, this LLFC mode also was shown to lower NO_x emissions, combustion noise, ringing intensity, and cyclic variability.
- The DFI concept was shown to reduce the amount of incandescence from soot at diesel-like conditions by up to two orders of magnitude without sacrificing combustion efficiency, indicating its promise as a pathway to achieving high-load LLFC. Further research is required to understand the physics governing the efficacy of DFI.

References

1. Burke, U., Pitz, W.J., and Curran, H.J., "Experimental and Kinetic Modeling Study of the Shock Tube Ignition of a Large Oxygenated Fuel: Tri-Propylene Glycol Mono-Methyl Ether," *Combust. Flame* **162**(7):2916–2927, 2015.
2. Dumitrescu, C.E., Mueller, C.J., and Kurtz, E., "Investigation of a Tripropylene-Glycol Monomethyl Ether and Diesel Blend for Soot-Free Combustion in an Optical Direct-Injection Diesel Engine." ASME-ATI-UIT 2015 Conference on Thermal Energy Systems: Production, Storage, Utilization and the Environment, Naples, Italy, May 17–20, 2015.
3. "ASTM Standard D6890-13b, Standard Test Method for Determination of Ignition Delay and Derived Cetane Number (DCN) of Diesel Fuel Oils by Combustion in a Constant Volume Chamber." ASTM International, West Conshohocken, PA, 2013.
4. Mueller, C.J., Cannella, W.J., Bruno, T.J., Bunting, B., Dettman, H., Franz, J., Huber, M.L., Natarajan, M., Pitz, W.J., Ratcliff, M.A., and Wright, K., "Methodology for Formulating Diesel Surrogate Fuels with Accurate Compositional, Ignition-Quality, and Volatility Characteristics," *Energy Fuels* **26**(6):3284–3303, 2012.
5. Bruno, T.J., Ott, L.S., Lovestead, T.M., and Huber, M.L., "Relating Complex Fluid Composition and Thermophysical Properties with the Advanced Distillation Curve Approach," *Chemical Eng. Tech.* **33**(3):363–376, 2010.
6. "ASTM Standard D4052-11, Standard Test Method for Density, Relative Density, and API Gravity of Liquids by Digital Density Meter." ASTM International, West Conshohocken, PA, 2011.
7. Gieleciak, R. and Fairbridge, C., "Detailed Hydrocarbon Analysis of FACE Diesel Fuels Using Comprehensive Two-Dimensional Gas Chromatography," CanmetENERGY Report: CDEV-2013-2065-RT, 2013. Online source, http://www.crcao.org/publications/advancedVehiclesFuelsLubricants/FACE/GCxGC%20analysis%20of%20FACE%20fuels%20-RG%20v4%200%20Nov2013.pdf.
8. Mueller, C.J., Cannella, W.J., Bays, J.T., Bruno, T.J., DeFabio, K., Dettman, H.D., Gieleciak, R.M., Huber, M.L., Kweon, C.-B., McConnell, S.S., Pitz, W.J., and Ratcliff, M.A., "Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties," *Energy Fuels*, 2016, doi:10.1021/acs.energyfuels.5b02879.
9. Gehmlich, R.K., Dumitrescu, C.E., Wang, Y., and Mueller, C.J., "Leaner Lifted-Flame Combustion Enabled by the Use of an Oxygenated Fuel in an Optical CI Engine," SAE Technical Paper 16PFL-0250 (in press), 2016.
10. 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 11, 2015), http://energy.gov/sites/prod/files/2015/06/f24/ft004_mueller_2015_o.pdf.

FY 2015 Publications

1. Mueller, C.J., Cannella, W.J., Bays, J.T., Bruno, T.J., DeFabio, K., Dettman, H.D., Gieleciak, R.M., Huber, M.L., Kweon, C.-B., McConnell, S.S., Pitz, W.J., and Ratcliff, M.A., "Diesel Surrogate Fuels for Engine Testing and Chemical-Kinetic Modeling: Compositions and Properties," *Energy Fuels*, 2016, doi:10.1021/acs.energyfuels.5b02879.
2. Gehmlich, R.K., Dumitrescu, C.E., Wang, Y., and Mueller, C.J., "Leaner Lifted-Flame Combustion Enabled by the Use of an Oxygenated Fuel in an Optical

CI Engine," SAE Technical Paper 16PFL-0250, in press, 2016.

3. Dumitrescu, C.E., Mueller, C.J., and Kurtz, E., "Investigation of a Tripropylene-Glycol Monomethyl Ether and Diesel Blend for Soot-Free Combustion in an Optical Direct-Injection Diesel Engine," *Applied Thermal Engineering*, 2015, doi:10.1016/j.applthermaleng.2015.12.068.

4. Dumitrescu, C.E., Polonowski, C.J., Fisher, B.T., Lilik, G.K., and Mueller, C.J., "Diesel Fuel Property Effects on In-Cylinder Liquid Penetration Length: Impact on Smoke Emissions and Equivalence Ratio Estimates at the Flame Lift-Off Length," *Energy Fuels* **29**(11):7689–7704, 2015.

5. Lilik, G.K., Mueller, C.J., Dumitrescu, C.E., and Gehrke, C.R., "The Visualization of Soot Late in the Diesel Combustion Process by Laser Induced Incandescence with a Vertical Laser Sheet," *SAE Int. J. Engines* **8**(2):716–734, 2015, doi:10.4271/2015-01-0801.

6. Cheng, A.S., Dumitrescu, C.E., and Mueller, C.J., "Investigation of Methyl Decanoate Combustion in an Optical Direct-Injection Diesel Engine," *Energy Fuels* **28**(12):7689–7700, 2014.

7. Nilsen, C.W. and Mueller, C.J., "Analysis of the Ducted Fuel Injection Concept for Compression-Ignition Engines," *Science Undergraduate Laboratory Internship (SULI) Program Final Report*, DOE Office of Science, September 3, 2015.

8. Dumitrescu, C.E., Mueller, C.J., and Kurtz, E., "Investigation of a Tripropylene-Glycol Monomethyl Ether and Diesel Blend for Soot-Free Combustion in an Optical Direct-Injection Diesel Engine," *ASME-ATI-UIT 2015 Conference on Thermal Energy Systems: Production, Storage, Utilization and the Environment*, Naples, Italy, May 17–20, 2015.

9. Mueller, C.J., and Dumitrescu, C.E., "Fuel Properties to Enable Leaner Lifted-Flame Combustion, Task 4.2: Sandia Optical-Engine Experiments," DOE FOA-239 Final Report, March 29, 2015.

10. Mueller, C.J., "Fuel Effects on Mixing-Controlled Combustion Processes in High-Efficiency Compression-Ignition Engines," *Proc. of DOE Advanced Engine Combustion and Fuels Program Review*, DOE Office of Vehicle Technologies Annual Report, 2014.

FY 2015 Presentations

1. Mueller, C.J., "Caterpillar/Sandia Collaborative Combustion Research: Recent Progress and Future Plans," Combustion and Air Systems Research Technical Meeting, Caterpillar Global R&D Headquarters, Peoria, IL (October 8, 2014).

2. Mueller, C.J., "Can Surrogate Fuels Improve CI Engine Performance?" **invited presentation**, Energy & Transportation Research Collaboration Meeting, Caterpillar Global R&D Headquarters, Peoria, IL (October 9, 2014).

3. Mueller, C.J., "Optical-Engine Experiments to Assess the Feasibility of LLFC with Oxygenated Fuels," DOE FOA 239 Project Meeting with Ford Motor Co., Southfield, MI, by teleconference (October 10, 2014).

4. 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, Phoenix, AZ (January 6, 2015).

5. Mueller, C.J., "DOE FOA-239 Project Summary, Task 4.2: Sandia Optical-Engine Experiments," DOE FOA-239 Project Summary Meeting, Ford World Headquarters, Southfield, MI, by teleconference (January 29, 2015).

6. Mueller, C.J., "Optical-Engine Experiments to Assess the Feasibility of Leaner Lifted-Flame Combustion (LLFC) with Oxygenated Fuels," Advanced Engine Combustion Program-Review Meeting, Livermore, CA (February 9, 2015).

7. Mueller, C.J., "The Visualization of Soot Late in the Diesel Combustion Process by Laser Induced Incandescence with a Vertical Laser Sheet," 2015 SAE International Congress and Exposition, Detroit, MI (April 22, 2015).

8. Cannella, W.J. and 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, Charlotte, NC (May 19, 2015).

9. 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 11, 2015).

10. Mueller, C.J., "CI Fuels Roadmap: Sooting Propensity," Advanced Combustion and Emissions Control (ACEC) Roadmap Meeting, Detroit, MI (June 18, 2015).

11. Mueller, C.J., "A Review of the CRC Program on Surrogate Diesel Fuels," **invited presentation**, 13th International Conference on Engines for Vehicles, Port Jefferson, NY (June 24, 2015).

12. Gehmlich, R.K. and Mueller, C.J., "Leaner Lifted-Flame Combustion in an Optical CI Engine with Conventional and Oxygenated Fuels," Advanced Engine Combustion Program-Review Meeting, Detroit, MI (August 18, 2015).

13. Nilsen, C.W. and Mueller, C.J., "Ducted Fuel Injection," Advanced Engine Combustion Program-Review Meeting, Detroit, MI (August 19, 2015).

14. Mueller, C.J., "Status Update on AVFL-18a: Improved Diesel Surrogate Fuels for Engine Testing and Kinetic Modeling," Coordinating Research Council FACE Working Group Meeting, St. Louis, MO (September 29, 2015).

15. Mueller, C.J. and Miles, P.C., "A History of Optically Accessible Engines and Their Impact on Our Understanding of Engine Combustion Processes," **invited presentation**, Coordinating Research Council FACE Working Group Meeting, St. Louis, MO (September 29, 2015).

Special Recognitions & Awards/ Patents Issued

1. US Patent #8,967,129: "Ducted Combustion Chamber for Direct Injection Engines and Method." Issued March 3, 2015.

2. US Patent Application #14,789,782: "Ducted Fuel Injection." Filed July 1, 2015.

VI. Index of Primary Contacts

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VII. Project Listings by Organizations

Argonne National Laboratory

Clean Air Power

Cummins Inc.

Ford Motor Company

George Washington University

Lawrence Livermore National Laboratory

National Renewable Energy Laboratory

Northwestern University

Oak Ridge National Laboratory

Oak Ridge National Laboratory (Continued)

Pacific Norhwest Natiional Laboratory

Sandia National Laboratories

University of Michigan

Valvoline

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